METAL COORDINATION STUDIES
OF
SULPHUR LIGANDS

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ABSTRACT

Transition metal complexes of ligands containing thioether sulphur have been investigated. Section I, concentrates on Cu(II) complexes, and to a lesser extent Cu(I) complexes, of mixed sulphur-nitrogen ligands. Some complexes of Co(II) and the d^8 metal ions, Ni(II), Pd(II) and Pt(II), have also been included. In Section II, complexes of the Group VIB metals (Cr(O), Mo(O), W(O)) are discussed.

SECTION I

All of the complexes have been investigated using infrared and electronic spectroscopy, with electronic spectra for some of the Cu(II) complexes also being recorded at 90K. The Cu(II) complexes have also been studied using electron spin resonance (esr) spectroscopy. For a variety of solvents at 77K, esr has been especially useful in revealing the complex behaviour of some of the compounds.

i) Complexes of 2-(3,3-dimethyl-2-thiabutyl)pyridine (tbmp)

The ligand has been used to prepare the Cu(II) complexes, $Cu(tbmp)_nX_2$ ($n=1$, $X=Cl^-$, Br^-; $n=2$, $X=BF_4^-$, ClO_4^-, Cl^-, Br^-), $[Cu(tbmp)_2X]BF_4$ ($X=Cl^-$, Br^-), and the Cu(I) complexes, $Cu(tbmp)_nBr$ ($n=1,2$) and $Cu(tbmpH)X_2$ ($X=Cl^-$, Br^-).

Crystallographic studies are reported for $Cu(tbmp)Br_2$, $Cu(tbmp)_2Br$ and $Cu(tbmpH)Br_2$.

$Cu(tbmp)Br_2$ crystallizes as discrete, non-centrosymmetric dibromo-bridged dimers ($[Cu(tbmp)Br_2]_2$), in which each Cu(II) centre has a distorted tetragonal pyramidal environment. The tetrahedrally distorted basal plane of each Cu(II) centre consists of one thioether sulphur ligand, (mean Cu(II)-S =

2.352(6) Å), one pyridyl nitrogen (mean Cu(II)-N = 2.06(2) Å) and two bromide ions [one terminal (mean Cu(II)-Br = 2.372(3) Å) and one bridging (mean Cu(II)-Br = 2.415(3) Å)]. The apex of each tetragonal pyramid is formed by a long bond to the bridging, basal bromide ion (mean Cu(II)-Br = 2.902(4) Å) of the second Cu(II) centre.

In monomeric, distorted tetrahedral Cu(tbmp)$_2$Br, each Cu(I) ion is bound by a terminal bromine (Cu(I)-Br = 2.426(2) Å), two thioether sulphur atoms (mean Cu(I)-S = 2.331(4) Å) and a pyridyl nitrogen (Cu(I)-N = 2.11(1) Å).

Cu(tbmpH)Br$_2$ forms centrosymmetric dimers ([Cu(tbmpH)Br$_2$]$_2$), in which the distorted tetrahedral Cu(I) centres are bridged by two bromide ions (mean Cu(I)-Br = 2.597(1) Å). The two remaining coordinating positions of each Cu(I) ion are occupied by a terminal bromide ion (Cu(I)-Br = 2.363(1) Å) and a sulphur-bound (Cu(I)-S = 2.276 (2) Å) tbmpH$^+$ cation.

The structural data for these and related complexes are used in attempting to understand the nature of Cu(I) and Cu(II) interactions with biologically relevant ligands.

The spectroscopic data suggests that the Cu(tbmp)$_2$X$_2$ complexes are cis-octahedral in the solid state, whereas the [Cu(tbmp)$_2$X]BF$_4$ complexes are tetragonal pyramidal.

An unstable deep blue species is formed by the addition of t-butyl thiolate to Cu(tbmp)$_2$X$_2$, where X is ClO$_4^-$ or BF$_4^-$. The displacement of tbmp (by pyridine) from Cu(tbmp)$_2$X$_2$ (X = Cl$^-$, BF$_4^-$) is also discussed.

With Co(II) and Ni(II), the cis-octahedral M(tbmp)$_2$X$_2$ (X=Cl$^-$,Br$^-$) and M(tbmp)$_2$(ClO$_4$)$_2$.nH$_2$O (n = 1,2) complexes have been characterized.

The nature of paramagnetic metal ion [M=Cu(II), Co(II)] interactions with tbmp under hydrophobic conditions are investigated using ^{1}H nmr spectroscopy.

ii) Complexes of 2-ethylthioethylamine (etea)

The tetragonal complexes Cu(etea)X_2 ($X=Cl^-$, Br^-), Cu$(etea)_2X_2$ ($X=BF_4^-$, ClO_4^-, Cl^-, Br^-) and $[Cu(etea)_2Cl]BF_4$ have been characterized and the displacement of etea from $Cu(etea)_2(ClO_4)_2$ (by pyridine), is discussed.

iii) Complexes of 2-methylthio-2-imidazoline (mti)

In the reactions of mti with M(II), the tetragonal complexes $Cu(mti)_4X_2$ ($X = BF_4^-$, Cl^-, Br^-) were successfully synthesized, together with a tetrahedral complex, $Co(mti)_3Cl_2$. In the latter, one mti molecule appears to remain uncomplexed.

With $Cu(mti)_4(BF_4)_2$, the ligand is not displaced by an excess of pyridine. A ^{1}H nmr line broadening experiment provides good evidence for Cu(II) binding to mti via its non-protonated nitrogen.

iv) Complexes of 2-(3,3-dimethyl-2-thiabutyl)quinoline (tbmq)

With this ligand, the pseudotetrahedral Cu(II) complexes, Cu(tbmq)X_2 ($X = Cl^-$, Br^-) and the Cu(I) complexes, Cu(tbmq)Br, Cu(tbmqH)Br_2 and $Cu(tbmq)_2ClO_4$, were synthesized. In contrast to tbmp and etea, tbmq does not form the six-coordinate complexes, $Cu(tbmq)_2X_2$ ($X = Cl^-$, Br^-).

v) Complexes of 3-(2-methylthiophenylimino)camphor (I)

Although I is susceptible to hydrolysis, the successful isolation and characterization of the pseudo-tetrahedral $CuI(ClO_4)_2$.acetone.xH_2O ($x = 0,2$) complexes was achieved from acetone solutions. A ^{1}H nmr line broadening experiment indicates that Cu(II)/S(thioether) interactions take place under hydrophobic conditions.

vi) Complexes of 1,2-bis(pentafluorophenylthio)ethane (fpte) and ethylthiopentafluorobenzene (C_6F_5SEt)

In order to determine the effects of the electronegative pentafluorophenyl substituents, the spectroscopic data for cis-$PtCl_2$fpte, cis-$PdCl_2$fpte and trans-$PtCl_2(C_6F_5SEt)_2$ are compared with the data for some related thioether ligand complexes. The results can be explained by a comparison of the ionisation potentials of the sulphur lone-pair electrons of fpte (as determined by photoelectron spectroscopy) with those of 3,4-bis(alkylthio)toluene (alkyl = methyl, ethyl) and meta- and para-bis(methylthio)benzene.

SECTION II

All of the carbonyl complexes in this Section have been characterized by infrared and electronic spectroscopy and in most cases, ^1H nmr spectroscopy.

i) Complexes of 3,4-bis(methylthio)toluene (bmtt) and 3,4-bis(ethylthio)toluene (bett)

The bridged-ligand complexes, $[M(CO)_5]_2$bmtt and $[M(CO)_5]_2$bett (M=Cr, W), and the chelated-ligand complexes, $M(CO)_4$bmtt and $M(CO)_4$bett (M=Cr, Mo, W) were characterized in this study. On the basis of force constant calculations and electronic spectra, it is apparent that for aryl thioether ligands such as bmtt and bett, the sulphur atom acts as a poorer σ-donor and, in general, a better π-acceptor than it does in aliphatic thioether ligands. A similar conclusion is reached for C_6F_5SEt (see above), with which unstable $M(CO)_5C_6F_5SEt$ (M=Cr, W) complexes were synthesized.

Reactivity studies are reported for $[W(CO)_5]_2$bett and the mass spectra of $[W(CO)_5]_2$bmtt and the $M(CO)_4$bmtt

(M=Cr, Mo, W) complexes are discussed.

^{13}C nmr spectra were recorded for $[W(CO)_5]_2$bmtt, $M(CO)_4$bett (M=Cr, W), $Cr(CO)_4$bmtt and the ligands. The ^{13}CO chemical shifts for $[W(CO)_5]_2$bmtt and the $W(CO)_5L$ complexes of phosphorus and nitrogen ligands are correlated with their Cotton-Kraihanzel carbonyl force constants.

ii) Complexes of 2-ethylthioethylamine (etea) and 2-(3,3-dimethyl-2-thiabutyl)pyridine (tbmp)

Both the bridged-ligand $[M(CO)_5]_2$etea (M=Cr,W) and the chelated-ligand $M(CO)_4$etea (M=Cr, Mo, W) complexes were characterized for etea. However, only the chelated-ligand complexes were isolated and characterized for tbmp.

^{13}C nmr spectra for etea, $Cr(CO)_4$etea and $Mo(CO)_4$etea (the carbonyl complexes showing two distinct trans-^{13}CO resonances) and reactivity studies for $[W(CO)_5]_2$etea and $W(CO)_4$etea, are also discussed.

iii) Complexes of 2-methylthioaniline (mta), 2-methylmercaptobenzimidazole (mmbi) and 2-methylthio-2-imidazoline (mti)

The combined spectroscopic data for the $M(CO)_5L$ complexes of these ligands, shows that mmbi and mti prefer to bind to the zero-valent Group VIB metals via one of their nitrogen donors. On the other hand, mta prefers to bind via the thioether sulphur.

Although the complexes of mta could not be isolated in an analytically pure form, good evidence for their identities was provided by their infrared and mass spectra and the observed replacement of mta from $W(CO)_5$mta, by triphenylphosphite.

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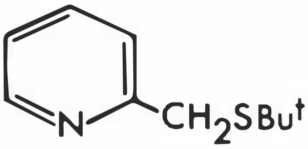

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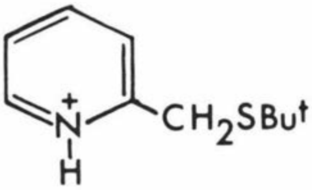

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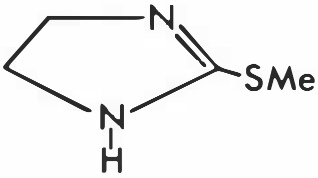
$EtSCH_2CH_2NH_2$

etea



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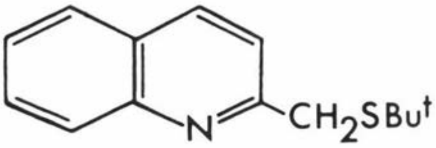

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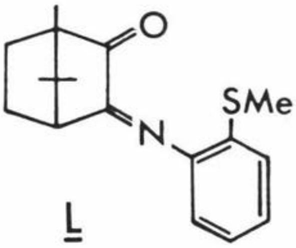

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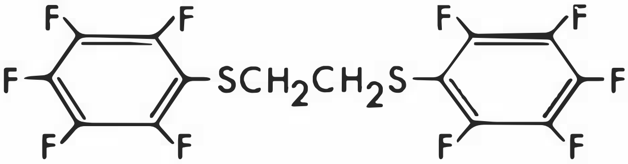

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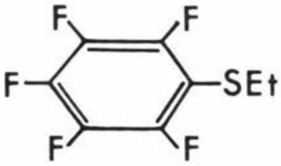

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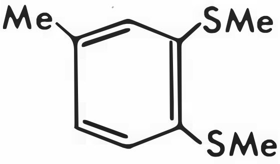

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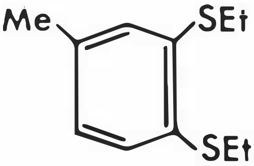

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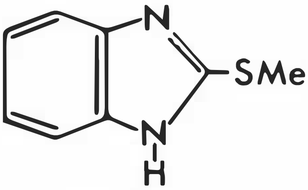

mmbi

THIS WORK

tbmp = 2-(3,3-dimethyl-2-thiabutyl)pyridine
tbmpH$^+$ = 2-(3,3-dimethyl-2-thiabutyl)pyridinium cation
etea = 2-ethylthioethylamine
mti = 2-methylthio-2-imidazoline
tbmq = 2-(3,3-dimethyl-2-thiabutyl)quinoline
tbmqH$^+$ is analogous to tbmpH$^+$ (above)
I =3-(2-methylthiophenylimino)camphor
fpte = 1,2-bis(pentafluorophenylthio)ethane
C_6F_5SEt = ethylthiopentafluorobenzene
bmtt = 3,4-bis(methylthio)toluene
bett = 3,4-bis(ethylthio)toluene
mta = 2-methylthioaniline
mmbi = 2-methylmercaptobenzimidazole.

LITERATURE DATA

A) SECTION I

CHAPTER 1

dmen = N,N-dimethylethylenediamine
∝-pic = 2-methylpyridine (∝-picoline)
tmen = N,N,N′,N′-tetramethylethylenediamine
maep = 2-(2-methylaminoethyl)pyridine
dth = 2,5-dithiahexane
BBTE = 5,8-dithiadodecane
pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane
EEE = 1,8-diamino-3,6-dithiaoctane
1-MeIm = 1-methylimidazole
L^0 = 3,4-bis(2-aminoethylthio)toluene
L^1 = N-(2-methylthiophenyl)(2-pyridyl)methylenimine

L^2 = bis(N,N-dimethylacetamido)thioether

L^3 = 1,4,8,11-tetrathiacyclotetradecane

L^4 = 2-methylthioethylamine

L^5 = [3,3′-ethylenedithiobis(o-phenyleneiminomethylidyne)bis(pentane-2,4-dionato)]$^{2-}$

L^6 = tricyclo[17.5.5.5^{7,13}]tetraaza-1,7,13,19-dioxa-4,16-tetrathia-10,22,27,32-tetratriacontane

L^7 = 1-oxa-4,13-dithia-7,10-diazacyclopentadecane

dmaep = 2-(2-dimethylaminoethyl)pyridine

aep = 2-(2-aminoethyl)pyridine

amp = 2-aminomethylpyridine

pib = N,N′-tetramethylenebis(2-pyridinaldimine)

tu = thiourea

dip = 2,2′-bipyridyl

tren = tris(2-aminoethane)amine

bipy = 2,2′-bipyridyl

tctd = 1,4,8,11-tetrathiacyclotetradecane

F_6acac = [1,1,1,5,5,5-hexafluoro-2,4-pentanedionato]$^-$

CHAPTER 2

trenMe_6 = hexamethyl N-substituted tris(2-aminoethane)amine

trienR_6 = hexaalkyl N-substituted 1,4,7,10-tetraazadecane

en = 1,2-diaminoethane (ethylenediamine)

CHAPTER 3

dto = 3,6-dithiaoctane

14-ane-S_4 = 1,4,8,11-tetrathiacyclotetradecane

py_2S_2 = bis(2-pyridyl)disulphide

$py_2Et_2S_2$ = bis[2-(2-pyridyl)ethyl]disulphide

pea = [2-(2-pyridyl)ethyl]bis[2-(ethylthio)ethyl]amine tal-i-C_3H_7 = N-(2-thenylidene)isopropylamine

C_8H_8 = cyclooctatetraene

DPPA = bis(diphenylphosphino)acetylene

tal-CH_3 = N-(2-thenylidene)methylamine

$(Me_2N)_2Et_2S_2$ = bis[2-(N,N-dimethylamino)ethyl] disulphide

CHAPTER 4

Hpymt = pyrimidine-2-thione

mmp = 2-methylthiomethylpyridine

NSSN = 1,6-bis(2-pyridyl)-2,5-dithiahexane

mmtq = 2-methyl-8-methylthioquinoline

A = 1,8-bis(2-pyridyl)-3,6-dithiaoctane

CHAPTER 6

N-R-sal = [N-salicylidenealkylaminato]$^-$

I^1 = N,N′-(1,7,7-trimethylbicyclo[2,2,1] heptane-2,3-diylidene)dianiline

CHAPTER 7

dmedt = 1,2-bis(methylthio)ethylene

dnxdt = 2-methyl-4,5-bis(n-butylthio)toluene

dbedt = 1,2-bis(benzylthio)ethylene

dmmnt = 1,2-bis(methylthio)ethylene dinitrile

SN = 1,2-bis(2-aminophenylthio)ethane

dpd = 1,12-bis(phenylthio)dodecane

pms = phenylmethylsulphide

p-bmtb = 1,4-bis(methylthio)benzene

B) SECTION II

CHAPTER 1

dmpe = 1,2-bis(dimethylphosphino)ethane

o-bmtb = 1,2-bis(methylthio)benzene

pte = 1,2-bis(phenylthio)ethane

bms = benzylmethylsulphide

m-bmtb = 1,3-bis(methylthio)benzene

3,8-dtd = 3,8-dithiadecane

tmdto = 2,2,7,7-tetramethyl-3,6-dithiaoctane

nte = 1,2-bis(p-nitrophenylthio)ethane

dad = 1,12-diaminododecane

2,9-dtd = 2,9-dithiadecane

CHAPTER 2

diphos = 1,2-bis(diphenylphosphino)ethane

L_2^{SMe} = 1,2-tetrakis(methylthio)ethylene

L_2^{SEt} = 1,2-tetrakis(ethylthio)ethylene

Me_4ed = N,N,N',N'-tetramethylethylenediamine

dte = 1,2-bis(p-dimethylaminophenylthio)ethane

mte = 1,2-bis(p-methoxyphenylthio)ethane

tmeda = N,N,N',N'-tetramethylethylenediamine

tn = trimethylenediamine

CHAPTER 3

bi = benzimidazole

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GENERAL INTRODUCTION

The wide distribution of copper containing proteins in plants and animals has stimulated interest[1] in the chemistry of Cu(I) and Cu(II) interactions with ligands containing biologically relevant donor groups. The intrinsic instability of Cu(II) interactions with thioether-sulphur ligands (e.g. tetrahydrothiophene; $\log K^{Cu^{2+}}_{CuL^{2+}} \sim 0.4$)[2] compared to nitrogen donor ligands (e.g. pyridine; $\log K^{Cu^{2+}}_{CuL^{2+}} = 2.54$)[3] and the instability of Cu(II) interactions with thiolate sulphur, have probably been partially responsible for a previous general lack of interest in the study of sulphur-ligand/Cu^{2+} chemistry. However, within the last five years or so, inorganic and bioinorganic chemists have become aware that coordinated cysteine thiolate and/or methionine thioether sulphur are probably responsible for the intense optical absorptions that are observed near 600 nm[4] in the "blue" copper proteins. The realisation that coordinated sulphur can impart such unusual optical properties on a Cu(II) chromophore, has thus resulted in a proliferation of studies into the chemistry of sulphur-ligand/Cu^{2+} interactions.

Widespread investigations into the chemical and physical properties of metal carbonyl complexes have arisen from attempts to understand and explain their bonding, spectroscopic and structural characteristics. However, there has also been an interest in the use of carbonyl complexes as catalysts in the chemical industry and as spectroscopic probes for the characterization and comparison of ligand bonding properties. The bonding characteristics of a particular type of ligand are often more easily interpreted from the study of metal carbonyl complexes. This is because the influence of the ligand on the spectroscopic and chemical properties of the complex can be conveniently studied by a variety of techniques: for example, IR, Raman, electronic, ^{1}H nmr and ^{13}C nmr spectroscopy, and crystallographic and reactivity studies.

Information obtained from the study of metal carbonyl complexes of biologically relevant ligands, can be used in considering the complexes of these or similar ligands with transition metal ions such as Cu(I) and Cu(II). Hence complementary studies, such as those that are described in this thesis, are of direct relevance in attempting to understand the behaviour of related ligands in biological systems.

SECTION I

COMPLEXES OF Cu(II), Cu(I), Co(II), Ni(II), Pd(II) AND Pt(II) WITH LIGANDS CONTAINING THIOETHER SULPHUR.

SECTION I

INTRODUCTION

Physical and chemical investigations into the unusual spectroscopic properties of the "blue-copper" proteins have implicated the binding of at least two histidine nitrogens, a cysteine sulphur and a fourth ligand, which has been proposed to be a methionine thioether sulphur, a tyrosine phenolate or a deprotonated, backbone nitrogen.[5] Furthermore, the results of both theoretical and "model" Cu(II)-complex studies suggested that a distorted tetrahedral Cu(II) geometry was likely.

The crystal structure analysis of oxidised, poplar-leaf plastocyanin[5] which has been recently completed, shows that Cu(II) in this Type I protein[4] has a distorted tetrahedral environment, consisting of two histidine nitrogens, a cysteine sulphur (thiolate) and a methionine sulphur (thioether). According to the Pearson classification of "hard" and "soft" acids and bases,[6] these ligands thus compromise the requirements of the Cu(I) and Cu(II) oxidation states.

The existence of the distorted tetrahedral Cu(II) environment has led Freeman _et al_[5] to suggest that the reduction of poplar-leaf plastocyanin can therefore proceed _without_ significant changes in the coordination environment. On the other hand, the results of crystallographic studies on "model" Cu(II)/Cu(I) complexes have led Rorabacher _et al_[7] to speculate that the reduction of Cu(II) in Cu-Zn superoxide dismutase (in which Cu(II) has a square planar environment of four nitrogen donors[8]) may be accompanied by significant geometric rearrangements at the active site. In each of the three comparative, crystallographic studies that have been reported for Cu(II) and Cu(I) complexes of thioether-containing ligands,[7,9,10,11]

it has been shown that a change in copper oxidation state is accompanied by significant structural changes. However this does not necessarily imply that such changes will be observed in the Cu-proteins because of the constraints that are imposed by the proteins' structure. Small changes may occur and these may be vital for the proteins' function. Such changes in the metal-ligand bonding and/or the coordination geometry of the metal ion (occurring for example, when it changes its oxidation state) may not be detectable by protein crystallography because of the limited resolution.[10] The crystallographic study of low molecular weight complexes containing biologically relevant ligands, is thus important in trying to detect subtle structural changes.

Although transition metal complexes of mixed sulphur-nitrogen ligands have been intensively studied,[12]

little attention has been paid to ligands that will force Cu(II) into accepting a distorted geometry, particularly distorted tetrahedral. Despite the relative ease with which simple, bidentate thioether-sulphur/nitrogen ligands can be synthesized, such studies have been been limited to 8-methylthioquinoline[13] and 2-methyl-8-methylthioquinoline (mmtq).[14] Spectroscopic studies suggested that the latter complexes ($Cu(mmtq)X_2$ where $X=Cl^-, Br^-$) are distorted tetrahedral.[14] No crystallographic studies have been reported for these complexes.

Studies on simple ligand systems such as the 2-alkylthioalkylpyridines, have been limited to some spectroscopic, preparative and stability-constant studies on the Cu(II) complexes of 2-methylthiomethylpyridine.[3,15] No attempt has been made to manipulate the coordination geometry of potential Cu(II) complexes by putting bulky, thioether sidechains in these ligand systems.

The synthetic, crystallographic and spectroscopic studies that are presented in Section I of this thesis were thus carried out for the following reasons:

i) to synthesize structurally distorted, low molecular weight Cu(II) and Cu(I) complexes, using suitably designed, biologically relevant, thioether-nitrogen ligands. Stability constant measurements show that the Cu(II) complexes of both thioether-sulphur and nitrogen donor ligands can be stabilized by the use of the chelate-ligand effect (Table 1). This is a very important factor when trying to isolate stable, but structurally distorted, Cu(II) complexes;

ii) to carry out extensive spectroscopic studies on these complexes; and

iii) to carry out crystallographic studies on a suitable Cu(II)/Cu(I) pair of complexes having similar ligand sets. Before this work was started, no crystallographic studies of this type had been carried out on the complexes of mixed thioether-nitrogen ligands. However, only very recently the crystal structures were reported for a Cu(II)/Cu(I) pair of complexes of 1,8-bis(2-pyridyl)-3,6-dithiaoctane.[11]

The Cu(II) and Cu(I) complexes of the following ligands have thus been considered:

- 2-(3,3-dimethyl-2-thiabutyl)pyridine	tbmp
- 2-(3,3-dimethyl-2-thiabutyl)quinoline	tbmq
- 3-(2-methylthiophenylimino)camphor	I
- 2-ethylthioethylamine	etea
- 2-methylthio-2-imidazoline	mti

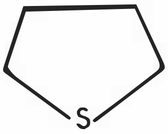
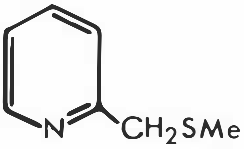
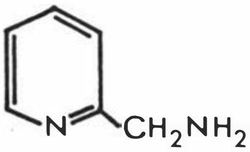
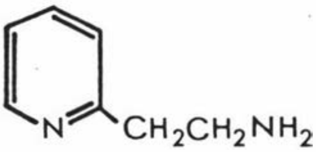
Of these ligands, tbmp, tbmq and I have not been previously synthesized. Although etea and mti are extensively indexed in the chemical literature, the studies on these ligands have been confined to their utilisation in the photographic and pharmaceutical industries.

This study has concentrated on Cu(II) and Cu(I) complexes. However some complementary studies on the Co(II) and Ni(II) complexes of tbmp have also been carried out, in order to assist in the interpretation of the spectroscopic data for the analogous Cu(II) complexes.

Little is known about the effects of electronegative substituents on both the reactivity of thioether ligands and the spectroscopic properties of their transition metal ion complexes. Consequently the reactions of 1,2-bis(pentafluorophenylthio)ethane and ethylthiopentafluorobenzene (both are previously unreported ligands) have been briefly investigated, together with some of the spectroscopic properties of their Pt(II) and Pd(II) complexes.

TABLE 1

STABILITY CONSTANT DATA

LIGAND	$\log K^{Cu^{2+}}_{CuL^{2+}}$	REFERENCE
Pyridine 	2.54	3
Tetrahydrothiophene 	<u>ca</u> 0.40	2
2-methylthiomethylpyridine 	3.27	3
2-methylthioethylamine $CH_3SCH_2CH_2NH_2$	5.30	16
2-aminomethylpyridine 	<u>ca</u> 9.30	16
2-(2-aminoethyl)pyridine 	7.30	16

CHAPTER I

DIMERIC COPPER(II) COMPLEXES OF 2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE (tbmp)

When tbmp is reacted with $CuCl_2.2H_2O$ or $CuBr_2$ in a 1:1 ratio, the dimeric Cu(II) complexes, $[Cu(tbmp)X_2]_2$ where X is Cl^- or Br^-, are formed.

The structure of $[Cu(tbmp)Br_2]_2$ has been determined by X-ray crystallography and the Cu(II) ions are found to have distorted tetragonal pyramidal environments. Molecular weight measurements and electronic, electron spin resonance and far-infrared spectral data, suggest that $[Cu(tbmp)Cl_2]_2$ has a similar structure.

TABLE 2

SUMMARY OF RESULTS - $[Cu(tbmp)X_2]_2$ DIMERS

COMPLEX	STATE	STRUCTURE	PHYSICAL TECHNIQUE
$[Cu(tbmp)Cl_2]_2$	solid	dist. tetrag. pyr. dimer	electronic, far-IR
	CH_2Cl_2 (rm.temp.)	dist. tetrag.pyr. dimer	electronic, M.W. meas.
	(77K)	trig. bipyr. dimer	esr
	MeOH (rm.temp.)	$Cu(tbmp)Cl_2.(MeOH)_n$ and $[Cu(tbmp)Cl.(MeOH)_n]^+$	electronic,conductivity
	(77K,90K)	tetrag.pyr. $[Cu(tbmp)_2Cl]^+$ + $Cu(MeOH)_n{}^{2+}$	electronic, esr
	CH_3NO_2 (77K)	trig.bipyr.dimer	esr
$[Cu(tbmp)Br_2]_2$	solid	dist.tetrag.pyr.dimer	X-ray
	CH_2Cl_2 (rm.temp.)	dist.tetrag.pyr.dimer	electronic,M.W. meas.
	(77K)	dist.tetrag.pyr.dimer	esr
	MeOH (rm.temp.)	$Cu(tbmp)Br_2.(MeOH)_n$ and $[Cu(tbmp)Br.(MeOH)_n]^+$	electronic, conductivity
	(77K, 90K)	tetrag.pyr. $[Cu(tbmp)_2Br]^+$ + $Cu(MeOH)_n{}^{2+}$	electronic, esr

1.1 CRYSTAL STRUCTURE OF BIS[DIBROMO(2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE)-COPPER(II)]

The experimental method that was followed in the elucidation of this structure, is outlined at the end of this Chapter. The observed and calculated structure factors can be found in the Appendices.

A. DESCRIPTION

The complex $[Cu(tbmp)Br_2]_2$ crystallizes as discrete, non-centrosymmetric, dibromo-bridged dimers. Each Copper(II) ion is bound by a chelated tbmp ligand and three bromide ions in a distorted tetragonal pyramidal environment (see Discussion below). The thioether sulphur and pyridyl nitrogen donors of tbmp, a terminal bromide ion and a bridging bromide ion, form the tetrahedrally distorted "basal plane" of each tetragonal pyramid. The apex of each pyramid is formed by a long bond to the bridging, basal bromide ion of the second Cu(II) centre (Figure 1a).

The t-butyl thioether side-chains are directed in such a manner as to apparently block the approach of a sixth ligand towards each Cu(II) ion.

The important structural details for $[Cu(tbmp)Br_2]_2$ can be found in Table 3a .

B. DISCUSSION

Tetragonal Pyramidal vs. Trigonal Bipyramidal Model

Because the complex has a distorted structure, it is not a trivial matter to choose the model which best describes it.

FIGURE 1

Structure of $[Cu(tbmp)Br_2]_2$

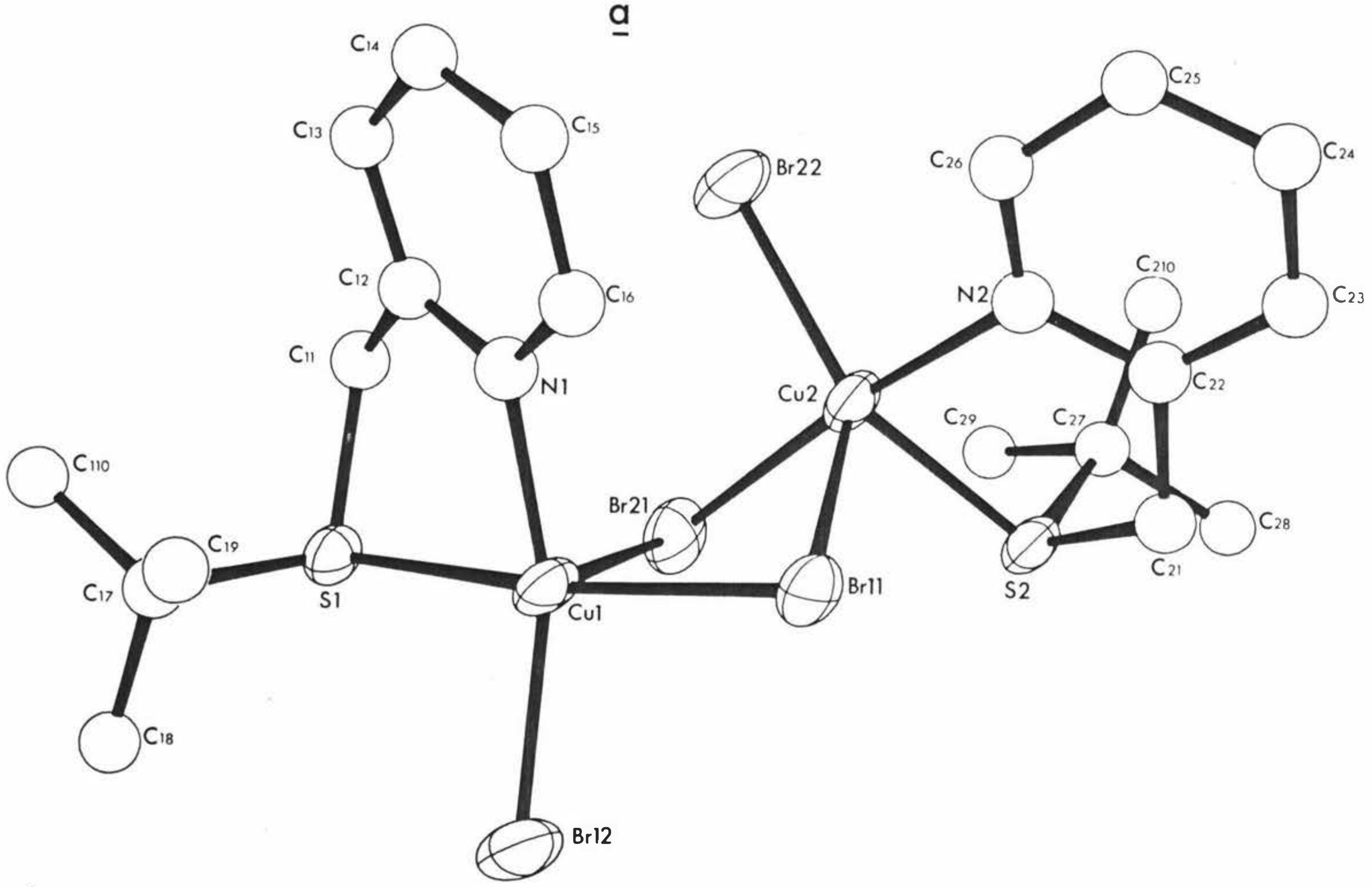


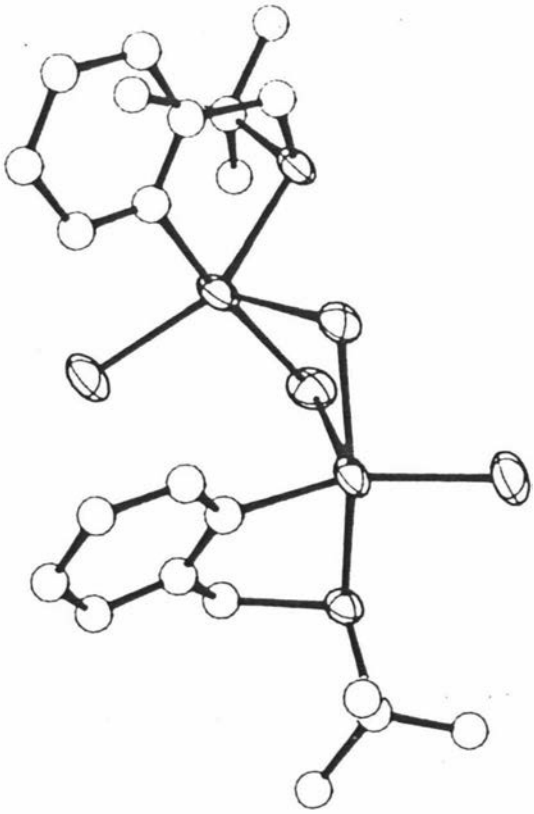
TABLE 3a

STRUCTURAL DETAILS FOR $[Cu(tbmp)Br_2]_2$

FROM ATOM	TO ATOM	DISTANCE/Å	FROM ATOM	TO ATOM	DISTANCE/Å
Cu1	Br11	2.412(3)	N2	C26	1.31(3)
Cu1	Br12	2.356(3)	N2	C22	1.36(3)
Cu1	Br21	2.965(4)	C11	C12	1.48(3)
Cu1	S1	2.353(5)	C12	C13	1.40(3)
Cu1	N1	2.04(2)	C13	C14	1.39(3)
Cu2	Br21	2.417(3)	C14	C15	1.42(3)
Cu2	Br22	2.388(3)	C15	C16	1.41(3)
Cu2	Br11	2.839(4)	C17	C18	1.54(3)
Cu2	S2	2.351(6)	C17	C19	1.56(3)
Cu2	N2	2.08(2)	C17	C110	1.55(3)
Cu1	Cu2	3.591(4)	C21	C22	1.51(3)
Br11	Br21	3.648(3)	C22	C23	1.40(3)
S1	C11	1.84(2)	C23	C24	1.38(3)
S1	C17	1.90(2)	C24	C25	1.41(3)
S2	C21	1.81(2)	C25	C26	1.43(3)
S2	C27	1.84(2)	C27	C28	1.58(3)
N1	C12	1.37(2)	C27	C29	1.58(3)
N1	C16	1.35(3)	C27	C210	1.54(3)

ANGLE	DEGREES	ANGLE	DEGREES
Cu1-Br11-Cu2	85.9(1)	C12-C11-S1	112(1)
Cu1-Br21-Cu2	83.0(1)	N1-C12-C13	122(2)
Br11-Cu1-S1	166.5(2)	N1-C12-C11	117(2)
Br11-Cu1-N1	93.1(5)	C13-C12-C11	121(2)
Br12-Cu1-Br11	93.9(1)	C12-C13-C14	118(2)
Br12-Cu1-Br21	103.4(1)	C13-C14-C15	120(2)
Br12-Cu1-S1	93.5(2)	C14-C15-C16	119(2)
Br12-Cu1-N1	153.9(5)	C15-C16-N1	121(2)
Br21-Cu1-Br11	84.8(1)	C18-C17-C19	114(2)
Br21-Cu1-S1	82.6(2)	C18-C17-C110	108(2)
Br21-Cu1-N1	102.3(5)	C18-C17-S1	103(2)
S1-Cu1-N1	85.1(5)	C19-C17-C110	111(2)
Br21-Cu2-Br11	87.5(1)	C19-C17-S1	111(1)
Br21-Cu2-S2	92.3(2)	C110-C17-S1	108(2)
Br21-Cu2-N2	171.0(5)	C22-C21-S2	113(2)
Br22-Cu2-Br21	92.7(1)	N2-C22-C23	120(2)
Br22-Cu2-Br11	125.3(1)	N2-C22-C21	119(2)
Br22-Cu2-S2	142.1(2)	C21-C22-C23	120(2)
S2-Cu2-Br11	92.4(2)	C22-C23-C24	119(2)
S2-Cu2-N2	85.3(5)	C23-C24-C25	120(2)
N2-Cu2-Br11	83.9(5)	C24-C25-C26	118(2)
N2-Cu2-Br22	94.6(5)	C25-C26-N2	121(2)
C11-S1-C17	106.8(9)	C28-C27-C29	109(2)
C11-S1-Cu1	91.9(7)	C28-C27-C210	108(2)
C17-S1-Cu1	109.7(7)	C28-C27-S2	108(2)
C21-S2-C27	104(1)	C29-C27-C210	113(2)
C21-S2-Cu2	95.4(7)	C29-C27-S2	105(2)
C27-S2-Cu2	106.9(7)	C210-C27-S2	114(2)
C16-N1-C12	120(2)		
C16-N1-Cu1	122(1)		
C12-N1-Cu1	117(1)		
C26-N2-C22	122(2)		
C26-N2-Cu2	120(2)		
C22-N2-Cu2	117(1)		

<u>NOTE</u>: - estimated standard deviations are in parentheses.



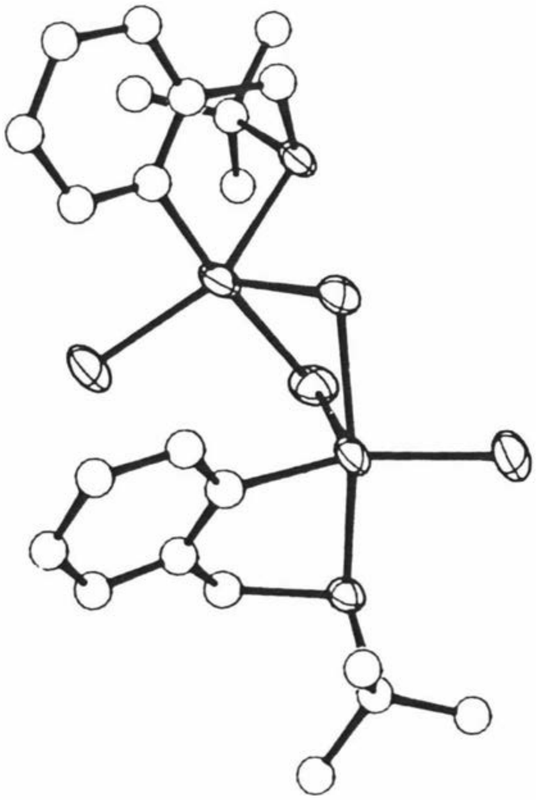


TABLE 3c

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR [Cu(tbmp)Br$_2$]$_2$

ATOM	x/a	y/b	z/c	B/Å^2
Br11	0.7661(3)	0.8560(2)	0.7960(2)	
Br12	0.9556(4)	0.6713(3)	0.6397(2)	
Br21	1.0882(3)	1.0648(2)	0.7433(2)	
Br22	0.7929(3)	1.1728(3)	0.7329(2)	
Cu1	0.8202(3)	0.7898(3)	0.6291(2)	
Cu2	0.8929(3)	1.1144(3)	0.8388(2)	
S1	0.9044(6)	0.7792(6)	0.4843(4)	
S2	1.0794(7)	1.2071(6)	0.9991(4)	
N1	0.625(2)	0.805(2)	0.574(1)	3.0
N2	0.720(2)	1.132(2)	0.922(1)	3.2
C11	0.803(2)	0.877(2)	0.482(2)	3.2
C12	0.640(3)	0.839(2)	0.503(2)	3.6
C13	0.508(3)	0.841(2)	0.453(2)	4.2
C14	0.364(3)	0.817(3)	0.483(2)	5.4
C15	0.348(3)	0.781(3)	0.556(2)	5.5
C16	0.482(3)	0.775(2)	0.599(2)	4.4
C17	0.783(3)	0.605(2)	0.363(2)	4.0
C18	0.906(3)	0.546(3)	0.349(2)	5.4
C19	0.617(3)	0.527(2)	0.376(2)	4.5
C110	0.748(3)	0.615(2)	0.269(2)	4.5
C21	0.921(3)	1.163(2)	1.058(2)	3.6
C22	0.763(3)	1.162(2)	1.021(2)	3.4
C23	0.656(3)	1.181(2)	1.083(2)	4.4
C24	0.507(3)	1.170(2)	1.044(2)	5.2
C25	0.462(3)	1.137(2)	0.941(2)	5.3
C26	0.577(3)	1.117(2)	0.881(2)	4.4
C27	1.165(3)	1.388(2)	1.069(2)	3.6
C28	1.272(4)	1.452(3)	1.184(2)	7.4
C29	1.284(4)	1.425(3)	1.008(2)	6.9
C210	1.034(3)	1.438(3)	1.079(2)	6.6

- estimated standard deviations are in parentheses.

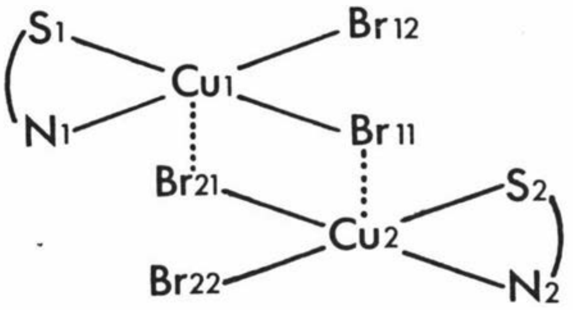
TABLE 3d

ANISOTROPIC THERMAL PARAMETERS FOR [Cu(tbmp)Br$_2$]$_2$

ATOM	B11	B22	B33	B12	B13	B23
Br11	0.0178	0.0124	0.0049	0.0088	0.0052	0.0063
Br12	0.0333	0.0230	0.0081	0.0223	0.0095	0.0112
Br21	0.0148	0.0143	0.0052	0.0072	0.0046	0.0060
Br22	0.0212	0.0152	0.0063	0.0099	0.0030	0.0077
Cu1	0.0143	0.0126	0.0046	0.0089	0.0041	0.0062
Cu2	0.0132	0.0136	0.0039	0.0081	0.0031	0.0056
S1	0.0106	0.0095	0.0037	0.0056	0.0027	0.0040
S2	0.0120	0.0128	0.0042	0.0075	0.0028	0.0056

i) <u>Cu1 Environment</u>: The angles that are subtended at Cu1 by any two of the <u>cis</u>-coordinated atoms in the Br11, Br12, S1, N1 basal plane, [N1-Cu1-Br11 (93°), N1-Cu1-S1 (85°), S1-Cu1-Br12 (93°) and Br12-Cu1-Br11(94°)] do not represent a large distortion from an ideal tetragonal pyramidal model. The long Cu1-Br21 bond (2.96 Å) and the displacement of Cu1 (-0.11 Å i.e. towards Br21) from the Br11, Br12, S1, N1 basal plane, (Table 3b) are consistent with Br21 being the apex of this tetragonal pyramid.

The equatorial planes that are possible for a trigonal bipyramidal Cu1 environment, are S1, Br21, Br11 and N1, Br 21, Br12 respectively. In the former "plane", S1-Cu1-Br11 (166°) and S1-Cu1-Br21 (83°) are both distorted by about 40° from an ideal geometry. In the N1, Br21, Br12 "plane", N1-Cu1-Br21 (102°) and Br12-Cu1-Br21 (103°) are intermediate between ideal trigonal bipyramidal and square pyramidal geometries. However, N1-Cu1-Br12 (154°) is significantly distorted and the "axial" Cu1-Br11 bond 2.412(3)Å is longer than the "equatorial" Cu1-Br12 bond 2.356(3)Å. The latter observation is contrary to that which is expected for trigonal bipyramidal d^9 complexes.[17,18]



ii) Cu2 Environment: Similar arguments can be applied in considering the Br21, Br22, S2, N2 basal plane of a tetragonal pyramidal model, in which the long Cu2-Br11 bond [2.839(4) Å] forms the apex of the pyramid. The Cu2 atom is displaced by 0.31 Å (Table 3b) out of the basal plane, towards Br11.

The most obvious equatorial plane of a trigonal bipyramidal model, would be defined by Br22, Br11 and S2. However, while Br22-Cu2-Br11 (125°) is consistent with this model, Br22-Cu2-S2 (142°) and Br11-Cu2-S2 (92°) are very distorted. The angles subtended at Cu2 [Br22-Cu2-N2 (171°), N2-Cu2-Br11 (84°), Br21-Cu2-Br11 (87°)] in the equatorial plane (Br21, Br11,N2) of the second trigonal bipyramidal model that is possible, are also very distorted.

The following discussion is thus based on the premise that the geometries of both Cu1 and Cu2 can be best described as being distorted tetragonal pyramidal.

Distortions in the Cu1 and Cu2 Environments

The extent of the tetrahedral distortions in the environments of Cu1 and Cu2 is shown by the dihedral angles*($w_1 = 28.9^{\circ}$ and $w_2 = 38.8^{\circ}$ respectively; these would be 0° for a square planar structure or 90° for a tetrahedral structure) and the displacements of the basal atoms from their mean least-squares planes (Table 3b).

---

* w_1 is defined by the planes through Cu1, S1, N1 and Br11, Br12, Cu1 while w_2 is defined by the planes through Cu2, S2, N2 and Br21, Br22, Cu2. See end of Chapter for equations.

TABLE 3b

ATOMIC DISPLACEMENTS FROM BASAL PLANES

Plane 1: Defined by Br11, Br12, S1, N1
Equation: $-0.3836X-0.7707Y-0.5089Z = 8.4320$

Plane 2: Defined by Br21, Br22, S2, N2
Equation: $-0.1179X-0.8940Y-0.4323Z = 10.8696$

BASAL PLANE	DISPLACEMENTS FROM PLANE (Å)
Plane 1	Br11[-0.350(3)], Br12[0.321(4)], Cu1[-0.112(3)], S1[-0.390(7)], N1[0.42(2)], Br21[-3.074(3)], Cu2[-2.729(3)]
Plane 2	Br21[0.400(3)], Br22[-0.428(3)], Cu2[0.313(4)], S2[-0.476(8)], N2[0.50(2)], Br11[3.025(3)], Cu1[3.268(4)]

The displacement of Cu1 and Cu2 out of their respective basal planes, towards their apical bromide ligands, is a normal observation for tetragonal pyramidal Cu(II) complexes.[19]

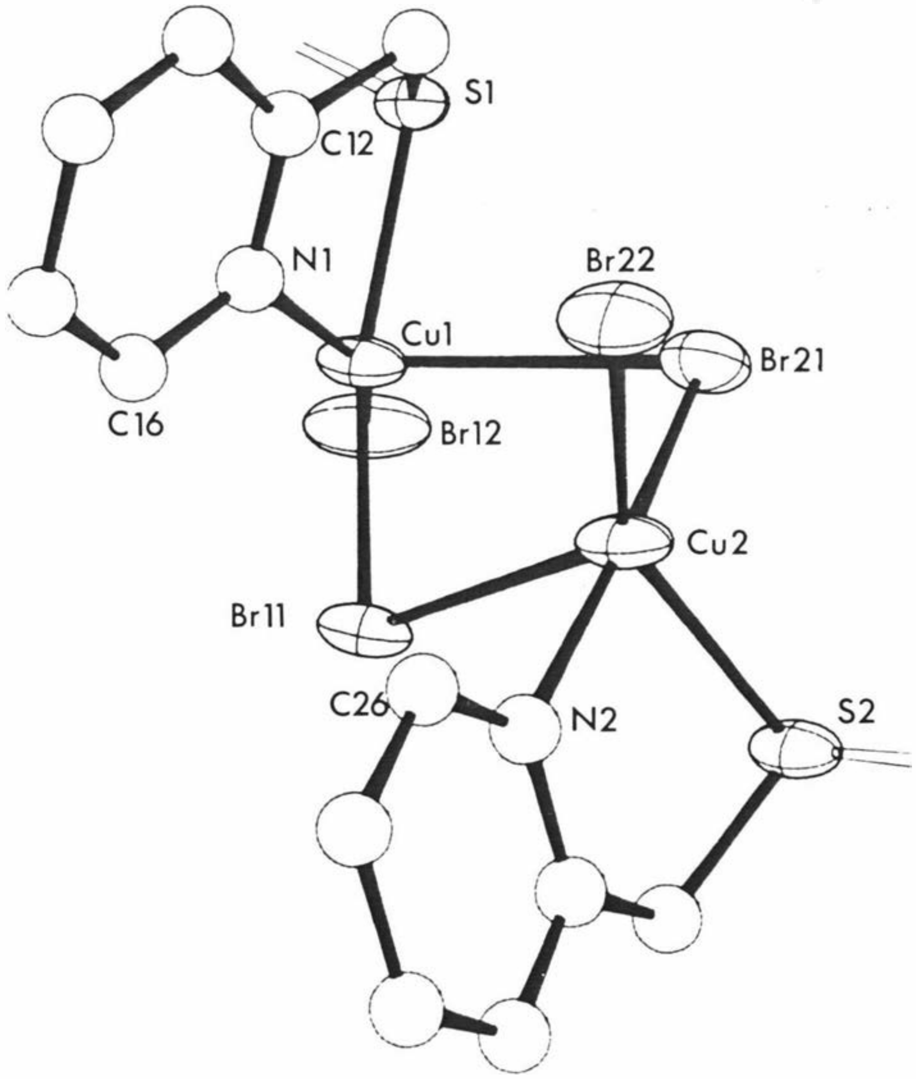
Possible Reasons For These Distortions.

In most square pyramidal complexes, the basal donor atoms are either coplanar (with the Cu(II) ion being displaced out of this plane, towards the fifth ligand), or only moderate distortions from planarity are observed.[19,20,21]

The large tetrahedral distortions that are seen in this complex are not unknown however. For example, in $[Cu(BBTE)Cl_2]_2$[18] (bis[dichloro(5,8-dithiadodecane)-copper(II)]) deviations from 0.41 Å to 0.68 Å are observed.

Electronic and electron spin resonance spectral investigations (see 1.2 and 1.3 respectively) suggest

1b



that the distortions also exist in solution and in various glasses at 77K. These observations thus imply that crystal packing forces can be ruled out as the source of the distortions in the solid state. This is also suggested by the observation that there are only two intermolecular contacts of less than 3.6 Å. These are Br12(x,y,z)...C18(1-x,$\bar{y}$,$\bar{z}$)[3.57 Å] and C23(x,y,z)....C24($\bar{x}$,1-y,1-z)[3.59 Å.] Neither of these contacts could explain the distortions in the structure of [Cu(tbmp)Br$_2$]$_2$.

i) <u>The Cu1-Br21 Bond</u>: This bond (2.965(4) Å) is about 0.13 Å longer than the corresponding Cu2-Br11 bond (2.839(4) Å) and it can be seen that its length will be limited by steric interactions between Br22 and C12 (Figure 1b) of the N1, C12-16 pyridyl ring. The Br22....C12 non-bonded contact (3.62 Å) in the present structure corresponds to the sum of the van der Waals radius of Br (1.95 Å)[22] and the half thickness (1.7 Å) of an aromatic ring system.[22] The two halves of the dimer cannot therefore, be brought any closer by a contraction in the Cu1-Br21 bond. Because the dimer is not symmetrical, there are no analogous steric restrictions on the length of the Cu2-Br11 bridging bond.

ii) <u>Tetrahedral Distortions in the Br11,Br12,S1,N1 Basal Plane</u>

The Br11...C16 contact (3.30 Å) within the Cu1(tbmp)Br$_2$ monomer, is about 0.30 Å closer than the normal van der Waals contact (<u>ca</u> 3.65 Å)[23] and it can be calculated that the Br11....C16 contact would be about 3.1 Å in an undistorted structure. Such a close contact (3.1 Å) would be quite unacceptable when it is considered that in $Cu(\alpha\text{-picoline})_2Cl_2$[24] an analogous Cl....C contact of 3.34 Å (van der Waals contact = 3.50 Å) results in significant distortions in the ∝-picoline ring that is involved.

It is apparent therefore, that the Cu1, S1, N1 plane in $[Cu(tbmp)Br_2]_2$ has twisted (Figure 1b) in order to minimize potential Br11....C16 interactions. The extent of this twisting is limited by the Br22....C12 contact that was discussed above. The corresponding twist of the Cu1, Br11, Br12 plane (in the opposite direction) thus also helps to bring the bridging Br11, closer to Cu2.

As a result of these distortions, N1-Cu1-Br21 (102^{o}) is increased and S1-Cu1-Br21 (83^{o}) is reduced from an ideal 90^{o} while S1-Cu1-Br11 (166^{o}) and N1-Cu1-Br12 (154^{o}) are significantly reduced from an ideal 180^{o}.

iii) Tetrahedral Distortions in the Br21, Br22, S2, N2 Basal Plane

The distortions are analogous to those that are observed in the Br11, Br12, S1, N1 basal plane. In an undistorted structure, the Br22....C26 contact (Figure 1a) would be about 3.0 Å as opposed to 3.26 Å in the present structure. The Cu2, S2, N2 and Cu2, Br21, Br22 planes must therefore undergo tetrahedral distortions in order to reduce this interaction. The twisting of the Cu2, Br21, Br22 plane again helps to bring the bridging Br21, closer to Cu1.

The result of these effects is that S2-Cu2-Br22 (142°) is significantly reduced from an ideal 180° and the Br22-Cu2-Br11 angle (125°) is increased by 35°. The remaining angles are only slightly distorted.

The tetrahedral distortions thus arise from attempts to minimise non-bonded contacts within each Cu(tbmp)Br_2 monomer. However, they also have the effect of bringing the bridging Br atoms (Br11 and Br21 respectively) closer to the opposing Cu atoms.

Other Intramolecular Contacts

The Br....Br, Br....S, Br....N and Br....CH_3 contacts in this molecule can be ruled out as possible sources of major distortions.

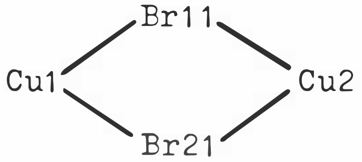
i) Br....Br contacts: The closest Br....Br intramolecular contact (Br21....Br22, 3.48 Å) is about 0.5 Å less than the sum of the van der Waals radii (3.90 Å).[22] However there is no evidence for anything other than a very minor effect on the Br22-Cu2-Br21 angle (93°). A comparable Br....Br contact (ca 3.40 Å) in the structure of dibromo-[2-(aminomethyl)pyridine]copper(II)[25] does not produce any major distortions either (Br-Cu-Br, 92°).

ii) Br....S contacts: The closest Br....S contact (Br12....S1, 3.43 Å) would be about 3.33 Å (van der Waals contact, 3.80 Å)[22] if the geometry about Cu1 was perfectly tetragonal pyramidal. However the difference (0.10 Å) is only minor. It is of interest to note that the Br21....S1 contact (3.54 Å) has been reduced from the 3.78 Å contact that would occur in an undistorted structure. This suggests that potential Br....S interactions do not play a very important role in determining the over all structure.

iii) Br....N contacts: These have been observed in the range from 3.10 to 3.20 Å in complexes such as dibromobis(2-methylpyridine)copper(II),[23] dibromo[2-(2-aminoethyl)pyridine]copper(II),[26] and dibromobis(2,3-dimethylpyridine)copper(II).[27] On the basis of these observations, the closest Br....N contact (Br11....N1, 3.25 Å) in $[Cu(tbmp)Br_2]_2$, can not be regarded as being severe.

iv) Br....CH_3 contacts: The closest Br....CH_3 contact (Br12....C18, 3.86 Å) is not significantly less than the sum of the Br and CH_3 van der Waals radii (3.95 Å)[22] and it is comparable to the contacts (3.82 Å, 3.79 Å) that are observed for dibromobis(2-methylpyridine)copper(II).[23]

Other Structural Features

The Cu(II)-Br bonding within the 

bridge (Table 3a) and the angles that are subtended at the bridging bromide ions (Cu1-Br11-Cu2=85.9(1)° and Cu1-Br21-Cu2=83.0(1)°) appear to be normal for this type of tetragonal pyramidal dimer, as is the Cu1....Cu2 separation [3.591(4) Å]. Relevant comparisons are made in Table 4a.

The chelate bite [85.2(5)°] is slightly greater

TABLE 4a

CRYSTALLOGRAPHIC DATA; BROMO-BRIDGED, DIMERIC Cu(II) COMPLEXES

COMPLEX	TERMINAL Cu-Br	BRIDGING Cu-Br	$Cu-\hat{Br}-Cu$	Cu....Cu	REFERENCE
$[Cu(tbmp)Br_2]_2$	2.356(3)	2.412(3)	85.9(1)	3.591(4)	This Work
	2.388(3)	2.417(3)	83.0(1)		
		2.965(4)			
		2.839(4)			
$[Cu(dmen)Br_2]_2$	2.401(1)	2.463(2)	83.71(5)	3.570(3)	19
		2.868(2)			
$[Cu(\alpha\text{-pic})Br_2]_2$	2.413(3)	2.426(3)	100.4(1)	4.926(6)	23
		3.872(5)			
$[Cu(tmen)Br_2]_2$	2.40	2.42	95.6(5)	4.20	28
		3.20			
Φ $[Cu(maep)Br_2]_2$	2.400(3)	2.468(2)	92.14(9)	3.803(4)	29
		2.802(4)			

Φ trigonal bipyramidal Cu(II), remaining complexes are tetragonal pyramidal.

\- bondlengths are Å, angles in degrees.

than the chelate bite of 2-aminomethylpyridine in one of its Cu(II) complexes [82.8(3)°] [25] but it is within the range (74-86°) observed for other rigid five-membered chelate ring systems.[25]

The chelate rings are puckered in a manner similar to that of the chelate ring in $Cu(tbmp)_2Br$ (see Chapter 3). In the Cu1, S1, N1, C11, C12 chelate ring, Cu1, N1, C11 and C12 are coplanar (see below), But S1 lies 0.851(6) Å out of the Cu1, N1, C11, C12 least-squares plane. Similarly, in the Cu2, S2, N2, C21, C22 chelate ring, S2 lies 0.650(8) Å out of the Cu2, N2, C21, C22 least-squares plane. Cu2, N2, C21 and C22 are also coplanar.

ATOMS IN PLANE	DEVIATIONS FROM PLANE (Å)				
<u>Equation</u>: $0.1023X - 0.6203Y - 0.7777Z = -8.5448$					
Cu1, N1, C11, C12	Cu1	N1	C11	C12	S1
	0.014(3)	-0.03(2)	-0.02(2)	0.04(3)	0.851(6)
<u>Equation</u>: $-0.0182X - 0.9102Y - 0.4138Z = -10.2334$					
Cu2, N2, C21, C22	Cu2	N2	C21	C22	S2
	-0.014(4)	0.04(2)	0.02(3)	-0.04(3)	-0.650(8)

The Cu(II)-S Bonding

The Cu(II)-S bonds (mean 2.352(6) Å) in $[Cu(tbmp)Br_2]_2$ are within the range (2.303(1) - 2.488(3) Å) observed for equatorial Cu(II)-S (thioether) bonding. (Table 4b). The Cu1-S1 and Cu2-S2 bonds of $[Cu(tbmp)Br_2]_2$ can be regarded as being essentially single bonds as an equatorial Cu(II)-S(thioether) single bond is calculated to be about 2.34 Å [assuming the covalent radius of S to be 1.04 Å[22] and the in-plane radius of Cu(II)[30] to be about 1.30 Å] . It is evident from Table 4b that Cu(II)-S bonds significantly longer than ca 2.34 Å are found. These may arise from unusual constraints that are imposed by specific ligands.

The mean of the equatorial Cu(II)-S bondlengths for Cu(II)-thioether complexes (Table 4b) is 2.342(2) Å. The difference between this mean and the Cu1-S1 (2.353(5) Å) and Cu2-S2 (2.351(6) Å) bonds of $[Cu(tbmp)Br_2]_2$, is insignificant.

On comparing the tetrahedrally distorted Cu(II)-S (thioether) bonding in $[Cu(tbmp)Br_2]_2$ and $[Cu(BBTE)Cl_2]_2$ (Cu(II)-S = 2.308(2), 2.369(2) Å),[18] with that of other Cu(II)-thioether complexes, there is no evidence to suggest that the Cu(II)-S bonding could have been weakened as a result of the tetrahedral distortions in these structures. Hence although in complexes such as $Cu(dth)_2(BF_4)_2$ (mean Cu(II)-S = 2.317(2) Å),[10] $CuL^3(ClO_4)_2$ (mean = 2.303(1) Å),[9] and $[Cu(pdto)ClO_4]ClO_4$ (mean = 2.313(2) Å),[11] it is apparent that the Cu(II)-S bonds are shorter than in $[Cu(tbmp)Br_2]_2$ and $[Cu(BBTE)Cl_2]_2$, longer Cu(II)-S equatorial bonds are found in complexes such as $CuL^4(ClO_4)_2$ (mean = 2.366(1) Å)[33] and CuL^2Cl_2 (Cu(II)-S=2.410(5) Å).[32]

TABLE 4b

Cu(II)-S(thioether) BONDLENGTH DATA

COMPLEX	MEAN Cu(II)-S/Å	STRUCTURE	REFERENCE
$[Cu(tbmp)Br_2]_2$	2.352(6)	Tetr. pyr.	This Work
$Cu(dth)_2(BF_4)_2$	2.317(2)	*trans*-tetr.	10
$[Cu(L^0)ClClO_4]_2$	2.438(6)	Dist.oct./dist.sq.pyr.	21
	2.587(6) ax.		
CuL^1Cl_2	2.341	Dist.tetr.pyr.	31
CuL^2Cl_2	2.410(5)	Dist.sq.pyr.	32
$CuL^3(ClO_4)_2$	2.303(1)	*trans*-tetr.	9
$CuL^4(ClO_4)_2$	2.366(1)	*trans*-tetr.	33
$[Cu(BBTE)Cl_2]_2$	2.338(2)	Tetr.pyr.	18
$[Cu(pdto)ClO_4]ClO_4$	2.313(2)	Tetr.pyr.	11
$[Cu(EEE)(1\text{-}MeIm)](ClO_4)_2$	2.414(2)	Tetr.pyr.	34
	2.560(2) ax.		
CuL^5	2.488(3)	Dist.tetr.	35
	2.607(2) ax.		
$[Cu_2L^6]^{4+}$	2.318(1)	Dist.tetr.pyr.	36
$[CuL^7](ClO_4)_2$	2.312(4)	Tetr.pyr.	37

NOTES: - ax. = axial, all other Cu(II)-S bonds are equatorially disposed.

TABLE 4c

Cu(II)-N(pyridyl) BONDLENGTH DATA

COMPLEX	MEAN Cu(II)-N	STRUCTURE	REFERENCE
$[Cu(tbmp)Br_2]_2$	2.06(2)	Tetr.pyr.	This Work
$[Cu(aep)_2Br]Br$	2.065(3)	Intermediate 5-coord.	38
$Cu(dmaep)Cl_2$	2.007(3)	Dist.tetrahedral	39
$[Cu(pdto)ClO_4]ClO_4$	2.010(5)	Tetr.pyr.	11
$Cu(aep)_2(ClO_4)_2$	2.024(2)	*trans*-tetr.	40
$Cu(\alpha\text{-}pic)_2Br_2$	1.982(6)	Tetr.pyr.	23
$Cu(amp)Br_2$	2.011(9)	Tetr.elongated oct.(poly.)	25
$Cu(\alpha\text{-}pic)X$	2.16(1) ax.	Tetr.pyr.	41

NOTES: - X = chloroacetate; ax. = axial

In all of these complexes, the coordinated thioether sulphur atoms are either equatorially coplanar, or they are distorted by no more than 0.07 Å from their respective equatorial planes.

The Cu(II)-N Bonding

While the Cu1-N1 and Cu2-N2 bonds (mean, 2.06(2) Å) of $[Cu(tbmp)Br_2]_2$ are longer than those of other Cu(II) complexes of substituted pyridyl ligands (Table 4c), the differences are not statistically significant. The Cu(II)-N bonds in this structure can be regarded as being single bonds as the equatorial Cu(II)-N single-bond is calculated to be about 2.04 Å (taking the in-plane radius of Cu(II) as 1.30 Å[30] and the single-bond covalent radius of N as 0.74 Å[22]).

As with the Cu(II)-S bonding, there is no evidence to suggest that the tetrahedral distortions seen here, have any significant effect on the Cu(II)-N bonding. This is supported by the fact that the Cu(II)-N bonds in the distorted tetrahedral monomer $Cu(dmaep)Cl_2$ (2.007(3) Å),[39] and in the tetragonal complex $Cu(aep)Br_2$[26] (2.021(5) Å; the coordinated pyridyl-nitrogen atoms are distorted from the equatorial, mean least-squares plane by up to 0.38 Å), are indistinguishable from those of complexes such as $[Cu(pdto)ClO_4]ClO_4$[11] (2.011(5), 2.008(5) Å) and $Cu(amp)Br_2$ (2.011(9) Å).[25] The latter complexes exhibit planar, equatorial Cu(II)-N bonding.

1.2 ELECTRONIC SPECTRA

The tentative assignments for the spectral maxima have been made by comparing the spectra of $[Cu(tbmp)X_2]_2$ with the spectra of the complexes that are discussed in subsequent chapters. Comparisons have also been made with published data, where they are relevant.

The spectra and the assignments are presented in Table 5a.

A) LIGAND FIELD TRANSITIONS

Introduction

The d^9 configuration of Cu(II) can theoretically give rise to a maximum of four d-d transitions but in the majority of complexes, it is usual for only one or two to be observed.[42,43] The single, unpaired electron of the e_g ground state will usually be found in either the $d_{x^2-y^2}$ or d_{z^2} orbital, depending on the stereochemistry of the complex. The largest proportion of complexes have a $d_{x^2-y^2}$ ground state[30], as these complexes have stereochemistries that can be derived from a basic tetragonal stereochemistry. However, considerable overlap occurs between the d-d transition energies of the various basic geometries and as a consequence, it is dangerous to draw conclusions about the structure of a complex on the basis of the electronic spectra alone.[44,45] Where it is possible, additional physical data such as the esr spectra, which can give information on the electronic ground state with greater certainty, and infrared spectra should also be considered.

It is in the interpretation of the degree of tetragonal distortion, that d-d absorption energies become valuable. Increasing the tetragonal distortion shifts the centre of gravity of the transitions to higher energies.[44]

The Spectra of $[Cu(tbmp)Br_2]_2$ and $[Cu(tbmp)Cl_2]_2$

i) Reflectance: The crystal structure of $[Cu(tbmp)Br_2]_2$ shows that the Cu(II) ions have a very distorted tetragonal pyramidal environment in which the basal atoms have undergone significant tetrahedral distortions. As a consequence of these distortions, the ligand field maximum (840 nm) is at quite low energy when compared to other complexes of this type, such as $Cu(\alpha\text{-picoline})_2Br_2$ (604 nm).[23,46]

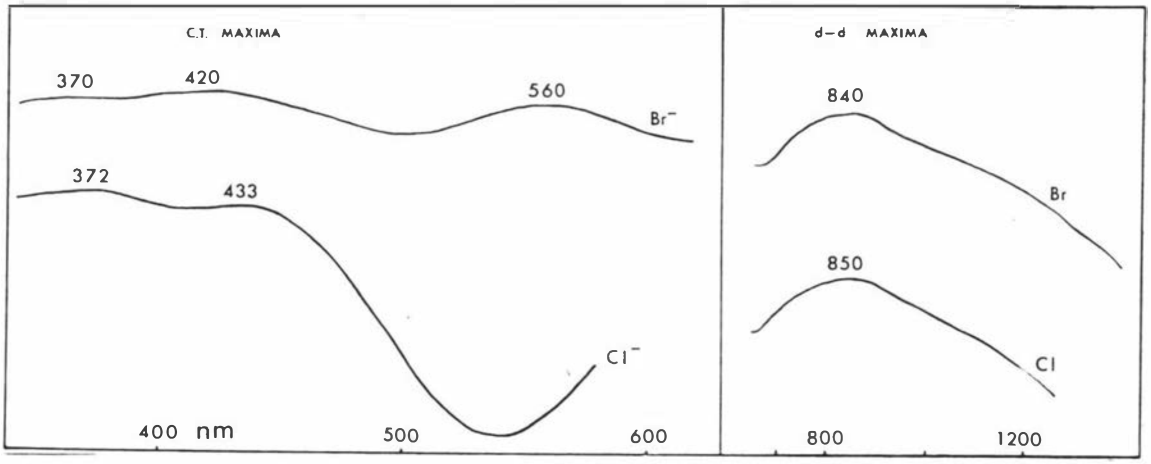
While there are no other known examples of $CuSNX_3$ five-coordinate chromophores with which comparisons can be made, $[Cu(BBTE).2Cl]_2$, (BBTE = 5,8-dithiadodecane) which is a distorted tetragonal pyramidal CuS_2Cl_3 dimer, has a ligand field maximum at about 800 nm, (mull, 80K).[18,47]
$[Cu(tbmp)Cl_2]_2$ has a reflectance spectrum similar to that of $[Cu(BBTE).2Cl]_2$ and $[Cu(tbmp)Br_2]_2$ and it is also dimeric in non-coordinating solvents. These observations are consistent with $[Cu(tbmp)Cl_2]_2$ having a structure similar to that of the bromide complex in the solid state.

The reflectance spectra of these complexes (Figure 2a), are in agreement with the criteria that were recently suggested for distinguishing between square pyramidal and trigonal bipyramidal

FIGURE 2

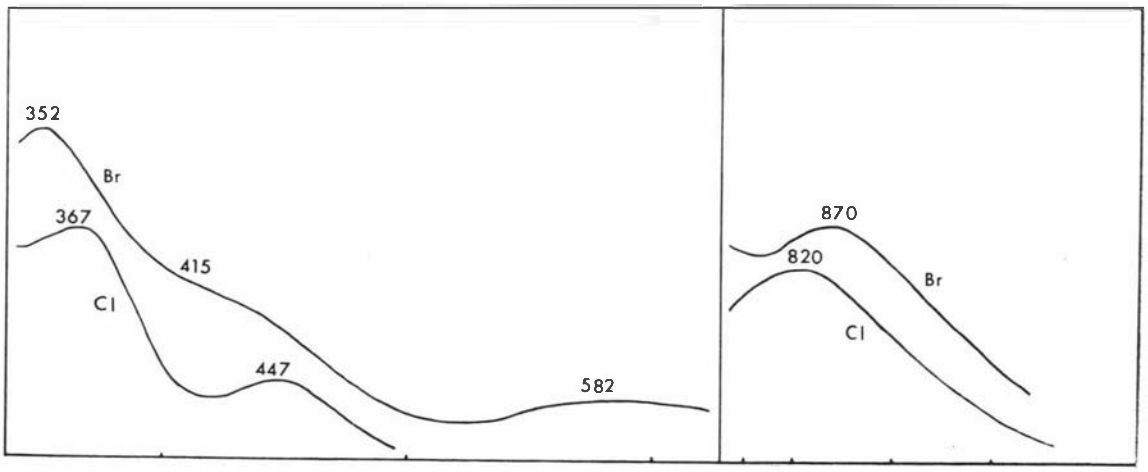
Electronic Spectra - $[Cu(tbmp)X_2]_2$ Dimers

2a



Reflectance

2b

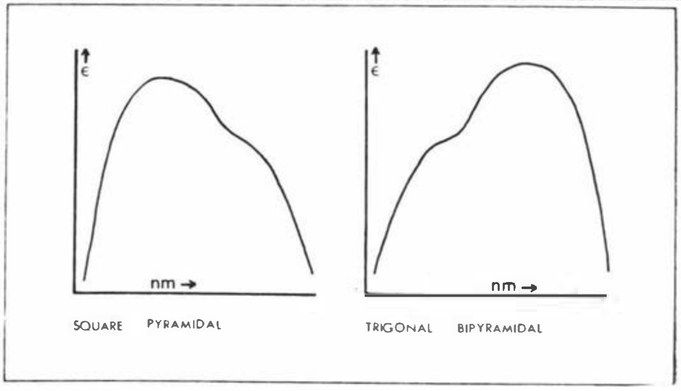


Dichloromethane solution

structures. From a study of $[CuN_5]^{2+}$ chromophores, Hathaway et al[48] noted that the lower energy transition of square pyramidal stereochemistries will be less intense than the main band, while in trigonal bipyramidal structures, the lower intensity shoulder will be blue-shifted in relation to the main absorption band as shown in Figure 2c.

FIGURE 2c

LIGAND FIELD MAXIMA OF FIVE-COORDINATE Cu(II) COMPLEXES.



It has also been suggested that d-d transitions for square pyramidal complexes are found in the general region from 550-670 nm while for trigonal bipyramidal structures, they are found from about 800-850 nm.[49] However, a limited number of examples taken from the literature (Table 5b) show that there is an overlap between these two extremes.

ii) Dichloromethane: The spectra in this solvent (Figure 2b) are very similar to the reflectance spectra and the dimeric nature of the complexes in chloroform (Table 8) implies that the distorted five-coordinate structures are being retained.

On the basis of Hathaway's criteria, the $[Cu(tbmp)X_2]_2$ dimers are more likely to have distorted tetragonal pyramidal structures in dichloromethane.

TABLE 5a

ELECTRONIC SPECTRA, $[Cu(tbmp)X_2]_2$ COMPLEXES

COMPLEX	REFLECTANCE	ASSIGNMENT	CH_2Cl_2 (ϵ)	ASSIGNMENT	MeCN (ϵ)	ASSIGNMENT
$[Cu(tbmp)Cl_2]_2$			292(5452)	apical$Cl^- \rightarrow Cu(II)$		
			ca 354(sh)	$\sigma(S) \rightarrow Cu(II)$	357(1177)	$\sigma(S) \rightarrow Cu(II)$
	372		367(3000)	$Cl^- \rightarrow Cu(II)$		
	433	$Cl^- \rightarrow Cu(II)$	447(1133)	$Cl^- \rightarrow Cu(II)$		
	850†	LF	820(308)†	LF	850(144)†	LF
$[Cu(tbmp)Br_2]_2$			*ca* 320(sh)	apical $Br^- \rightarrow Cu(II)$	309(2062)	$Br^- \rightarrow Cu(II)$
	ca 370(sh)		352(5097)	$\sigma(S) \rightarrow Cu(II)$	358(1276)	$\sigma(S) \rightarrow Cu(II)$
	420	$Br^- \rightarrow Cu(II)$	*ca* 415	$Br^- \rightarrow Cu(II)$		
	560	$Br^- \rightarrow Cu(II)$	582(631)	$Br^- \rightarrow Cu(II)$		
	840†	LF	870(391)†	LF	850(267)†	LF

NOTES: - absorption maxima are nm.; extinction coefficients are $l.mol.^{-1}$ $cm.^{-1}$

- sh = shoulder; LF = Ligand Field

† = asymmetric

- tbmp has intense intra-ligand charge transfer absorptions at about 265 nm.

TABLE 5b

ELECTRONIC SPECTRA OF 5-COORDINATE Cu(II) COMPLEXES

COMPLEX	LF MAXIMA	STATE	REFERENCE	
TETRAGONAL PYRAMIDAL			X-Ray	Spectrum
$Cu(\alpha\text{-pic})_2Cl_2$	517(sh),585, 625(sh)	Refl.	24	46
$Cu(\alpha\text{-pic})_2Br_2$	604	Refl.	23	46
$[Cu(tmen)Cl_2]_2$	ca 675	Mull, 80K	47	47
$[Cu(BBTE)Cl_2]_2$	ca 800	Mull, 80K	18	47
$[Cu(tmen)SO_4.(H_2O)_2].H_2O$	676	Mull	50	50
TRIGONAL BIPYRAMIDAL				
$Cu(pib)tu(ClO_4)_2$	670	Refl.	51	52
$Cu(dip)_2tu(ClO_4)_2$	770	Refl.	51	52
$[Cu(tren)NCS]SCN$	680(sh),840	Refl.	53	54
$[Cu(bipy)_2I]I$	800	Refl.	55	56
$Cu(NH_3)_2Ag(SCN)_3$	690(sh),781	Refl. 80K	57	54

NOTES: - LF maxima are nm.

- sh = shoulder

TABLE 5c

C.T. ASSIGNMENTS FOR $[Cu(tbmp)X_2]_2$ AND $[Cu(BBTE)X_2]_2$.

COMPLEX	C.T. MAXIMA/nm	ASSIGNMENT
$[Cu(BBTE)Cl_2]_2$	363	$Cl^- \longrightarrow Cu(II)$
	449	$\sigma(S) \longrightarrow Cu(II)$
$[Cu(tbmp)Cl_2]_2$	ca 354(sh)	$\sigma(S) \longrightarrow Cu(II)$
	367	$Cl^- \longrightarrow Cu(II)$
	447	$Cl^- \longrightarrow Cu(II)$
ϕ $[Cu(BBTE)Br_2]_2$	358(sh)	$Br^- \longrightarrow Cu(II)$
	ca 420	$\sigma(S) \longrightarrow Cu(II) + Br^- \longrightarrow Cu(II)$
	544	
$[Cu(tbmp)Br_2]_2$	352	$\sigma(S) \longrightarrow Cu(II)$
	ca 415	$Br^- \longrightarrow Cu(II)$
	582	$Br^- \longrightarrow Cu(II)$

NOTE: ϕ mull data (80K) for this complex, otherwise CH_2Cl_2 solution.

iii) Methanol: The disappearance of the charge transfer absorptions that are assigned to "in-plane" Cu-X ($X=Cl^-$, Br^-) bonding, (see below), indicates that the dimeric structure is not retained. Partially solvated species such as $Cu(tbmp)X_2.(MeOH)_n$ and $[Cu(tbmp)X.(MeOH)_n]^+$ would account for the low energy, ligand field maxima (850 nm for both complexes) and the partial electrolytic behaviour (Table 8) of the complexes in this solvent. Thus,

$[Cu(tbmp)X_2]_2 \xrightarrow{MeCH} Cu(tbmp)X_2.(MeCH)_n$ and

$[Cu(tbmp)X.(MeOH)_n]^+$

where n= 1 or 2.

B) CHARGE TRANSFER TRANSITIONS (L ⟶ Cu(II))

Introduction[43]

Ligand ⟶ Cu(II) charge transfer spectra are more easily interpreted and are better understood than L ⟶ Co(II) and L ⟶ Ni(II) charge transfer spectra. In the latter group, transitions to metal states that have different interelectronic repulsion parameters result in a greater number of overlapping L ⟶ M(II) charge transfer transitions.

Halogen ligands and thioether sulphur donors have σ and π-symmetry lone pair electrons and as a consequence, two types of L ⟶ Cu(II) charge transfer absorption can theoretically be observed:

i) $\sigma \longrightarrow$ singly occupied Cu(II) d-orbital, and

ii) $\pi \longrightarrow$ singly occupied Cu(II) d-orbital.

If more than one ligand is bound to Cu(II) or if spin-orbit coupling is sufficient to lift the degeneracy of some of the orbitals, several absorptions of a specific type may be observed.

Where the ligands do not have any π-symmetry orbitals (e.g. amine ligands), only $\sigma(L) \longrightarrow Cu(II)$ charge transfer absorptions can occur.

The Spectra of $[Cu(tbmp)Br_2]_2$ and $[Cu(tbmp)Cl_2]_2$

i) $X^- \longrightarrow Cu(II)$: Apical ligation of halide ions should result in "weak" $X^- \longrightarrow Cu(II)$ charge transfer absorptions at relatively high energies[47] but the assignments of Schugar *et al* apply to mull spectra, for which the intensities are not known. In the spectra of $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$ (see Chapter 5), the absorptions that are assigned as apical $X^- \longrightarrow Cu(II)$ charge transfer transitions (CH_2Cl_2 solution) are reasonably strong, and are observed at 283 nm (ϵ = 6825 l.mol.$^{-1}$cm^{-1}) and 327 nm respectively. Similar absorptions (Table 5a) are also observed (CH_2Cl_2 solution) for $[Cu(tbmp)Cl_2]_2$ and $[Cu(tbmp)Br_2]_2$ at 292 nm (ϵ =5452) and *ca* 320(sh) nm respectively and these are thus assigned as apical $X^- \longrightarrow Cu(II)$ charge transfer absorptions.

The remaining $X^- \longrightarrow Cu(II)$ charge transfer absorptions are consistent with the equatorially disposed Cu(II)— X bonding that is shown by the structure of $[Cu(tbmp)Br_2]_2$ and they are in agreement with the assignments for square planar CuX_4^{2-} systems.[58,59]

Support for these assignments comes from the disappearance of the absorptions in methanol, the implication being that the dimeric structure is disrupted.

All of the $X^- \longrightarrow Cu(II)$ charge transfer transitions will arise from π-orbitals on the halide ions,[58] the $\sigma(X^-) \longrightarrow Cu(II)$ absorptions being found only at very high energies, (ca 200 nm).

ii) $\sigma(S) \longrightarrow Cu(II)$: These absorptions (Table 5a) remain relatively constant in going from dichloromethane [$X=Cl^-$, ca 354(sh) nm; $X=Br^-$, 352 nm (ϵ =5097)] to methanol solution [357 nm (ϵ =1177) and 358 nm (ϵ = 1276) resp.] and on changing the halogen.

iii) Discussion: The spectra of $[Cu(tbmp)Cl_2]_2$ and $[Cu(tbmp)Br_2]_2$ are very similar to those of the tetragonal pyramidal dimers, $[Cu\ BBTE.2X]_2$ ($BBTE = BuSCH_2CH_2SBu$, $X = Cl^-, Br^-$) whose spectra have been discussed by Schugar et al.[47] However their assignments differ from those of this work, being based on the assumption that the $\sigma(S) \longrightarrow Cu(II)$ charge transfer absorption occurs near 440 nm as assigned for $Cu(BBTE)_2(ClO_4)_2$. The charge transfer absorptions for the $[Cu(tbmp)X_2]_2$ and $[CuBBTE.2X]_2$ complexes are compared in Table 5c.

C) ELECTRONIC SPECTRA AT 90K (in 20% Glycerol/MeOH)

The respective spectra are virtually identical to those of the $Cu(tbmp)_2X_2$ ($X = Cl^-, Br^-$) and $[Cu(tbmp)_2X]BF_4$ ($X=Cl^-, Br^-$) complexes (at 90K) that are discussed in Chapter 2. Hence the tetragonal pyramidal, $[Cu(tbmp)_2X]^+$ monomers (derived according to equation (i)) are probably responsible for these spectra (Table 11). The existence of a solvated Cu(II) species, $Cu(MeOH)_n{}^{2+}$, is apparent in the esr spectra (1.3) of the dimers in 20%-Glycerol/MeOH (at 77K), but this is not immediately obvious in the electronic spectra at 90K.

(i) $[Cu(tbmp)X_2]_2 \xrightarrow{nMeOH} [Cu(tbmp)_2X]^+ + Cu(MeOH)_n^{2+} + 3X^-$

1.3 ELECTRON SPIN RESONANCE SPECTRA

i) Introduction

Two of the most important factors that determine the esr spectrum of a Cu(II) complex, are the stereochemistry of the complex[30] and the ligand type.[60]

Tetragonal Cu(II) stereochemistries that have a $d_{x^2-y^2}$ ground state, result in $|A_{\parallel}|$ values that fall approximately in the range from 150×10^{-4} to 200×10^{-4} cm^{-1} and $g_{\parallel}$ is greater than $g_{\perp}$. Several studies have now successfully shown that, in agreement with theoretical predictions, distorting a square planar stereochemistry towards a tetrahedral stereochemistry generally results in a relative increase in $g_{\parallel}$ and a decrease in $|A_{\parallel}|$ for the same ligand donor sets.[61,62,63] For a given geometry, smaller $g_{\parallel}$ values can be achieved by substituting "hard" donor ligands with "soft" donor ligands and this is exemplified by the $CuS_4{}^{2+}$ chromophores of $Cu(dth)_2(BF_4)_2$ ($g_{\parallel} = 2.122$ and

$Cu(tctd)(ClO_4)_2$ ($g_{\parallel}$ = 2.085).[60]

The spectral characteristics of the idealised five-coordinate Cu(II) complexes are also well established now. Trigonal bipyramidal Cu(II) complexes have a d_{z^2} ground state and these are recognised by $g_{\parallel}$ being ca 2.00 and $g_{\perp} > g_{\parallel}$, while $|A_{\parallel}|$ and $|A_{\perp}|$ lie approximately in the range from 60×10^{-4} to $100 \times 10^{-4} cm^{-1}$.[64,65] However, a complex where $|A_{\parallel}|$ is as low as $38 \times 10^{-4} cm^{-1}$ $[Cu\text{-}Zn(F_6acac)_2H_2O]$, has been characterized.[66] While the Cu(II) complexes of thioether donor ligands can have $g_{\parallel}$ values that are characteristic of a d_{z^2} ground state[60], trigonal bipyramidal complexes are easily recognised by their "reversed" spectra. An excellent example of this type, is the powder spectrum of $Cu\text{-}Zn(F_6acac)_2.H_2O$.[66] Square pyramidal complexes have a $d_{x^2-y^2}$ ground state and this usually results in the spectra and esr parameters being similar to those of tetragonal complexes.[67,68]

Intermediate five-coordinate geometries have received little attention, although criteria were recently suggested by Bencini et al,[64] for recognising these geometries in frozen solution spectra. Strong rhombic distortions, which result in one of the g values being less than 2.04, a more diffuse spectrum in the high field region and a normal tetragonal-like low field region, characterize these spectra.

ii) The Spectra of $[Cu(tbmp)Br_2]_2$ and $[Cu(tbmp)Cl_2]_2$

The calculation of the g and A parameters, and the experimental conditions, are described in the Appendices. The data for these complexes is given in Table 6, for various glasses at 77K.

Dichloromethane and Chloroform: Molecular weight measurements (Table 8) indicate that these complexes retain their dimeric nature in chloroform and this is reflected in the poorly resolved esr spectra[69] (Figure 3). The broadening of the spectra is probably due to exchange-coupling effects.[70]

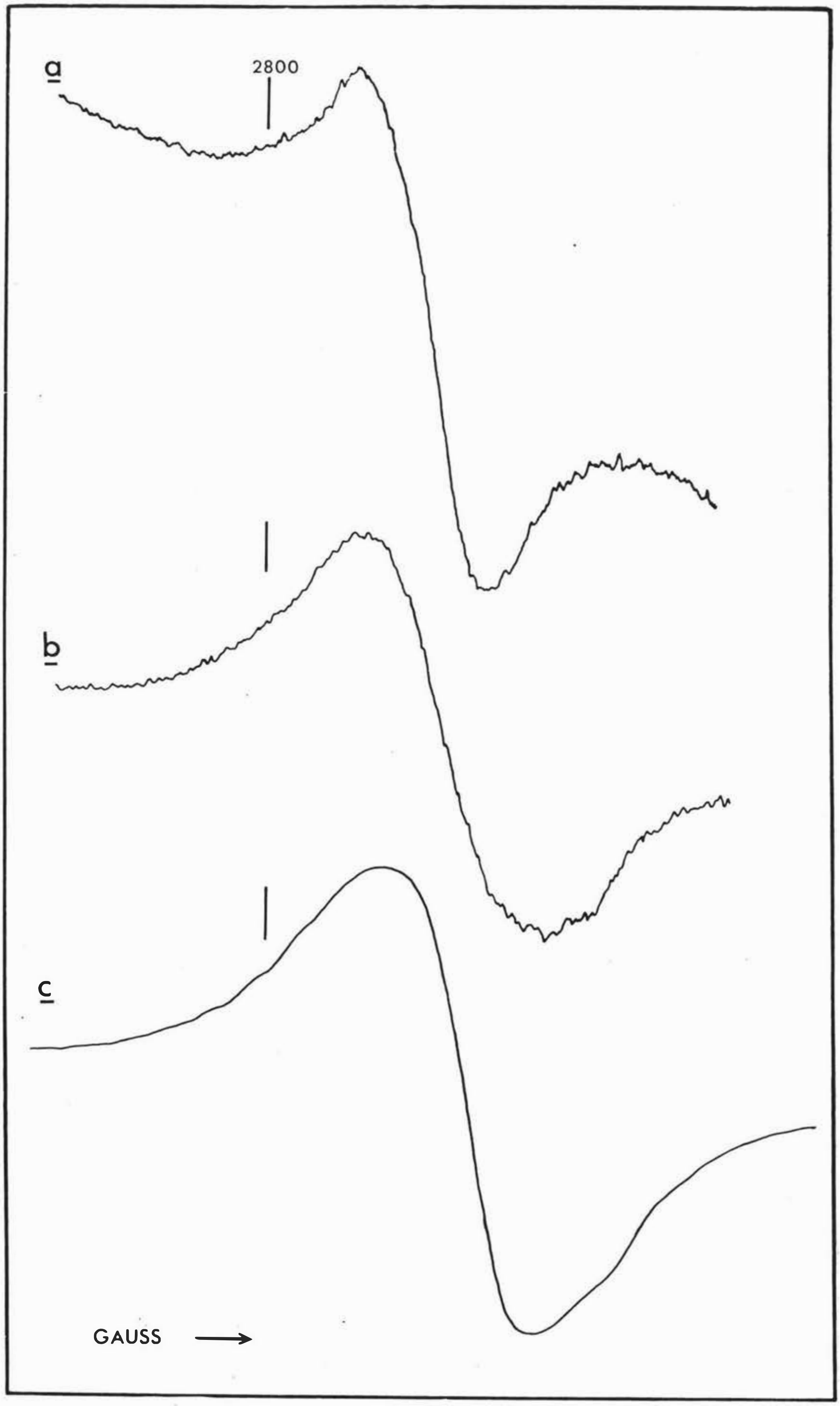
The spectrum of $[Cu(tbmp)Br_2]_2$ in dichloromethane (Figure 3) could not be improved sufficiently to enable the calculation of g and A values. The diffuse nature of the spectrum at high fields would be consistent with a distorted five-coordinate structure.

Although the high-field region for $[Cu(tbmp)Cl_2]_2$ in dichloromethane is only weakly resolved (Figure 3) (which may be indicative of an intermediate five-coordinate geometry),[64] the g (ca 2.000, ca 2.349) and A (ca 93, ca 71 x $10^{-4}cm^{-1}$) values strongly suggest that its structure is trigonal bipyramidal.

Nitromethane: For $[Cu(tbmp)Cl_2]_2$, the spectrum (Figure 3) is quite well-resolved. The g value calculated for the weakly resolved peaks on the high-field of the major spectral line is consistent with a trigonal bipyramidal structure ($g \sim 2.00$, $|A| \sim 31 \times 10^{-4} cm^{-1}$). However, the difference between the

FIGURE 3

ESR Spectra - $[Cu(tbmp)X_2]_2$ Dimers (at 77K)



Key to Figure 3

a - $[Cu(tbmp)Cl_2]_2$ in chloroform

b - $[Cu(tbmp)Br_2]_2$ in dichloromethane

c - $[Cu(tbmp)Cl_2]_2$ in dichloromethane

d - $[Cu(tbmp)Cl_2]_2$ in nitromethane

e - $[Cu(tbmp)Br_2]_2$ in methanol

f - Cu(II) in methanol

NOTE: In all of the esr spectra that are presented in this thesis, the 2800 Gauss field line is given as a reference point.

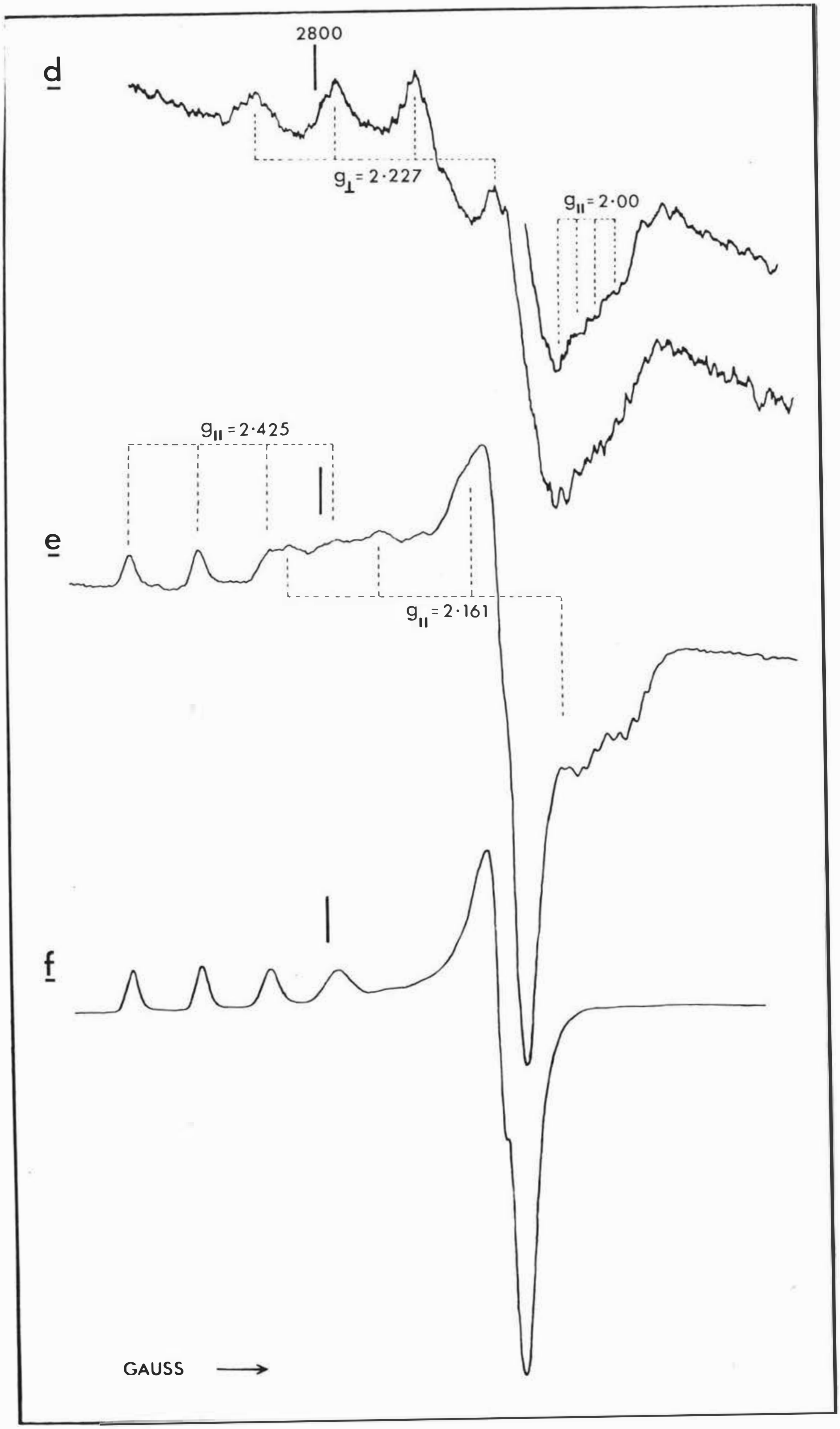

d
2800
g⊥ = 2·227
g∥ = 2·00
e
g∥ = 2·425
g∥ = 2·161
f
GAUSS →

TABLE 6

ESR SPECTRA, $[Cu(tbmp)X_2]_2$ COMPLEXES

COMPLEX	SOLVENT		$g_{\parallel}$	$10^4 \lvert A_{\parallel} \rvert / cm^{-1}$	$g_{\perp}$	$10^4 \lvert A_{\perp} \rvert / cm^{-1}$	g_{iso}	$^{14}N_{shfs}$
$[Cu(tbmp)Cl_2]_2$	CH_3NO_2		ca 2.00	ca 31	2.227	135		
	CH_2Cl_2		ca 2.00	ca 93	ca 2.349	ca 71		
	$CHCl_3$						2.115	
	Acetone						2.136	
	MeOH	a)	2.430	125				
		b)	2.279	144				
	Glyc/MeOH	a)	2.426	123				
		b)	2.270	143				ca 19 G
$[Cu(tbmp)Br_2]_2$	CH_3NO_2						2.104	
	CH_2Cl_2						2.108	
	Acetone						2.131	
	MeOH	a)	2.425	127				
		b)	ca2.161	ca151				ca 19 G
	Glyc/MeOH	a)	2.424	121				
		b)	2.288	150				18 G

NOTES:
- iso. = isotropic; shfs = superhyperfine splitting; G = Gauss;
- all spectra recorded at 77K.
- Glyc/MeOH=20% Glycerol/Methanol
- in methanol glasses, species a) is $Cu(MeOH)_n^{2+}$ while species b) is tetragonal pyramidal $[Cu(tbmp)_2X]^+$

low-field and high-field $|A|$ values (135×10^{-4} and $31 \times 10^{-4} cm^{-1}$ resp.) is greater than previously observed for trigonal bipyramidal complexes. According to these studies, $|A_{\parallel}|$ and $|A_{\perp}|$ should be of comparable magnitudes.[71]

Methanol and 20% Glycerol/MeOH: There are two major species present in these glasses (Figure 3). One of the species is solvated Cu(II) $[Cu(MeOH)_n{}^{2+}]$ as the $g_{\parallel}$ and $|A_{\parallel}|$ parameters correspond to those that are measured for Cu(II) under the same conditions. For $[Cu(tbmp)Cl_2]_2$, the identity of the second complex is not immediately clear although the electronic spectra at 90K suggested that a tetragonal pyramidal $[Cu(tbmp)_2Cl]^+$ chromophore is present. The two high-field peaks in the esr spectra of $[Cu(tbmp)Br_2]_2$ correspond to those that are observed for $Cu(tbmp)_2Br_2$ and $[Cu(tbmp)_2Br]BF_4$ under the same conditions (see Chapter 2). Hence the tetragonal pyramidal monomer $[Cu(tbmp)_2Br]^+$, is probably present.

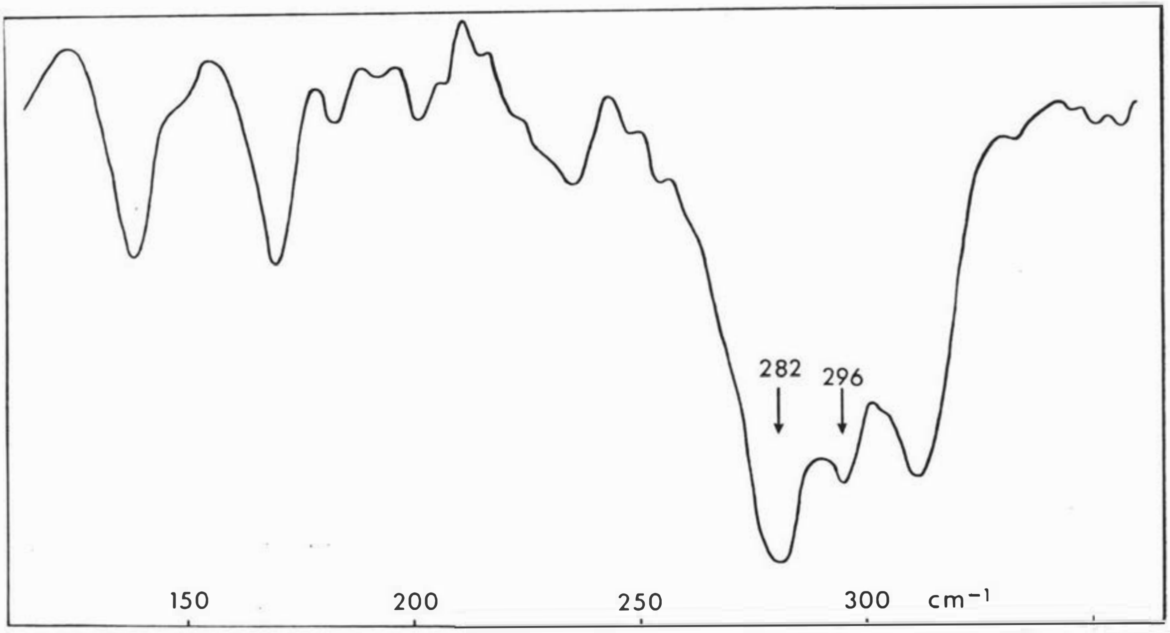
1.4 INFRARED SPECTRA

FAR INFRARED

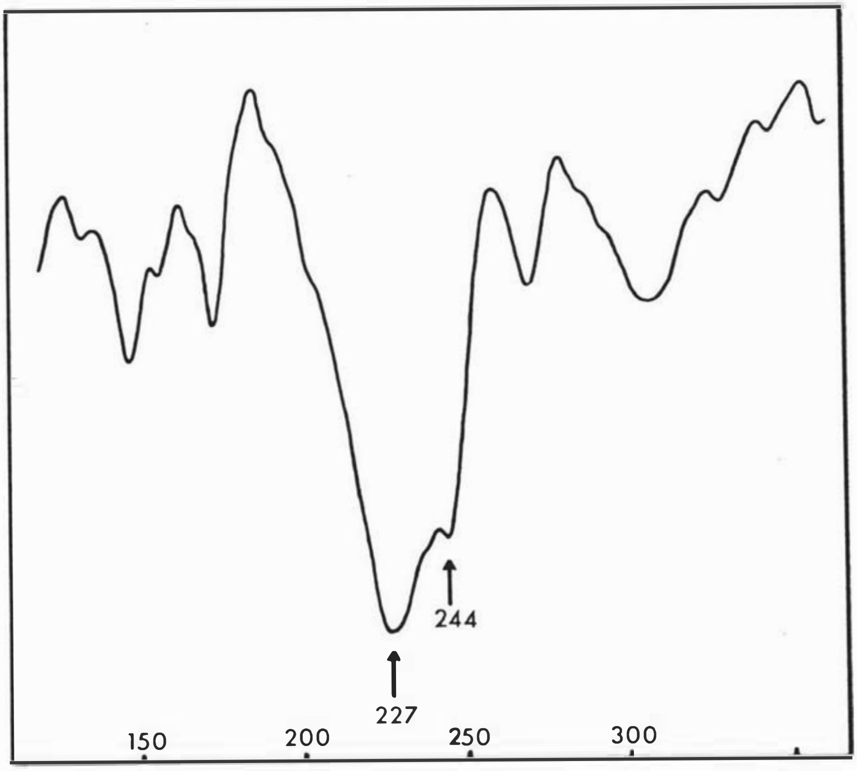
In both spectra (Figure 4) there are two absorptions ($X=Cl^-$; 282, 296 cm^{-1}: $X=Br^-$; 227,244 cm^{-1}) that can be assigned as stretching vibrations of the "equatorial" Cu—X bonding, but there are no absorptions that can be readily assigned as stretching vibrations of the apical Cu—X bonding. The

FIGURE 4

Far-IR Spectra - $[Cu(tbmp)X_2]_2$ Dimers



X=Cl⁻   ν(Cu-Cl) absorptions shown



X=Br⁻   ν(Cu-Br) absorptions shown

assignments are in agreement with those of similar dimeric Cu(II) complexes, such as $[Cu(\alpha\text{-picoline})_2X_2]_2$ (X=Cl^-; 305 cm^{-1}: X=Br^-; 233 cm^{-1}) [23,24,72] and $[Cu(dmen)X_2]_2$ (X=Cl^-; 302 cm^{-1}: X=Br^-; 233 cm^{-1}).[19,72]

EXPERIMENTAL

DETERMINATION OF STRUCTURE OF $[Cu(tbmp)Br_2]_2$

i) General

The approximate unit cell dimensions of the black crystals of $[Cu(tbmp)Br_2]_2$ were determined by preliminary oscillation, Weissenberg and precession photography. The crystals were prepared as described in the SYNTHESES. Density measurements and molecular weight determinations indicated that there were two dimers per unit cell, suggesting the space group $P\bar{1}$ as the most logical choice. Accurate cell dimensions were calculated after a crystal had been aligned on a four-circle X-ray diffractometer. The least-squares analysis of the positions of twelve general reflections was used to define the crystal orientation.

TABLE 7a

CRYSTAL DATA FOR $[Cu(tbmp)Br_2]_2$

M.W.	809.30 g.	
CRYSTAL SYSTEM	Triclinic	
SPACE GROUP	$P\bar{1}$	
CELL DIMENSIONS	a=9.040(1)Å	α=120.26(1)°
	b=13.100(2)	β=92.80(1)
	c=15.455(2)	γ=111.31(1)
CELL VOLUME	U=1411 $Å^3$	
DENSITY	$D_M^* = 1.896$ g cm^{-3} $D_{CALC} = 1.905$ g. cm^{-3}(Z =2)	
RADIATION	Mo - $K\alpha$	
μ(Mo-$K\alpha$)	77.2 cm^{-1}	

NOTE: * Determined by flotation method.
Measured in CH_3I/p-dibromobenzene/bromobenzene

ii) Data Collection and Reduction

The data was collected on a computer controlled Hilger and Watts four-circle X-ray diffractometer for a crystal which had dimensions of approximately 0.03 x 0.01 x 0.02 cm and which was mounted about its a axis.

TABLE 7b

DATA COLLECTION FOR $[Cu(tbmp)Br_2]_2$

λ Mo-Kα	0.7107 Å
Background Count Time	9 s. each side
Counting Steps	30
Counting Time/step	1.5 s.
Standard Reflections	(-3, -1,0);(0,0,8)

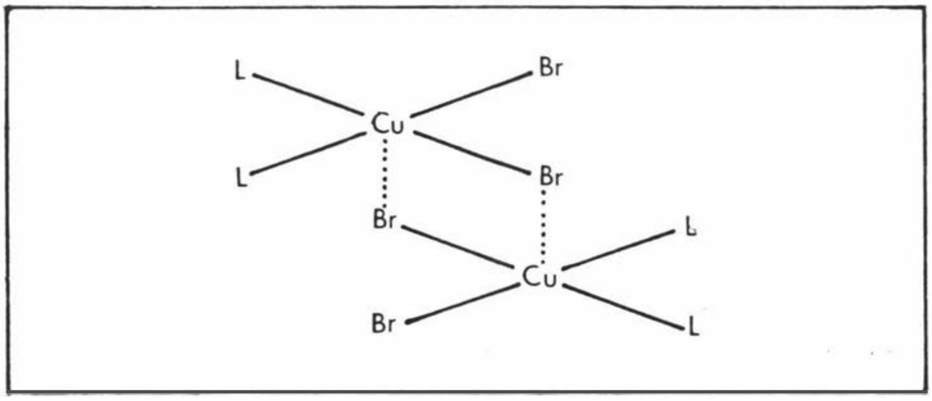
The checks that were made on the standard reflections did not reveal any significant , non-random, intensity changes. The data was collected (6341 measurements) for the hkl, $\bar{h}kl$, $\bar{h}\bar{k}l$ and $h\bar{k}l$ reflections in two shells ($0^\circ < \theta < 20^\circ$ and $20^\circ < \theta < 26^\circ$). Equivalent reflections were then merged to give 5504 independent reflections of which 3070 had intensities greater than 2σ . Lorentz and polarization corrections were applied to the data, but no absorption corrections were made.

iii) Structure Solution and Refinement

Although it was apparent that quite a few of the major vectors in the Patterson vector map were related, the solution of this map was not obvious. The program DANFIG, a locally adapted version of ORTEP,[73] was used to calculate the distances of the major vectors from the origin, as well as the angles that are subtended at the origin, by these vectors. A copper atom was assigned to the origin and this gave a set of Cu-Br, Cu-Cu and Br-Br vectors that were consistent with a dimeric structure, such as that shown in Figure 5.

FIGURE 5

POSSIBLE STRUCTURE, AS INDICATED BY PATTERSON VECTORS



The coordinates of the two copper and four bromine atoms, that had been deduced from the Patterson map, were used to calculate an electron density map phased on these atoms. The space group was assumed to be P1 and copper (1) was kept at the origin. This electron density map revealed the positions of the remaining copper and bromine atoms and also the sulphur and nitrogen atoms. The coordinates of all of the atoms that had been found gave reasonable environments for each of the four copper atoms in the unit cell.

On close examination of the atomic coordinates at this stage, it was noticed that pairs of atoms in both dimers were related by an apparent inversion centre centre. The space group thus appeared to be P$\bar{1}$ as anticipated, and so the coordinates of the atoms were adjusted accordingly. A second electron density map was calculated after the new x,y,z parameters had been given one cycle of least-squares refinement. From this map, all of the remaining twenty carbon atoms were located.

The structure was refined using the full-matrix least-squares program, CUCLS.[74] The least-squares refinement was carried out on F, with the quantity $\sum w(|F_o| - |F_c|)^2$ being minimised and the weight (w) being $4(F_o)^2/[\sigma(F_o)^2]^2$.

Four cycles of least-squares refinement, with all of the atoms being given isotropic temperature factors, reduced R to 0.174. A difference Fourier which was calculated at this stage, indicated that there were no unaccounted-for atoms in the unit cell. However, Br12 had a pair of peaks of about 10 e.Å^{-3} associated with it and the other heavy atoms had accompanying pairs of peaks of up to 7 e.Å^{-3}. This suggested that perhaps the unit cell was not truly centrosymmetric. Various attempts to break the apparent centre of symmetry were unsuccessful and so it was decided to retain the centrosymmetric space group. The bromine and copper atoms were given anisotropic temperature factors and refined. This was followed by a cycle in which anisotropic temperature factors were also given to the sulphur atoms and R was reduced to 0.080. Corrections for anomalous dispersion were applied to the bromine and copper atoms (as for $Cu(tbmp)_2Br$) and two further least-squares refinement cycles resulted in R converging at 0.079 (R'=0.097).

A difference Fourier indicated that there was still some unaccounted-for density around the bromine, copper and sulphur atoms. The highest pair of peaks (ca 2.0 e.Å^{-3}) was associated with Br22, the remaining heavy atoms having peaks of ca 1.8 - 1.0 e.Å^{-3}.

No attempt has been made to locate or calculate the positions of the hydrogen atoms in this structure.

The anisotropic atoms have the following RMS components of thermal displacement along the principal axes, R:

ATOM	R = 1	R = 2	R = 3
Br11	0.1404 Å	0.2125	0.2624
Br12	0.1576	0.2208	0.3777
Br21	0.1652	0.2231	0.2737
Br22	0.1495	0.2612	0.2841
Cu1	0.1339	0.1822	0.2599
Cu2	0.1370	0.1876	0.2660
S1	0.1550	0.1740	0.2221
S2	0.1398	0.1828	0.2575

TABLE 7c

MEAN LEAST-SQUARES PLANE EQUATIONS

ATOMS IN PLANE	EQUATION
Cu1, S1, N1	-0.0930X-0.8299Y-0.5501Z = -8.2009
Br11, Br12, Cu1	-0.5632X-0.6917Y-0.4521Z = -8.3277
Cu2, S2, N2	0.1568X-0.9658Y-0.2066Z = -8.0053
Br21, Br22, Cu2	-0.2934X-0.7205Y-0.6283Z = -11.9320
Br11, Cu1, S1, N1	-0.0649X-0.9015Y-0.4279Z = -7.6152
Br12, Cu1, S1, N1	-0.2490X-0.6620Y-0.7070Z = -8.9242
Br22, Cu2, S2, N2	0.2030X-0.7943Y-0.5726Z = -11.2541
Br21, Cu2, S2, N2	0.1091X-0.9857Y-0.1287Z = -7.2846
N1, C12-16	0.1091X-0.6651Y-0.7388Z = -8.4952
N2, C22-26	0.0001X-0.9357Y-0.3527Z = -9.6056

SYNTHESES

General comments that relate to these syntheses can be found in the experimental section of the Appendices.

Bis[Dichloro-[2-(3,3-dimethyl-2-thiabutyl)pyridine]-copper(II)]

2 mmole of $CuCl_2.2H_2O$ (0.340 g.) were added to 2 mmole of ligand (0.363 g.) to give a dark green solution. Shiny dark green crystals were precipitated from this solution after it had been concentrated in vacuo.

YIELD: 0.418 g. (66%)

Bis[Dibromo-[2-(3,3-dimethyl-2-thiabutyl)pyridine]-copper(II)]

With the solution volume at a minimum, 1 mmole of ligand (0.181 g.) was added to an excess of anhydrous $CuBr_2$ ($>$ 0.223 g.). Cooling the black solution produced black crystals.

<u>TABLE 8</u>

<u>MISCELLANEOUS PHYSICAL DATA</u>

COMPLEX	COLOUR	M.P/°C	ANALYSES:Calc.(Found)/%				CONDUCTIVITY/ohm^{-1}mol^{-1}cm^{2}		M.W:Meas.(Calc)
			C	H	N	Other	CH_3NO_2	MeOH	
$[Cu(tbmp)Cl_2]_2$	d.green	128-130	38.04 (38.24)	4.79 (4.80)	4.44 (4.15)		4	67	$CHCl_3$-662 g. (631) Acetone-662 g.
$[Cu(tbmp)Br_2]_2$	black	108-110	29.68 (29.81)	3.74 (3.85)	3.46 (3.41)	Br39.50 (39.32)	10	74	$CHCl_3$-785 g. (809) Acetone-799 g.

<u>NOTES</u>: - molar conductivities at 25°C: Nitromethane 1:1 (70-90), 2:1 (150-170)
Methanol (100-130), (210-250).

- d = dark

CHAPTER 2

BIS [2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE] COPPER(II) COMPLEXES

The $Cu(tbmp)_2X_2$ complexes ($X=BF_4^-$, ClO_4^-, Cl^-, Br^-) that are described in this Chapter, are formed by the reaction of the respective Cu(II) salts with tbmp in a 1:2 ratio. In the solid state, far-infrared spectroscopic investigations ($X=Cl^-$, Br^-) suggest that these complexes have distorted cis-octahedral structures (Figure 6a) and the electronic spectral data is not inconsistent with these results. Molecular model studies also suggest that the binding of anions will be less sterically hindered if the tbmp ligands bind in a cis configuration.

In solution their behaviour is varied and the species that are formed can be both solvent and temperature dependent.

If LiBr and LiCl are reacted with $Cu(tbmp)_2(BF_4)_2$ in 1:1 ratios, the respective $[Cu(tbmp)_2X]BF_4$ complexes ($X=Cl^-$, Br^-) are formed. These appear to have tetragonal pyramidal structures (Figure 6b) in the solid state and in non-ligating solvents.

FIGURE 6

Possible Structures for $Cu(tbmp)_2X_2$ and $[Cu(tbmp)_2X]BF_4$ Complexes

$Cu(tbmp)_2X_2$; $X = Cl^-, Br^-$

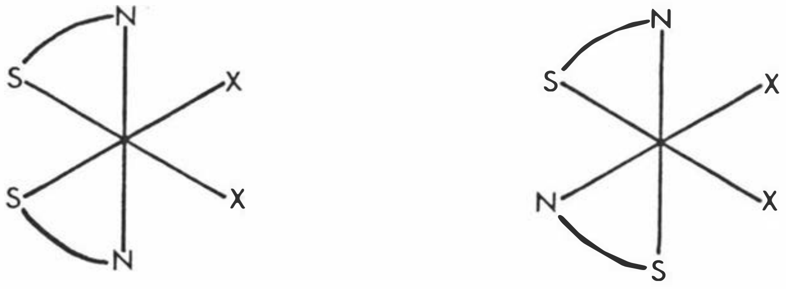


Figure 6a

$[Cu(tbmp)_2X]BF_4$; $X = Cl^-, Br^-$

Figure 6b

TABLE 9

SUMMARY OF RESULTS - $Cu(tbmp)_2X_2$ COMPLEXES

COMPLEX	STATE	STRUCTURE	PHYSICAL TECHNIQUE
$Cu(tbmp)_2X_2$	solid	*cis*-octahedral	electronic
($X=BF_4^-$, ClO_4^-)	non-ligating solvent		
	(rm.temp.)	*cis*-$[Cu(tbmp)_2]^{2+}$	electronic, conductivity
	(77K)	$[Cu(tbmp)_2]^{2+}$ minor sp. without excess tbmp. Major species with excess tbmp.	esr
	ligating solvent		
	(rm.temp.)	$[Cu(tbmp)_2.(solvent)_2]^{2+}$	electronic, conductivity
	(77K)	$Cu(tbmp)(solvent)_n^{2+}$ (n=2 or 4, without excess tbmp) $[Cu(tbmp)_2(solvent)_n]^{2+}$(n=0 or 2, with excess tbmp)	esr
$Cu(tbmp)_2Cl_2$	solid	*cis*-octahedral	electronic, far-IR
	non-ligating solvent		
	(rm.temp.)	dist.tetrag.pyr. $[Cu(tbmp)Cl_2]_2$	electronic
	(77K)	*cis*-$Cu(tbmp)_2Cl_2$ with and without excess tbmp	esr
	ligating solvent		
	(rm.temp.)	$Cu(tbmp)_2Cl_2 \rightleftharpoons [Cu(tbmp)_2Cl.(solvent)]^+ + Cl^-$ (In H_2O, both Cl^- dissociate)	electronic, conductivity
	(77K, 90K)	tetrag.pyr. $[Cu(tbmp)_2Cl]^+$ with and without excess tbmp	electronic, esr
		cis-$Cu(tbmp)_2Cl_2$ in CH_3NO_2, with excess tbmp	esr
$Cu(tbmp)_2Br_2$	solid	*cis*-octahedral	electronic, far-IR
	non-ligating solvent		
	(rm.temp.)	dist.tetrag.pyr. $[Cu(tbmp)Br_2]_2$	electronic
	(77K)	trig.bipyr. $Cu(tbmp)_2Br_2$ or $[Cu(tbmp)_2Br]^+$	esr
	ligating solvent		
	(rm.temp.)	$Cu(tbmp)_2Pr_2 \rightleftharpoons [Cu(tbmp)_2Br.(solvent)]^+ + Br^-$	electronic, conductivity
	(77K, 90K)	tetrag.pyr. $[Cu(tbmp)_2Br]^+$ (2 isomers)	electronic, esr
$[Cu(tbmp)_2X]BF_4$	solid	tetrag.pyr. $[Cu(tbmp)_2X]^+BF_4^-$	electronic, infrared
($X=Cl^-$, Br^-)	non-ligating solvent		
	(rm.temp.)	tetrag.pyr. $[Cu(tbmp)_2X]^+$	electronic
	ligating solvent		
	(rm.temp.)	$[Cu(tbmp)_2X.(solvent)]^+$	electronic, conductivity
	(77K, 90K)	tetrag.pyr. $[Cu(tbmp)_2X]^+$	electronic, esr

2.1 ELECTRONIC SPECTRA

Where possible, the spectral maxima have been tentatively assigned, the assignments being based on comparions made within this series of complexes and according to arguments presented in the literature. The spectra and the assignments for $Cu(tbmp)_2X_2$ ($X=ClO_4^-$, BF_4^-, Cl^-, Br^-) and $[Cu(tbmp)_2X]BF_4$ ($X=Cl^-$, Br^-) are presented in Table 10.

A) LIGAND FIELD TRANSITIONS

i) $Cu(tbmp)_2(ClO_4)_2$ and $Cu(tbmp)_2(BF_4)_2$

Reflectance: The ligand field maxima (600, 595 nm resp.) are consistent with the complexes having distorted tetragonal geometries where the anions are weakly coordinated and this is supported by the infrared spectra of these complexes. The spectra are very similar to those of the related complexes $Cu(mmp)_2(ClO_4)_2$ (mmp = 2-methylthiomethylpyridine)[15] and $Cu(etmp)_2(BF_4)_2$(etmp = 2-ethylthiomethylpyridine)[75] which have been postulated to have tetragonal structures. The ligand field maxima of these two complexes are at ca 620 nm (shoulders at 600 and 710 nm) and 602 nm respectively.

Solution: The spectra are unchanged in dichloromethane and in nitrobenzene ($X=ClO_4^-$ only) and acetone, they move to slightly lower energies. A red-shift of 150 nm occurs in methanol, implying that a solvated, cationic complex such as $[Cu(tbmp)_2.(MeOH)_2]^{2+}$ is being formed.

ii) $Cu(tbmp)_2Cl_2$ and $Cu(tbmp)_2Br_2$

Reflectance: Two absorptions are apparent

($X=Cl^-$; 730, ca 970(sh); $X=Br^-$; 840 nm) although the low-energy shoulder in each spectrum is not clearly resolved. The spectra are consistent with the complexes having distorted six-coordinate geometries.[15]

The far-infrared spectra of these complexes suggest that the structures are distorted cis-octahedral.

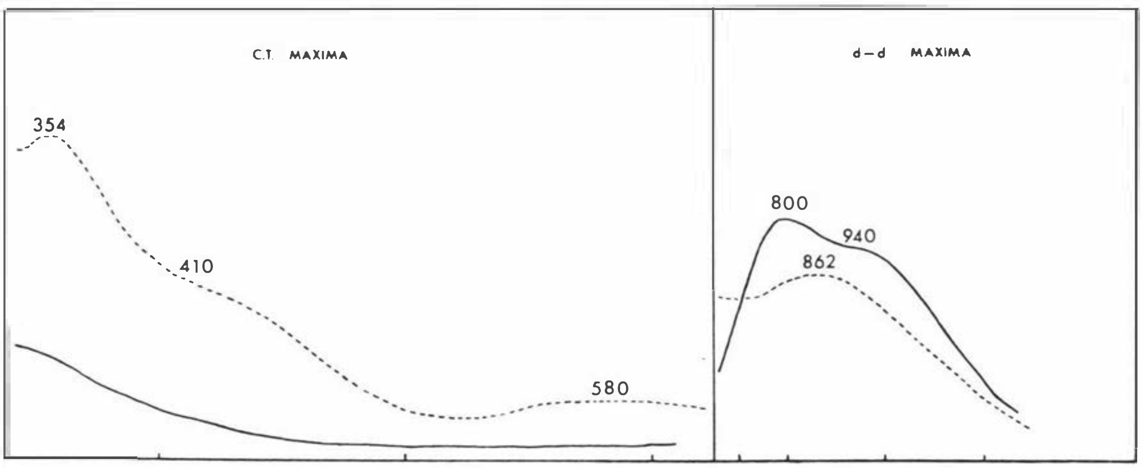
Few distorted cis-octahedral Cu(II) complexes have been characterized and consequently it is uncertain whether or not there is a basic difference between the d-d absorptions of cis- and trans-tetragonal Cu(II) complexes. The most well known cis-octahedral complex, $[Cu(bipy)_2ONO]NO_3$, and a series of closely related complexes, have two distinct d-d maxima of about equal intensity at about 640-700 nm and 925-1090 nm in the solid state, at room temperature.[76] Similar distinctive splittings though, have been observed for trans-tetragonal complexes and related to the degree of tetragonal distortion.[77]

Solution: In coordinating solvents such as methanol, two absorptions (Table 10, Figure 7) are readily apparent. It is probable that partial solvation is occurring as these complexes exhibit appreciable conductivities in nitromethane and methanol (Table 14) and in the latter solvent, the spectra are similar to those of the $[Cu(tbmp)_2X]BF_4$ complexes ($X=Cl^-$, Br^-) under the same conditions.

In deionised water the 2:1 electrolytic behaviour (Table 14) of $Cu(tbmp)_2Cl_2$ suggests that at least two

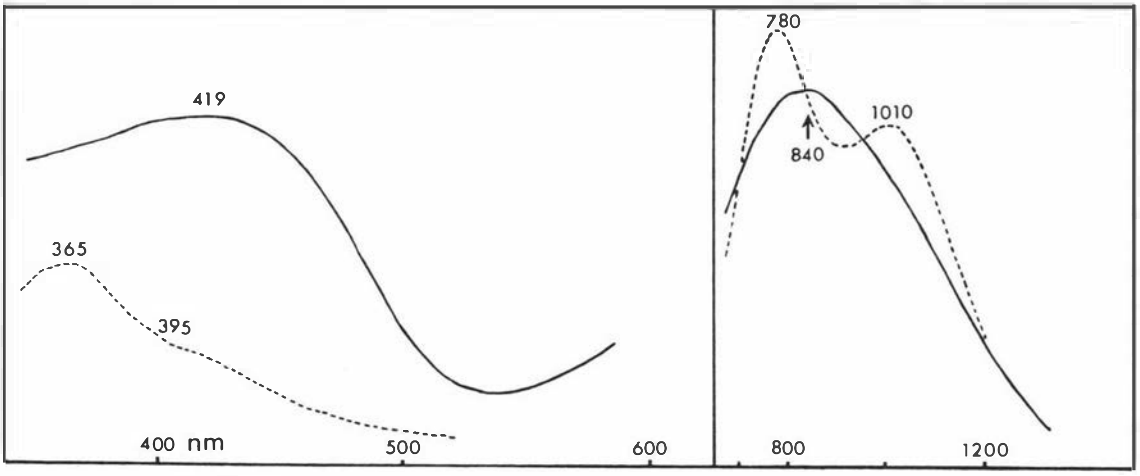
FIGURE 7

Electronic Spectra - $Cu(tbmp)_2Br_2$ and $[Cu(tbmp)_2Br]BF_4$



$Cu(tbmp)_2Br_2$: (----) Dichloromethane solution

(——) Methanol solution



$[Cu(tbmp)_2Br]BF_4$: (----) Dichloromethane solution

(——) Reflectance

TABLE 10

ELECTRONIC SPECTRA, $Cu(tbmp)_2X_2$ AND $[Cu(tbmp)_2X]BF_4$ COMPLEXES

COMPLEX	REFLECTANCE	ASSIGNMENT	$CH_2Cl_2(\epsilon)$	ASSIGNMENT	$MeOH(\epsilon)$	ASSIGNMENT	ACETONE	OTHER
								ϕNO_2
$Cu(tbmp)_2(ClO_4)_2$	420	$\sigma(S)\rightarrow Cu(II)$	390†	$\sigma(S)\rightarrow Cu(II)$	346(1023)	$\sigma(S)\rightarrow Cu(II)$	ca 380(sh)	
	ca 440(sh)	$\sigma(S)\rightarrow Cu(II)$					405(1562)	
	600	LF	600	LF	750(60)†	LF	635(389)	637(556)
$Cu(tbmp)_2(BF_4)_2$	407	$\sigma(S)\rightarrow Cu(II)$	ca 370(sh)	$\sigma(S)\rightarrow Cu(II)$	344(1086)	$\sigma(S)\rightarrow Cu(II)$	381(3166)	
	ca 455(sh)	$\sigma(S)\rightarrow Cu(II)$	387	$\sigma(S)\rightarrow Cu(II)$				
	595	LF	595	LF	745(74)†	LF	612(379)	
							ca 850(sh)	
$Cu(tbmp)_2Cl_2$			ca 286(5370)	apical $Cl^-\rightarrow Cu(II)$				H_2O
			368(2537)	mixed	361(1480)	mixed	ca 351(sh)	343(1058)
	ca 410(sh)	mixed	448(926)	$Cl^-\rightarrow Cu(II)$			448(1061)	
	730	LF	812(195)†	LF	810(209)	LF	820(178)†	765(91)†
	ca 970(sh)	LF			ca 965(sh)	LF		
$Cu(tbmp)_2Br_2$			ca 320(sh)	apical $Br^-\rightarrow Cu(II)$	310(1892)	$Br^-\rightarrow Cu(II)$		
			354(4685)	mixed	ca 342(sh)	mixed	352(4078)	
	ca 450(sh)	mixed	ca 410(sh)	$Br^-\rightarrow Cu(II)$			ca 415(sh)	
			580(546)	$Br^-\rightarrow Cu(II)$			577(403)	
	840†	LF	862(327)	LF	800(350)	LF	875(318)†	
					ca 940(sh)	LF		
$[Cu(tbmp)_2Cl]BF_4$			ca 280(sh)	$Cl^-\rightarrow Cu(II)$				CH_3NO_2
	ca 375	mixed	380(1700)†	mixed	363(1468)	mixed		
	810	LF	760(500)	LF	800(212)	LF		760(467)
	ca 960(sh)	LF	1020(504)	LF	950(194)	LF		1010(476)
$[Cu(tbmp)_2Br]BF_4$			365(2896)	$\sigma(S)\rightarrow Cu(II)$	355(1610)†	mixed		
	419†	mixed	ca 395(sh)	$Br^-\rightarrow Cu(II)$				
	840†	LF	780(645)	LF	805(300)	LF		
			1010(507)	LF	ca 950(sh)	LF		

NOTES: † asymmetric maxima, implying a second, unresolved maximum,

- where charge transfer maxima are assigned as being "mixed", maximum probably consists of $\sigma(S)\rightarrow Cu(II)$ and $X^-\rightarrow Cu(II)$ charge transfer maxima.
- $Cu(tbmp)_2X_2$ (where X is ClO_4^- and BF_4^-) were only partially soluble in CH_2Cl_2.
- sh = shoulder; LF = Ligand Field; all maxima are in nm.
- extinction coefficients are $l.mol.^{-1}cm^{-1}$

of the Cu(II) coordination sites will be occupied by water molecules.

Possible equilibria are:

$Cu(tbmp)_2X_2 \rightleftharpoons [Cu(tbmp)_2X.(solvent)]^+ + X^-$ ($X=Cl^-$, Br^-)

where the solvent is methanol or nitromethane, but in water

$Cu(tbmp)_2X_2 \rightleftharpoons [Cu(tbmp)_2(H_2O)_2]^{2+} + 2X^-$.

In contrast, the spectra in the poorer ligating solvents, dichloromethane and acetone, show only slightly asymmetric d-d absorption envelopes (Figure 7). These are very similar both in energy ($X=Cl^-$; 812 nm: $X=Br^-$; 862 nm) and form, to those of the distorted five-coordinate $[Cu(tbmp)X_2]_2$ dimers ($X=Cl^-$, Br^-) in dichloromethane (Chapter 1) and the charge transfer absorption maxima are also very similar. These results suggest that the $Cu(tbmp)_2X_2$ ($X=Cl^-$, Br^-) complexes are dimerizing in dichloromethane and acetone;

i.e. $2[Cu(tbmp)_2X_2] \longrightarrow [Cu(tbmp)X_2]_2 + 2tbmp$.

iii) $\underline{[Cu(tbmp)_2Cl]BF_4}$ and $\underline{[Cu(tbmp)_2Br]BF_4}$

Reflectance: The infrared spectra (see 2.3) of these complexes give good evidence for the tetrafluoroborate anion being unbound in the solid state and so the spectra are assigned to the five-coordinate chromophores $[Cu(tbmp)_2X]^+$. The form of the d-d absorption envelopes (Figure 7) ($X=Cl^-$; 810, ca 960(sh): $X=Br^-$; 840(asym) nm) suggests that these chromophores are tetragonal pyramidal (see Chapter 1.2).

Solution: In dichloromethane (and nitromethane where $X=Cl^-$), these complexes have two, well-defined absorptions at 760-780 nm and 1010-1020 nm respectively

(Figure 7). Similar spectra are commonly observed for trigonal bipyramidal complexes such as $[Cu(trenMe_6)X]X$ in solution[67,78,79] but they are also not unknown for square pyramidal complexes[67] where the maxima are observed at higher energy. A consideration of the conductivities (Table 14) and the infrared spectra (see 2.3) of the $[Cu(tbmp)_2X]BF_4$ complexes suggests that these spectra are due to five-coordinate, $[Cu(tbmp)_2X]^+$ chromophores. The intensity arguments (see 1.2) applied by Hathaway <u>et al</u>[48] imply that in dichloromethane and nitromethane, $[Cu(tbmp)_2Cl]BF_4$ may assume an intermediate geometry as both absorptions are of about equal intensity. $[Cu(tbmp)_2Br]BF_4$ appears to retain a tetragonal pyramidal structure in dichloromethane.

B) CHARGE TRANSFER TRANSITIONS

i) $Cu(tbmp)_2(ClO_4)_2$ and $Cu(tbmp)_2(BF_4)_2$

The assigned $\sigma(S)\longrightarrow Cu(II)$ charge transfer absorptions are in agreement with other studies on simple Cu(II)/thioether complexes where the absorptions have been specifically assigned[47,69,80] or recognised as being charge transfer arising from thioether ligands.[81-83]

It is apparent from these studies that $\sigma(S)\longrightarrow Cu(II)$ charge transfer absorptions will be found from about 300 nm to 460 nm.

The two $\sigma(S)\longrightarrow Cu(II)$ charge transfer absorptions in the $Cu(tbmp)_2X_2$ ($X=ClO_4^-$, BF_4^-) reflectance spectra are indicative of a <u>cis</u>-ligand arrangement.[60,80] The spectra in dichloromethane suggest that this ligand arrangement is retained.

ii) Cu(tbmp)$_2$Cl$_2$ and Cu(tbmp)$_2$Br$_2$

Poor resolution at the blue end of the visible region in the reflectance spectra does not allow specific assignments to be made. In dichloromethane solution, the charge transfer maxima of the [Cu(tbmp)X$_2$]$_2$ dimers that are formed are discussed in Chapter 1.

iii) [Cu(tbmp)$_2$Cl]BF$_4$ and [Cu(tbmp)$_2$Br]BF$_4$

"In-plane" Cu(II)—Br bonding is implicated by the assignment of a Br$^-$ ⟶ Cu(II) charge transfer absorption at about 395 nm in dichloromethane, as it is probably too low in energy to have arisen from apical Cu—Br interactions (see Chapter 5.1(B)).[47] A similar structure is inferred from the spectra of [Cu(tbmp)$_2$Cl]BF$_4$.

C) ELECTRONIC SPECTRA AT 90K (in 20% Glycerol/MeOH)

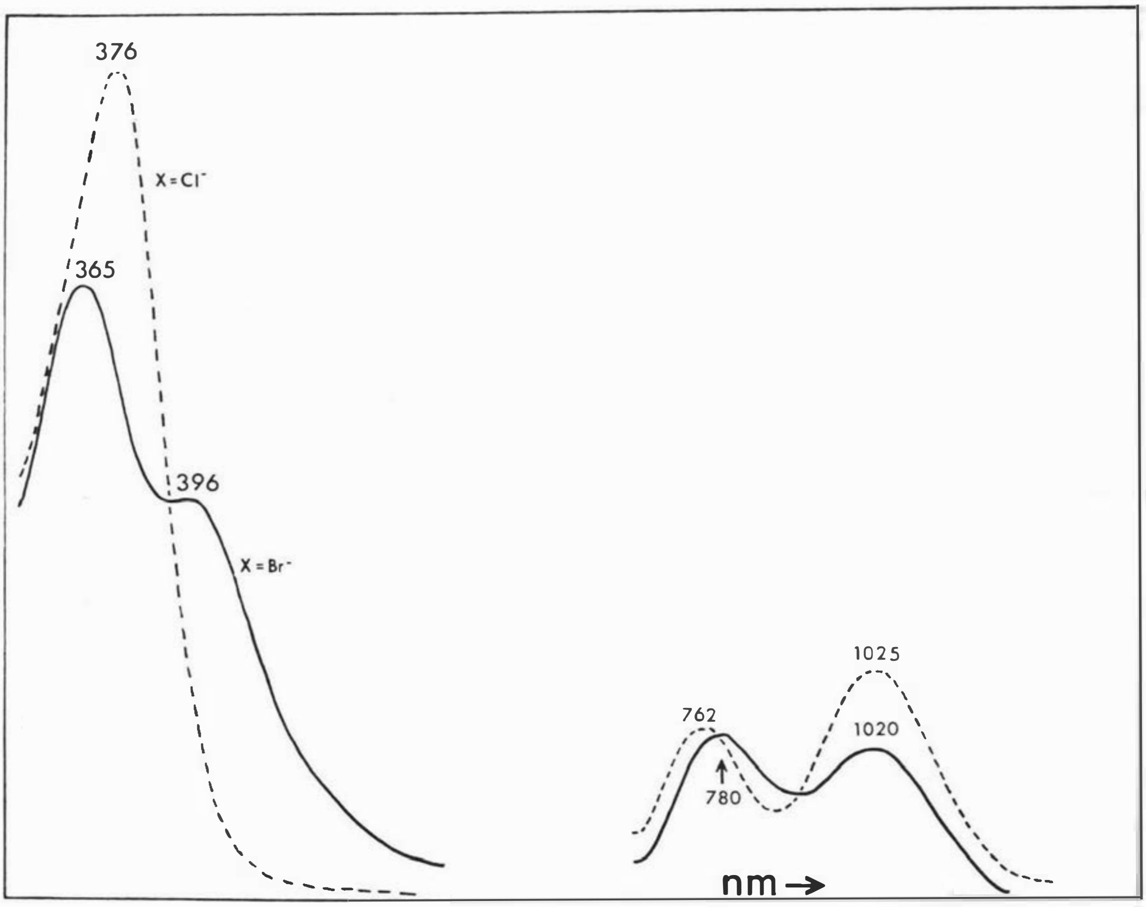
The spectra and assignments for these complexes are presented in Table 11 and typical spectra for the anions X=Cl$^-$ and X=Br$^-$ are shown in Figure 8.

i) Cu(tbmp)$_2$X$_2$(X=ClO$_4^-$, Cl$^-$, Br$^-$)

Ligand Field Transitions: The net similarity of the two well resolved d-d absorptions suggests that the same type of species is responsible for each of these spectra. Where X is chloride and bromide, the spectra are identical to those of the five-coordinate [Cu(tbmp)$_2$X]BF$_4$ complexes (X=Cl$^-$, Br$^-$ respectively) in dichloromethane solution and this strongly implies that similar five-coordinate chromophores are responsible for these spectra at 90K. Electron spin resonance evidence is consistent with both ligands remaining coordinated and the complexes

FIGURE 8

Electronic spectra - $[Cu(tbmp)_2X]BF_4$ Complexes at 90K



- spectra recorded for 20% Glycerol/MeOH glasses,
- for the respective anions, spectra of $[Cu(tbmp)X_2]_2$ and $Cu(tbmp)_2X_2$ are identical to these spectra.

TABLE 11

ELECTRONIC SPECTRA AT 90K

COMPLEX	ABSORPTION/nm	ϵ/l.mol.$^{-1}$cm^{-1}	ASSIGNMENT
$Cu(tbmp)_2(ClO_4)_2$	362(asym)		$\sigma(S) \longrightarrow Cu(II)$
	695	142	LF
	1020	81	LF
$Cu(tbmp)_2Cl_2$	372(asym)		mixed
	750		LF
	1010		LF
$[Cu(tbmp)_2Cl]BF_4$	376(asym)	2449	mixed
	762	455	LF
	1025	631	LF
$[Cu(tbmp)Cl_2]_2$	367(asym)	1303	mixed
	762	336	LF
	1025	354	LF
$Cu(tbmp)_2Br_2$	366	2606	$\sigma(S) \longrightarrow Cu(II)$
	395(sh)	1796	$Br^- \longrightarrow Cu(II)$
	780	914	LF
	1020	862	LF
$[Cu(tbmp)Br_2]_2$	369		$\sigma(S) \longrightarrow Cu(II)$
	390(sh)		$Br^- \longrightarrow Cu(II)$
	785		LF
	1010		LF
$[Cu(tbmp)_2Br]BF_4$	365		$\sigma(S) \longrightarrow Cu(II)$
	396(sh)		$Br^- \longrightarrow Cu(II)$
	780	709	LF
	1020	669	LF

NOTES:
- where extinction coefficients have not been given, they were considered to be unreliable.
- "mixed" implies that maximum probably consists of $\sigma(S) \longrightarrow Cu(II)$ and $Cl^- \longrightarrow Cu(II)$ C.T. maxima.
- $Cu(tbmp)_2(ClO_4)_2$ appeared to be reducing
- sh = shoulder; asym = asymmetric, implying a second, unresolved absorption.
- ϵ is uncorrected for contraction on cooling.

having tetragonal pyramidal structures under these conditions (see 2.2).

Charge Transfer Transitions: Thioether binding is implicated by the absorption at about 365 nm which appears in each of these complexes and is assigned as a $\sigma(S)\rightarrow Cu(II)$ charge transfer transition. In the chloride complex, this absorption probably overlaps a $Cl^- \rightarrow Cu(II)$ charge transfer transition, the analogous $Br^- \rightarrow Cu(II)$ transition being observed at 395 nm in $Cu(tbmp)_2Br_2$. The latter assignments are more consistent with in-plane Cu-X bonding.

ii) $[Cu(tbmp)_2X]BF_4$ $(X=Cl^-, Br^-)$

The spectra at 90K (Figure 8) are virtually identical to those of the respective complexes in dichloromethane at room temperature (Figure 7) and to those of $Cu(tbmp)_2X_2$ ($X=Cl^-$, Br^- respectively) at 90K (Table 11). Electron spin resonance spectra at 77K in 20% Glycerol/MeOH are consistent with the $[Cu(tbmp)_2X]^+$ chromophores being closer to having tetragonal pyramidal structures rather than trigonal bipyramidal structures.

2.2 ELECTRON SPIN RESONANCE SPECTRA

The data for these complexes is given in Table 12, for various glasses at 77K.

i) $Cu(tbmp)_2(BF_4)_2$

Acetone: Two species are present, both having similar $|A_{\parallel}|$ values (169×10^{-4} and $165 \times 10^{-4} cm^{-1}$) but with different $g_{\parallel}$ (2.264, 2.320 resp.) values (Figure 9). On adding excess ligand, a significant increase in the concentration of the minor species is observed (Figure 9) but there is no change in the $g_{\parallel}$ and $A_{\parallel}$

values of either complex. The spectral changes suggest that the $g_{\parallel} = 2.320$ complex is basically a $[Cu(tbmp)_2]^{2+}$ chromophore where tetrahedral distortions and/or decreased covalent bonding in the Cu(II) coordination sphere have increased $g_{\parallel}$ [60].

Nitromethane and Methanol: The complex also breaks down in these solvents and dramatic spectral changes (Figure 9) can be induced by adding excess ligand. In the absence of excess ligand, the spectra are probably due to a tetragonal solvated $[CuNS]^{2+}$ chromophore such as $[Cu(tbmp)(solvent)_n]^{2+}$ where n = 2 or 4. In methanol, a very small quantity of a species having similar $g_{\parallel}$ (ca 2.30) and $|A_{\parallel}|$ (ca 150-165 x $10^{-4}cm^{-1}$) values to one of the complexes in acetone, is also formed.

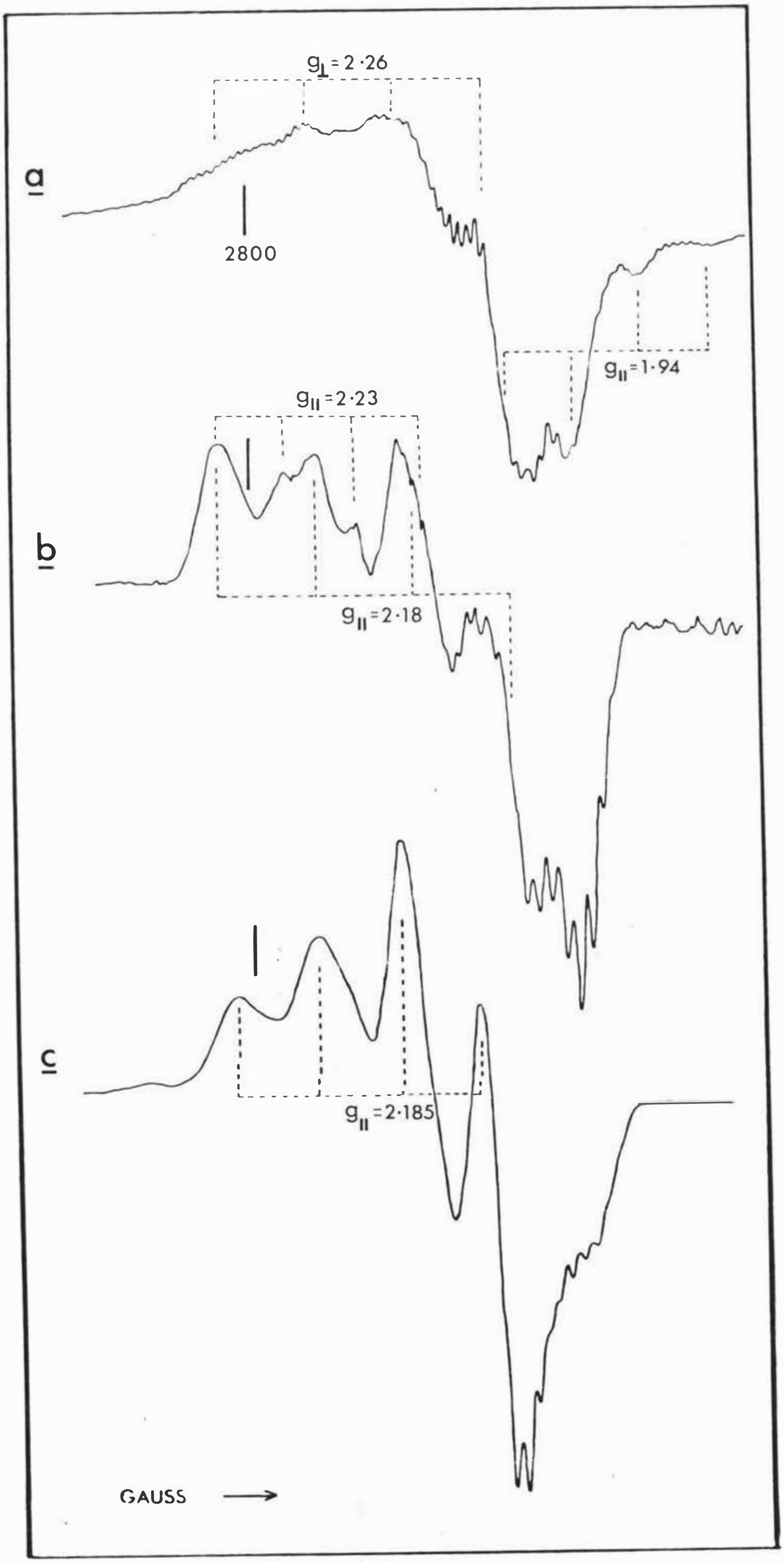
In the presence of excess ligand, the spectra are typical of a tetragonal Cu(II) chromophore, with or without nitromethane and methanol in the Cu(II) coordination sphere. The spectra are thus assigned to a $[Cu(tbmp)_2(solvent)_n]^{2+}$ species (n = 0 or 2).

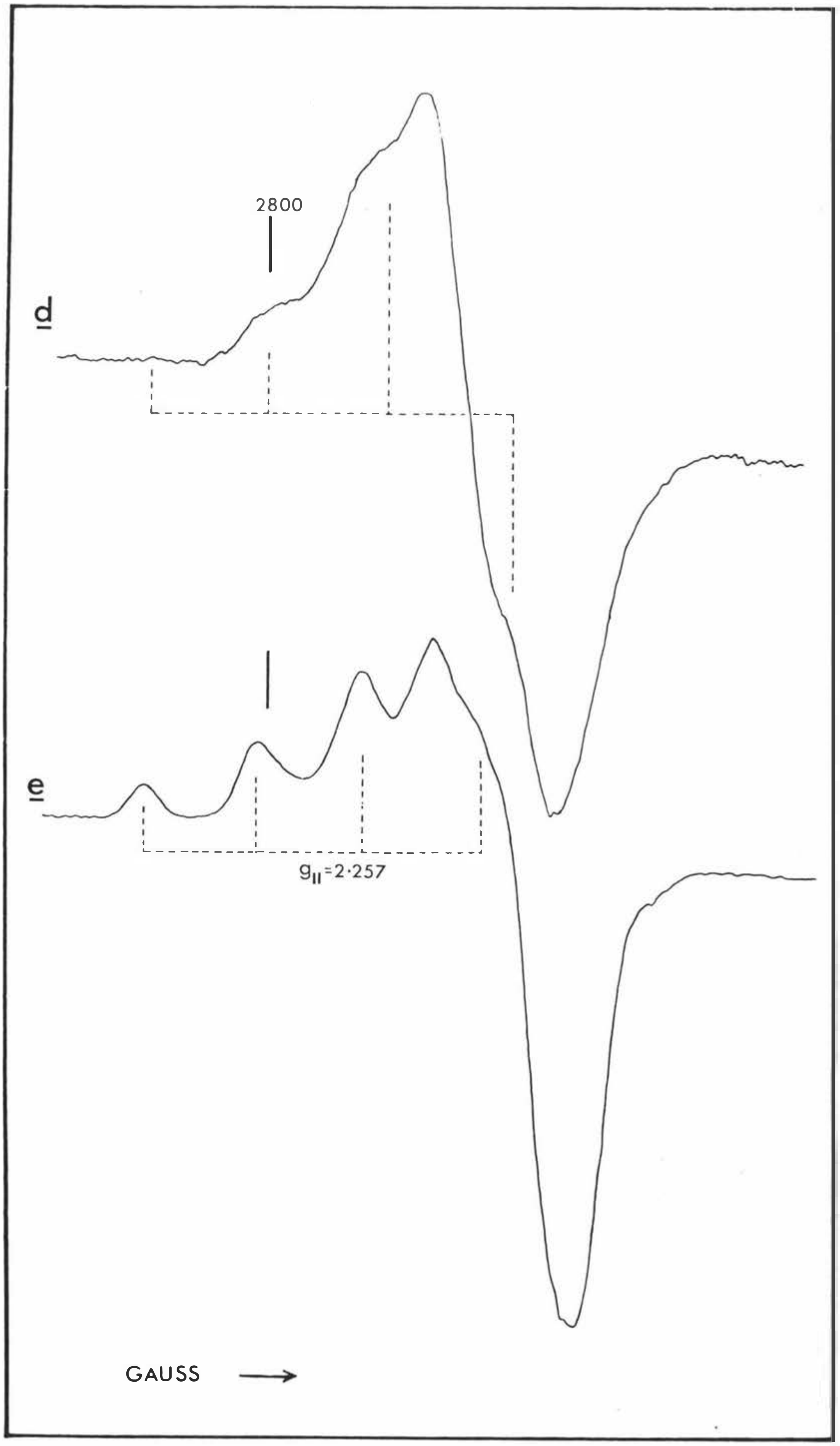
ii) $Cu(tbmp)_2X_2$ ($X=Cl^-$, Br^-)

Dichloromethane: It was apparent from the electronic spectra that these complexes form $[Cu(tbmp)X_2]_2$ five-coordinate dimers in this solvent at room temperature but there is no esr evidence for the presence of these dimers at 77K. The addition of excess ligand gives a better resolved spectrum (Figure 9) where X is chloride, but the $g_{\parallel}$ and $|A_{\parallel}|$ values suggest

FIGURE 9

ESR Spectra - Cu(tbmp)$_2$X$_2$ Complexes (at 77K)




2800
d
e
g_{II}=2·257
GAUSS →

Key to Figure 9

a - $Cu(tbmp)_2Br_2$ (+ excess tbmp) in dichloromethane

b - $Cu(tbmp)_2Br_2$ in 20% Glycerol/MeOH

c - $Cu(tbmp)_2Cl_2$ in methanol

d - $Cu(tbmp)_2Cl_2$ in dichloromethane

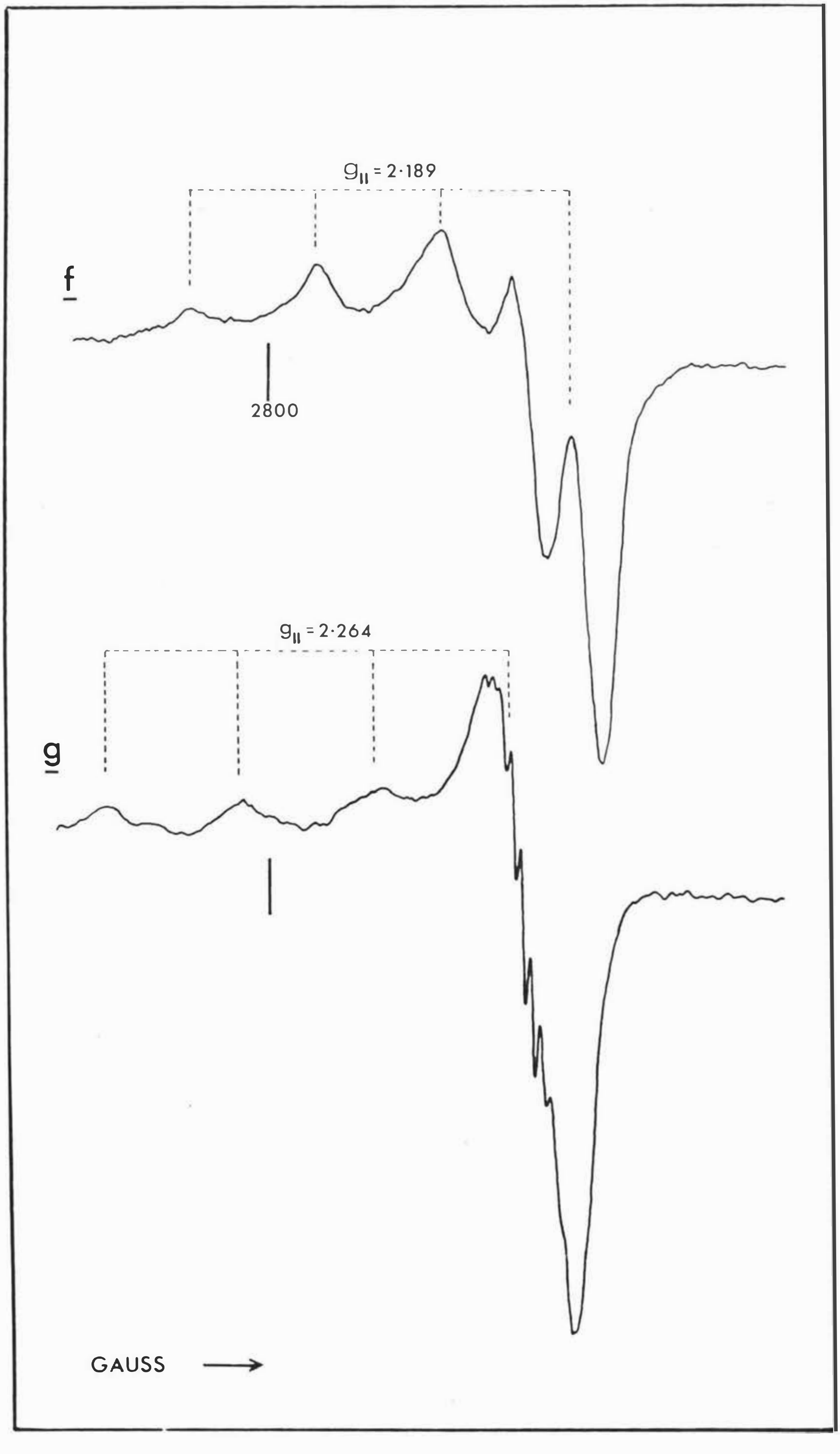
e - $Cu(tbmp)_2Cl_2$ (+ excess tbmp) in dichloromethane

f - $Cu(tbmp)_2(BF_4)_2$ in nitromethane

g - $Cu(tbmp)_2(BF_4)_2$ (+ excess tbmp) in nitromethane

h - $Cu(tbmp)_2(BF_4)_2$ in acetone

i - $Cu(tbmp)_2(BF_4)_2$ (+ excess tbmp) in acetone


$g_{\parallel} = 2{\cdot}189$
f
2800
$g_{\parallel} = 2{\cdot}264$
g
GAUSS →

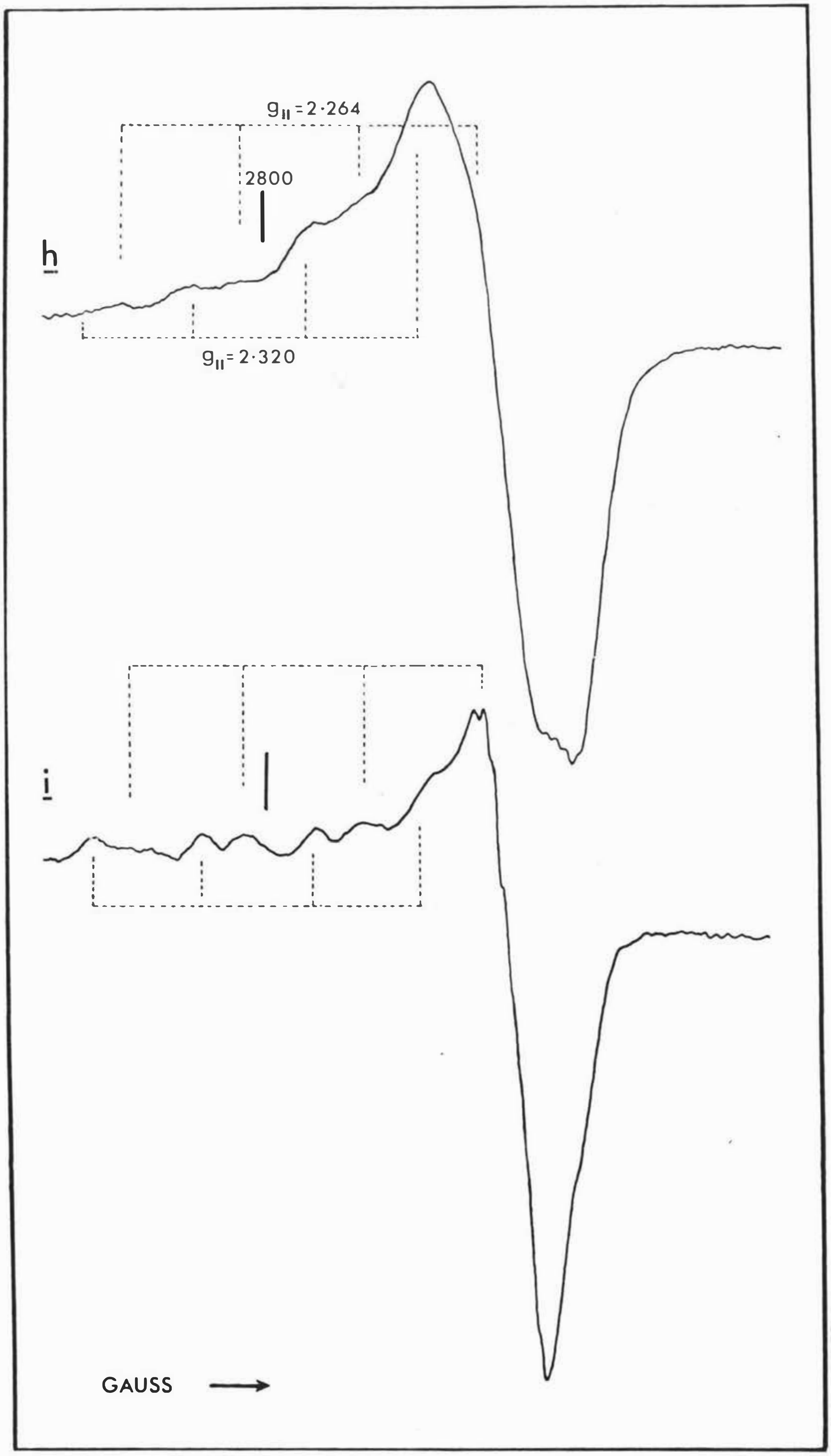

$g_{\parallel} = 2{\cdot}264$
2800
h
$g_{\parallel} = 2{\cdot}320$
i
GAUSS

TABLE 12

ESR SPECTRA, $Cu(tbmp)_2X_2$ AND $[Cu(tbmp)_2X]BF_4$ COMPLEXES

COMPLEX	SOLVENT	$g_\parallel$	$10^4\lvert A_\parallel\rvert$	$^{14}N_{shfs}$	$g_\perp$	$10^4\lvert A_\perp\rvert$
$Cu(tbmp)_2(BF_4)_2$	CH_3NO_2	2.189	169			
	+ excess L	2.264	190	14	*ca* 2.055	
	Acetone	a) 2.264	169			
		b) 2.320	165			
	+ excess L	a) 2.263	169			
		b) 2.312	163			
	MeOH	a) 2.296	150			
		b) 2.363	151			
	+ excess L	a) 2.252	173			
		b) 2.194	164			
	Glyc./MeOH	a) 2.293	147			
		b) 2.338	162			
	+ excess L	2.249	144			
$Cu(tbmp)_2(ClO_4)_2$	CH_3NO_2	2.180	172			
$Cu(tbmp)_2Cl_2$	CH_2Cl_2	*ca* 2.24	*ca* 162			
	+ excess L	2.257	157		*ca* 2.068	
	CH_3NO_2	a) *ca* 2.26	*ca* 100	*ca* 16		
		b) *ca* 2.26	*ca* 159			
	+ excess L	2.260	158	14	2.060	
	MeOH	2.185	124	*ca* 18		
	Glyc./MeCH	2.179	124	17		
	+ excess L	2.185	119	*ca* 18		
	H_2O	2.120(g_{iso})				
$Cu(tbmp)_2Br_2$	CH_2Cl_2	*ca* 1.95	*ca* 97		*ca* 2.23	*ca* 126
	+ excess L	*ca* 1.94	*ca* 92	*ca* 10($g_\perp$) *ca* 12($g_\parallel$)	*ca* 2.26	*ca* 140
	CH_3NO_2	2.104(g_{iso})				
	MeOH	a) *ca* 2.18	*ca* 142	19		
		b) *ca* 2.23	*ca* 104			
	+ excess L	a) 2.191	136	20		
		b) *ca* 2.23	*ca* 104			
	Glyc./MeOH	a) *ca* 2.18	*ca* 144	*ca* 19		
		b) *ca* 2.23	*ca* 109			
$[Cu(tbmp)_2Cl]BF_4$	CH_3NO_2	2.183	117	*ca* 17		
	+ excess L	2.183	117	*ca* 20		
	MeOH	2.183	133	*ca* 17		
	+ excess L	2.188	131	*ca* 17		
	Glyc./MeOH	2.191	126	18		
$[Cu(tbmp)_2Br]BF_4$	CH_3NO_2	a) 2.181	129	*ca* 20		
		b) 2.225	97			
	MeOH	*ca* 2.19	*ca* 138			
	+ excess L	a) 2.180	122	17		
		b) 2.220	107			
	Glyc./MeOH	a) 2.180	142	18		
		b) 2.225	104			
	+ excess L	a) 2.185	138	19		
		b) 2.225	104			

NOTES:
- units of $\lvert A_\parallel\rvert$ and $\lvert A_\perp\rvert$ are cm^{-1},
- units of $^{14}N_{SHFS}$ are Gauss,
- iso = isotropic; shfs = superhyperfine splitting,
- all spectra recorded at 77K,
- Glyc./MeCH = 20% Glycerol/Methanol,
- unless otherwise indicated, $^{14}N_{SHFS}$ lines appear in $g_\perp$ region.

that the same complex, (probably cis-$Cu(tbmp)_2Cl_2$) is present both with and without excess ligand.

Cis-distorted octahedral complexes have a d_{z^2} ground state and should thus exhibit a lowest-g value of ca 2.00, however a lower than ideal geometry, which is likely to be the case here can raise this low g value.[30,76] ESR parameters for what were deduced to be cis and trans- $[Cu(bipyridyl)_2(solvent)_2]^{2+}$ systems have been reported recently[84], but the dissimilarity between the studies described herein and those described by Marov et al, does not make a comparison very meaningful.

Under the same conditions, $Cu(tbmp)_2Br_2$ behaves differently than $Cu(tbmp)_2Cl_2$. With and without excess ligand, the spectra exhibit poorly resolved, low-field hyperfine structure ($g_{\parallel}$) and this is overlapped by a complicated ^{14}N superhyperfine structure in the presence of excess ligand (Figure 9). The number of species contributing to the spectra is difficult to determine. It is clear from the high-field region that the major contributor to the spectrum is a distorted trigonal bipyramidal species. This could be either $[Cu(tbmp)_2Br]^+$ or $Cu(tbmp)_2Br_2$ if one ligand is monodentate. The $g_{\parallel}$ for this complex ($g_{\parallel} \sim 1.94$) is characteristic of trigonal bipyramidal complexes containing coordinated halogens and it probably arises from a combination of spin-orbit coupling with a bromide ligand[67] and Cu(II)-thioether interactions.[60]

Nitromethane: Two species are apparent for $Cu(tbmp)_2Cl_2$ and the addition of ligand causes the disappearance of one of these ($g_{\parallel} \sim 2.26$; $|A_{\parallel}| \sim 100 \times 10^{-4} cm^{-1}$) leaving the spectrum of what is probably <u>cis</u>-octahedral $Cu(tbmp)_2Cl_2$.

The spectrum of $Cu(tbmp)_2Br_2$ is poorly resolved and neither the addition of excess ligand nor varying the concentration resulted in an improved spectrum.

<u>Methanol and 20% Glycerol/Methanol</u>: $Cu(tbmp)_2Cl_2$ gives identical spectra (Figure 9) to $[Cu(tbmp)_2Cl]BF_4$ in methanol, glycerol/methanol and nitromethane glasses and there is no change on adding excess ligand. The $g_{\parallel}$ (<u>ca</u> 2.185) and $|A_{\parallel}|$ (<u>ca</u> $123 \times 10^{-4} cm^{-1}$) values are consistent with the complexes having tetragonal pyramidal geometries at 77K [67,68,85] where $|A_{\parallel}|$ has been lowered from typically tetragonal values by increased axial interactions.[85] These result in a concomitant increase in the 4s orbital population, compared to <u>cis</u>-octahedral $Cu(tbmp)_2Cl_2$ postulated in nitromethane (plus excess ligand) and dichloromethane glasses (above). The possibility that $Cu(tbmp)_2Cl_2$ is six-coordinate is ruled out by a consideration of its electronic spectrum in 20% Glycerol/MeOH at 90K. (see 2.1(C)).

Superior resolution of the $g_{\parallel}$ lines for the two species arising from $Cu(tbmp)_2Br_2$ in methanol glass is achieved by adding excess ligand. No resolution problems are encountered with 20% Glycerol/MeOH. The spectra (Figure 9) are virtually the same as those of $[Cu(tbmp)_2Br]BF_4$ in methanol (plus excess ligand), 20% Glycerol/MeOH and nitromethane glasses, with two species being observed. Their relative concentrations are unaffected by excess ligand. Species (a) ($g_{\parallel} \sim 2.18$; $|A_{\parallel}| \sim 142 \times 10^{-4} cm^{-1}$) appears to be analogous to the tetragonal pyramidal monomer which is postulated to be responsible for the spectra of $Cu(tbmp)_2Cl_2$ and $[Cu(tbmp)_2Cl]BF_4$ in methanol containing glasses. Species (b) ($g_{\parallel} \sim 2.23$; $|A_{\parallel}| \sim 104 \times 10^{-4} cm^{-1}$) may also have a tetragonal pyramidal stereochemistry although $g_{\parallel}$ and $|A_{\parallel}|$ are equally consistent with a pseudotetrahedral $[CuN_2S_2]^{2+}$ chromophore where $g_{\parallel}$ has been lowered by Cu(II)-thioether interactions.[60] However, the electronic spectra at 90K do not support the latter suggestion. It is plausible that the esr spectra are due to two of the isomers that are possible for a tetragonal pyramidal $[Cu(tbmp)_2Br]^{2+}$ species. The low $|A_{\parallel}|$ values for the two species rule out the possibility that tetragonal pyramidal ↔ square planar interconversion, similar to that postulated for $CutrienR_6X_2$ ($X=Cl^-$, Br^-) complexes,[67] is occurring.

iii) <u>$[Cu(tbmp)_2X]BF_4$ ($X=Cl^-$, Br^-)</u>

<u>Methanol, 20% Glycerol/Methanol</u>: The spectra are virtually identical to the respective $Cu(tbmp)_2X_2$ complexes (where X is chloride and bromide) that were discussed above. There is one minor difference though, in that only one species is apparent for $[Cu(tbmp)_2Br]BF_4$ in methanol, the spectrum being poorly resolved.

<u>Nitromethane</u>: The spectra are similar to those of the respective complexes in methanol and 20% Glycerol/MeOH (Table 12). However, they differ from those of $Cu(tbmp)_2Cl_2$ and $Cu(tbmp)_2Br_2$ in nitromethane glasses in which

the cis-octahedral Cu(tbmp)$_2$X$_2$ chromophores are probably predominant.

2.3 INFRARED SPECTRA

FAR-INFRARED (Cu(II)-halogen stretching)

One ν(Cu-X) absorption (X=halogen) is expected for trans-tetragonal CuL$_4$X$_2$ complexes (D_{4h} symmetry) whereas two absorptions are expected for the cis complexes (C_{2v} symmetry).[86] The tbmp complexes will be of lower symmetry because of the asymmetrical nature of the ligands and so predictions regarding the expected number of ν(Cu-X) absorptions, in the absence of more detailed structural information, can not be accurately made.

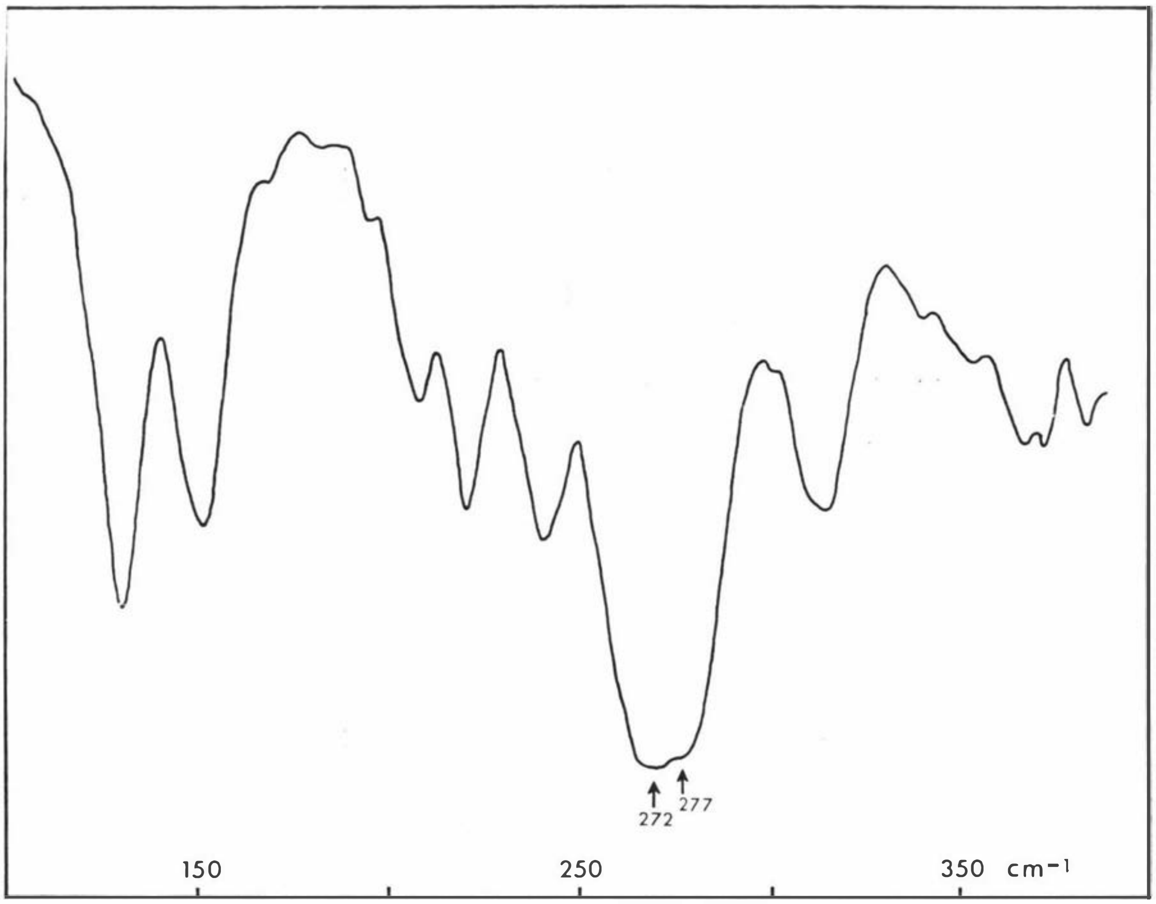
Some crystal structure-correlated far-infrared data for Cu(II) complexes is presented in Table 13a and this can be compared with the data for the Cu(tbmp)$_2$X$_2$ (X=Cl$^-$, Br$^-$) and [Cu(tbmp)$_2$X]BF$_4$ (X=Cl$^-$, Br$^-$) complexes in Table 13b. The tentatively assigned ν(Cu-X) absorptions of these complexes are consistent with equatorial Cu-X bonding and they can be compared with the low frequency ν(Cu-X) absorptions that have been assigned for the trans-tetragonal Cu(etea)$_2$X$_2$ complexes (Chapter 5.3, Table 29). Two ν(Cu-Cl) absorptions are observed for Cu(tbmp)$_2$Cl$_2$ (Figure 10) and the spectrum is similar to those of Ni(tbmp)$_2$Cl$_2$ and Co(tbmp)$_2$Cl$_2$ for which distorted cis-octahedral structures also seem to be likely (Chapter 4).

GENERAL INFRARED

i) Anion coordination: Semi-coordination of perchlorate and tetrafluoroborate anions results in a

FIGURE 10

Far-IR Spectrum - $Cu(tbmp)_2Cl_2$



- the two ν(Cu-Cl) absorptions (indicating that the chloride ions are <u>cis</u> with respect to each other) are shown.

TABLE 13a

SOME FAR-IR DATA FOR Cu(II) COMPLEXES

COMPLEX	STRUCTURE	REF.	ν(Cu-X)/cm^{-1}	REF.
$Cu(en)Cl_2$	Polymeric tetr.; briding Cl^-	87	267	72
$Cu(en)Br_2$	Isomorphous with $Cu(en)Cl_2$	88	187	72
$[Cu(en)_2Cl.H_2O]Cl$	Tetr.; axial Cu-Cl and Cu-H_2O	89	<200 ϕ	90
$[Cu(en)_2Br.H_2O]Br$	Tetr.; axial Cu-Br and Cu-H_2O	91,97	<200 ϕ	90
$[Cu(dmen)Cl_2]_2$	Dichloro-bridged, tetr.pyr. dimer	19	302	72
$[Cu(dmen)Br_2]_2$	Dibromo-bridged, tetr.pyr. dimer	19	233	72
$Cu(\alpha\text{-pic})_2Cl_2$	Chloro-bridged, tetr.pyr. dimer	24	305	72
$Cu(\alpha\text{-pic})_2Br_2$	Bromo-bridged, tetr.pyr. dimer	23	233	72
$Cu(4\text{-}EtPy)_2Cl_2$	Tetr., long Cu-Cl br.sq.planar CuN_2Cl_2	92	310	72
$Cu(py)_2Cl_2$	Tetr., long Cu-Cl br.sq.planar CuN_2Cl_2	93	295, 234	86
$Cu(py)_2Br_2$	Tetr., long Cu-Br br.sq.planar CuN_2Br_2	94	256	86
$Cu(\beta\text{-isosparteine})Cl_2$	Distorted tetrahedral	95	282, 275	96

NOTES: - tetr. = tetragonal; pyr. = pyramidal; br. = bridging; sq. = square.

ϕ ν(Cu-X) below the range of the instrument that was used.

TABLE 13b

FAR-IR DATA, tbmp/Cu(II) COMPLEXES

COMPLEX	ν(Cu-X)/cm^{-1}	PROPOSED STRUCTURE
$Cu(tbmp)_2Cl_2$	272,277(sh)	cis-octahedral,monomeric
$[Cu(tbmp)Cl_2]_2$	282,296	tetragonal pyramidal,dimeric
$[Cu(tbmp)_2Cl]BF_4$	292	tetragonal pyramidal,monomeric
$Cu(tbmp)_2Br_2$	184	cis-octahedral,monomeric
$[Cu(tbmp)Br_2]_2$	227,244	tetragonal pyramidal,dimeric (X-rayed)
$[Cu(tbmp)_2Br]BF_4$	183	tetragonal pyramidal,monomeric

NOTES: - spectra recorded for paraffin mulls, room temperature.
- structures proposed on basis of collective spectroscopic data.

TABLE 13c

GENERAL IR DATA, tbmp/Cu(II) COMPLEXES

COMPLEX	ν(pyridyl ring)	$\nu_3(ClO_4^-/BF_4^-)$	$\nu_1(ClO_4^-/BF_4^-)$
tbmp	1593(s),1570(m)		
$Cu(tbmp)_2(ClO_4)_2$	1612(s),1576(w)	1090(vs),1050(vs)	933(w)
$Cu(tbmp)_2(BF_4)_2$	1611(m),1577(w)	1098(s),1061(s) 991(s)	φ
$Cu(tbmp)_2Cl_2$	1607(s),1574(m)		
$Cu(tbmp)_2Br_2$	1609(m),1566(w)		
$[Cu(tbmp)Cl_2]_2$	1606(m)		
$[Cu(tbmp)Br_2]_2$	1599(m),1565(m)		
$[Cu(tbmp)_2Cl]BF_4$	1605(s),1572(w)	1054(vs)	φ
$[Cu(tbmp)_2Br]BF_4$	1607(s),1569(w)	1055(vs)	φ

NOTES: φ strong ligand band occurs at about 760 cm^{-1}
- frequencies are cm^{-1}, spectra recorded for Nujol Mulls.
- s = strong; m = medium; w = weak; v = very
- ionic ClO_4^-, ν_3 occurs at ca 1100 cm^{-1}, ν_1 at ca 930 cm^{-1}
- ionic BF_4^-, ν_3 occurs at ca 1100 cm^{-1}, ν_1 at ca 760 cm^{-1}.

splitting of the intense ν_3 mode (found at about 1100 cm^{-1}) and there is an increase in the intensity of the weak ν_1 mode which is found at about 930 cm^{-1} (perchlorate) and 760 cm^{-1} (tetrafluoroborate) respectively.[91] The ν_1 mode, which is formally infrared inactive in the uncoordinated anions (T_d symmetry), becomes infrared active as a result of the lower symmetry (C_{3v}) of the semi-coordinated anion and the previously degenerate ν_3 mode, loses some of its degeneracy.

The spectra of $Cu(tbmp)_2(ClO_4)_2$ and $Cu(tbmp)_2(BF_4)_2$ suggest that the anions are semi-coordinating (Table 13c) as a splitting of the ν_3 mode is observed, however the single ν_3 absorption in the spectra of $[Cu(tbmp)_2Cl]BF_4$ and $[Cu(tbmp)_2Br]BF_4$ is good evidence for the non-coordination of the tetrafluoroborate anions.

ii) <u>Ring Stretching modes</u>: Two ring stretching modes are normally observed for 2-substituted pyridine ligands[98] and the effects of ligand complexation to metal ions, on these frequencies, have been well documented.[99,100] The strong, sharp absorption at 1578 cm^{-1} for pyridine film[99] is shifted to 1593 cm^{-1} in tbmp and Gill <u>et al</u> report that it is this absorption (Band I) which shifts to higher frequencies in metal-pyridine complexes. Other workers have reported similar shifts in the complexes of substituted pyridine ligands.[100,101] The $Cu(tbmp)_2X_2$ ($X=ClO_4^-$, BF_4^-, Cl^-, Br^-) and $[Cu(tbmp)_2X]BF_4$ ($X=Cl^-$, Br^-) complexes exhibit shifts of up to 19 cm^{-1} in Band I (Table 13c) and these are consistent with pyridyl — Cu(II) coordination. The blue-shifts are greater than those observed in the carbonyl complexes, $M(CO)_4$tbmp (M=Cr, Mo, W) (Section II, Chapter 3,), but similar to those of the $[Cu(tbmp)X_2]_2$ dimers (Chapter 1), which have also been included in Table 13c.

2.4 INTERACTION OF THIOLS WITH $Cu(tbmp)_2X_2$ ($X=ClO_4^-$, BF_4^-)

The addition of a few drops of a freshly prepared alcohol solution of $NaSC(CH_3)_3$ to methanol solutions of $Cu(tbmp)_2X_2$ ($X=ClO_4^-$, BF_4^-) at dry-ice/acetone temperatures, produces a deep blue solution which goes colourless after about ten minutes. In ice-cold solutions, the colour disappears almost instantly. The characterization of this deep blue species was attempted using electronic spectroscopy.

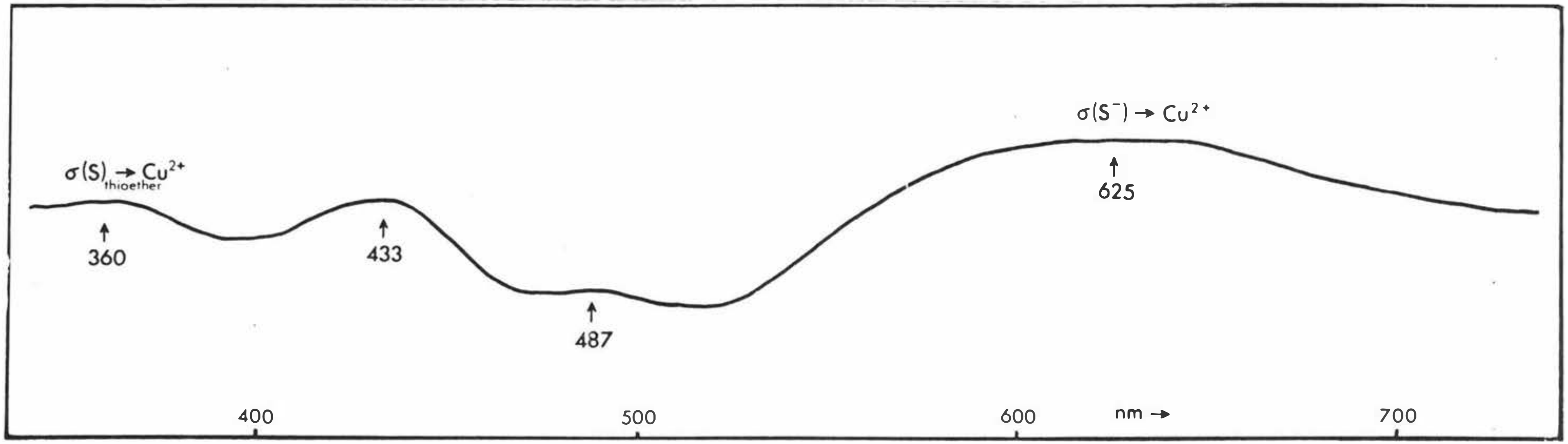
Electronic Spectra

The electronic spectrum (measured at 90K) for the reaction of t-butylthiolate with $Cu(tbmp)_2(ClO_4)_2$ in methanol is shown in Figure 11.

A comparison of the spectrum (at room temperature) of $Cu(tbmp)_2(ClO_4)_2$ (Table 10) with this system shows that at least three new absorptions appear in the latter spectrum. These are at 433, ca 487 and 625 nm, the latter not being a d-d maximum because of its greater relative intensity than the higher energy charge transfer absorptions. By analogy with $Cu(tbmp)_2(ClO_4)_2$, the 360 nm absorption can probably be assigned as a σ(thioether)$\longrightarrow$ Cu(II) charge transfer transition but the assignments of the other absorptions are not as obvious. A comparison with similar work on Cu(II) —

FIGURE 11

Electronic Spectrum (90K) - Addition of $t\text{-BuS}^-$ to $Cu(tbmp)_2(ClO_4)_2$ in Methanol



thiolate interactions[80] suggests that the 625 nm transition is probably a thiolate → Cu(II) charge transfer absorption. The remaining two absorptions may also be derived from S → Cu(II) charge transfer.

2.5 REACTIVITY STUDIES

These were designed to test the stability of tbmp towards replacement of pyridine.

i) Addition of pyridine to $Cu(tbmp)_2Cl_2$

Without pyridine, an ethanol solution of $Cu(tbmp)_2Cl_2$ exhibits two ligand field absorptions and the changes in the lower energy maximum can be followed in Figure 12. The changes on adding successive aliquots of pyridine are consistent with adduct formation when these spectra are compared with the spectrum of a dilute ethanol solution of $Cu(tbmp)_2Cl_2$. The adduct appears to be quite stable because even in the presence of a ten-fold excess of pyridine where a blue precipitate characteristic of $Cu(py)_2Cl_2$ forms, the d-d maxima of the solution remain unchanged. An ethanol solution of $CuCl_2$ and pyridine has a d-d absorption at about 662 nm.

ii) Addition of pyridine to $Cu(tbmp)_2(BF_4)_2$ (in acetone)

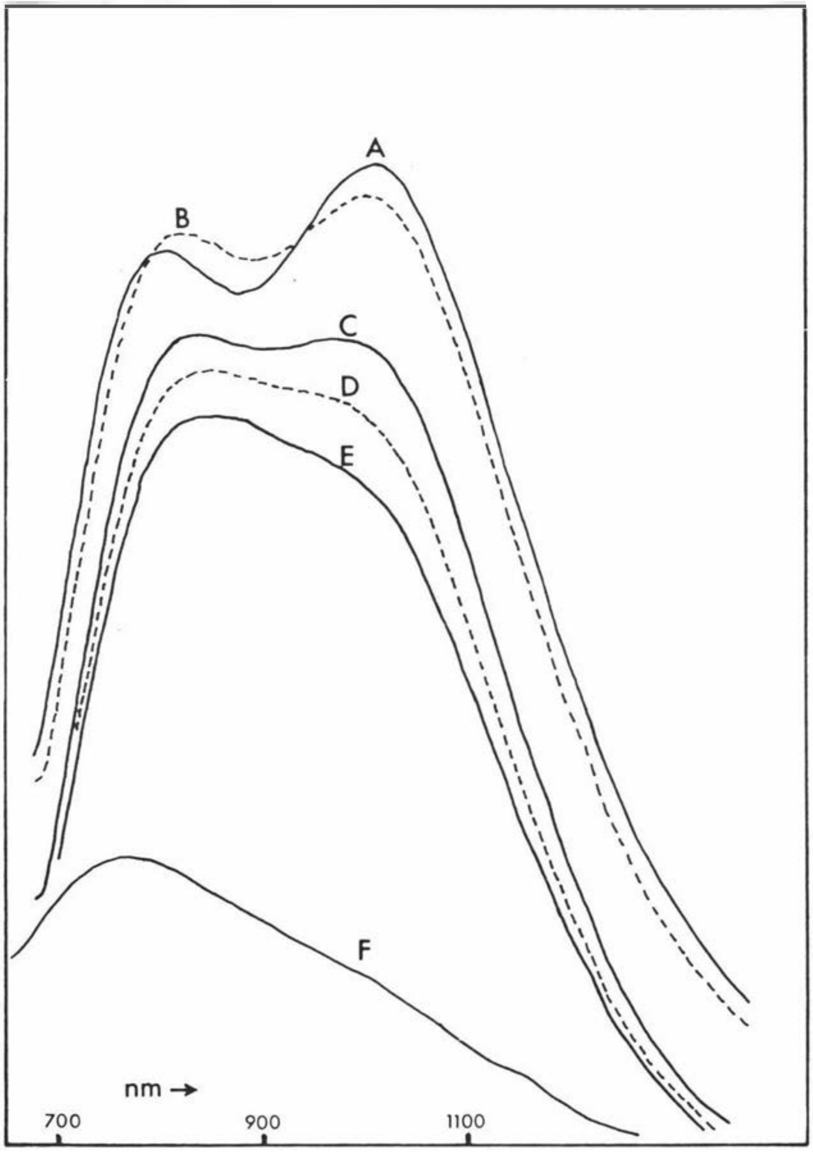
Although the initially green/black solution turns blue with the successive addition of aliquots of pyridine, a purple precipitate does not form until a ten-fold excess of pyridine is reached. The infrared spectrum and colour of this precipitate are consistent with it being $Cu(py)_4(BF_4)_2$.

iii) Discussion

These experiments show that chelated tbmp is

FIGURE 12

Electronic Spectra-Addition of pyridine to $Cu(tbmp)_2Cl_2$



- changes in the ligand field maxima are shown.

A - no pyridine (green solution)
B - pyridine : Cu(II) = 1:1
C - pyridine : Cu(II) = 3:1
D - pyridine : Cu(II) = 6:1
E - pyridine : Cu(II) = 10:1 (blue-green solution)
F - large excess of pyridine (blue solution)

quite stable towards replacement by pyridine as relatively high pyridine : Cu(II) ratios are needed. This stability can be compared to the relative ease with which the displacement of 2,5-dithiahexane and 3,6-dithiaoctane can be achieved,[82,102] using a two-fold excess of pyridine, in polar solvents.

2.6 PARAMAGNETIC ^1H nmr LINE BROADENING EXPERIMENT

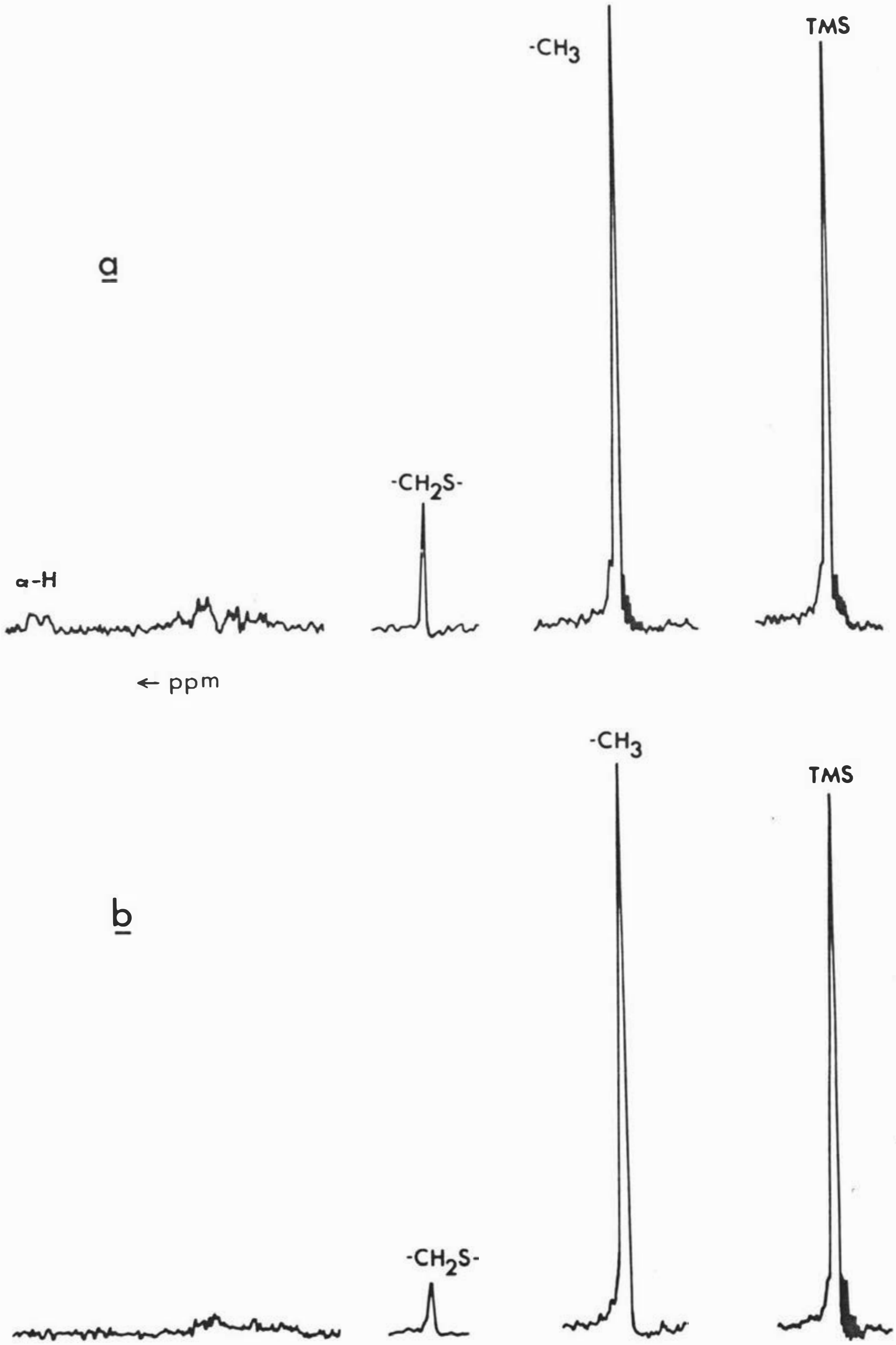
^1H nmr line broadening experiments using paramagnetic ions such as Cu(II)[103], have become an important tool in determining the nature of metal ion interactions with thioether ligands in solution. This is especially so in studies of ligands that have more than one possible binding site, such as S-methyl-L-cysteine, L-methionine[104], S-2′-aminoethylcysteine[105] and (S)-β-(2-pyridylethyl)-L-cysteine.[106] Selective broadening of the ^1H nmr signals of protons close to the binding site of the ligand is caused by rapid $M^{2+} + L \rightleftharpoons ML^{2+}$ exchange if M^{2+} is paramagnetic.[107] This provides a means of determining the type of metal-ligand interaction that exists under the conditions of the experiment.

Discussion

The effect of adding Cu(II) to the ligand (tbmp) is illustrated by the changes in the signals of the α-proton and methylene protons. (Figure 13). The α-proton resonance disappears and the height of the methylene proton peak is significantly reduced in comparison to the slight changes observed for the TMS and methyl proton signals. In an experiment where $CuCl_2\cdot 2H_2O$ crystals were added to a $CDCl_3$ solution of the

FIGURE 13a

^{1}H nmr - Addition of Cu(II) to tbmp (in $CDCl_3$)

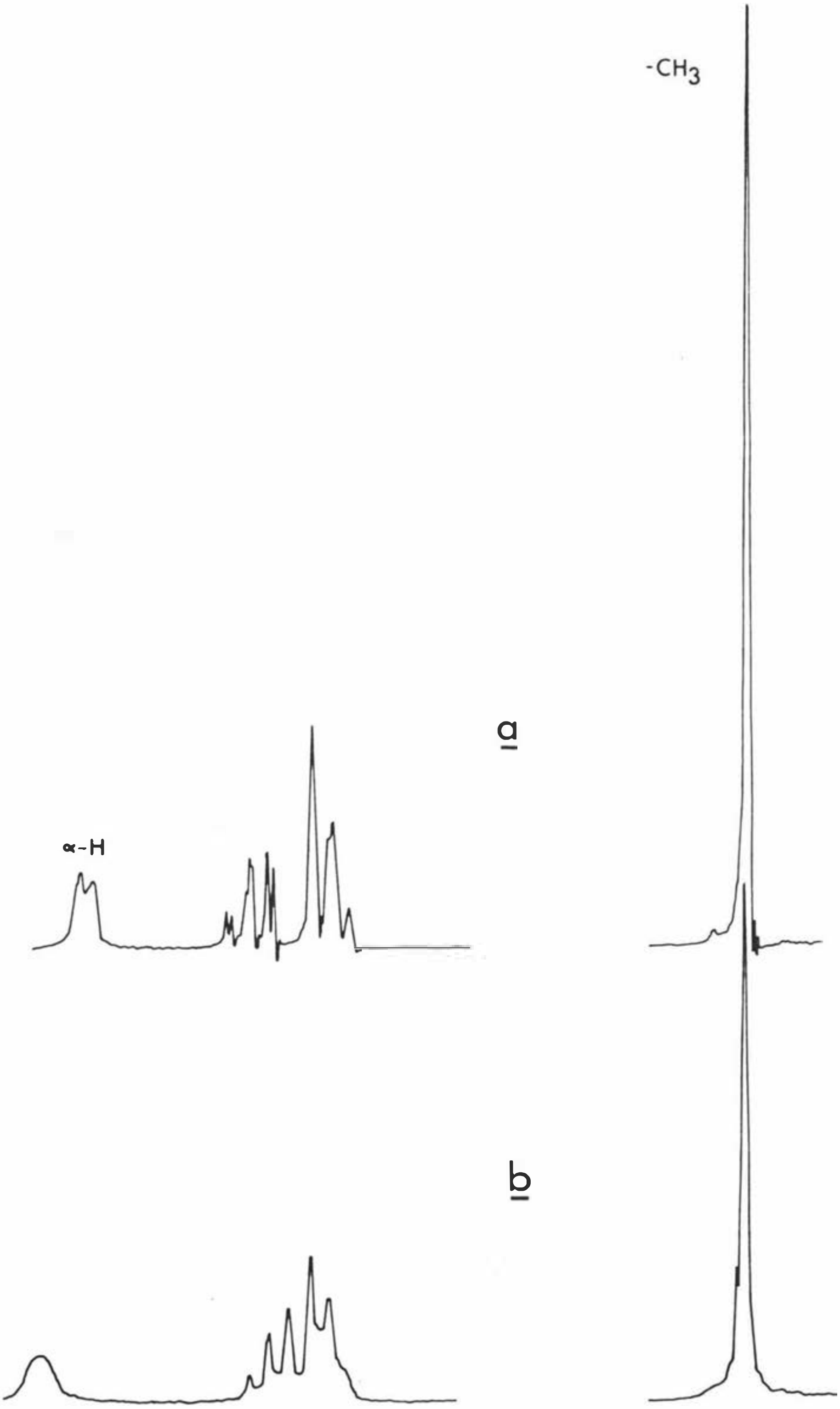


a - tbmp in absence of Cu(II)

b - tbmp in presence of Cu(II) [3.3×10^{-4}mol.l^{-1}]

FIGURE 13b

^{1}H nmr - Addition of Co(II) to 2-methylpyridine (in CH_2Cl_2)



a - 2-methylpyridine in absence of Co(II)

b - 2-methylpyridine in presence of Co(II) ligands, the methylene protons' resonance disappeared. The paramagnetic effect is greater for Cu(II) than Co(II) and this is discussed in Chapter 4.

It is apparent from this experiment that Cu(II) exchange occurs at the pyridyl nitrogen. However, it is possible that the changes in the methylene protons' resonance are also due to this exchange. This can be demonstrated by adding Co(II) to a sample of 2-methylpyridine (Figure 13). It can be seen that the methyl protons' resonance is significantly affected by Co(II)-pyridyl interactions. As a result of these observations, the presence or absence of Cu(II)-thioether interactions can not be confidently established. It is unlikely that the methyl protons of tbmp will be perturbed by Cu(II) exchange at the thioether donor as similar studies with $BuSCH_2CH_2SBu$ show that only the $-CH_2SCH_2-$ protons are affected.[47]

SYNTHESES

Some general comments that relate to all of these syntheses can be found in the experimental section of the Appendices.

Diperchloratobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]-copper(II)

1 mmole of $Cu(ClO_4)_2.6H_2O$ (0.371 g.) was added to 2 mmole of tbmp (0.363 g.) and this resulted in the immediate formation of a dark green precipitate. When it had been filtered and washed with Abs. EtOH, the semi-dry product was carefully transferred to a bottle to complete the drying *in vacuo*.

YIELD : 0.424 g. (68%)

Ditetrafluoroboratobis[2-(3,3-dimethyl-2-thiabutyl)-pyridine]copper(II)

2 mmole of $Cu(BF_4)_2.6H_2O$ (0.690 g.) were added to 4 mmole of ligand (0.725 g.) to give a dark green precipitate.

YIELD : 0.845 g. (70%)

Dichlorobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]-copper(II)

2 mmole of $CuCl_2.2H_2O$ (0.340 g.) were added to 4 mmole of ligand (0.725 g.) to give a dark green solution. This was concentrated *in vacuo* then cooled to yield a lime green precipitate. The precipitate was washed with a small quantity of Abs. EtOH and then ether, after it had been filtered.

YIELD : 0.655 g. (66%)

Dibromobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]copper(II)

1 mmole of anhydrous $CuBr_2$ (0.223 g.) was added to 2 mmole of ligand (0.363 g.) to give a green-black

solution. The solution was reduced in volume and then cooled to precipitate a dark green solid. Ether was added to the filtrate to precipitate some more of the complex which was filtered off and washed with Abs. EtOH and then ether.

YIELD : 0.365 g. (62%)

Chlorobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]-copper(II)tetrafluoroborate

1 mmole of anhydrous LiCl (0.042 g.) in ethanol-acetone was added to an acetone solution of 2 mmole of tbmp and 1 mmole of $Cu(BF_4)_2.6H_2O$. The lime green solution was concentrated and then cooled to crystallize impure, green $[Cu(tbmp)_2Cl]BF_4$. Pure $[Cu(tbmp)_2Cl]BF_4$ was isolated after recrystallizing the impure product from an Abs. EtOH solution at dry ice/acetone temperatures.

Bromobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]copper(II)-tetrafluoroborate

An acetone solution (containing a few drops of triethylorthoformate) of 2 mmole of tbmp and 1 mmole of $Cu(BF_4)_2.6H_2O$ was filtered before adding an Abs. EtOH solution of anhydrous LiBr. The light green solution was concentrated *in vacuo* and cooled. The lime green complex was crystallized by scratching the flask with a spatula.

YIELD : 0.076 g. (13%)

TABLE 14

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES:Calc.(Found)%				CONDUCTIVITY/ohm^{-1}mol.$^{-1}$ cm^{2}		
			C	H	N	Other	CH_3NO_2	MeCN	Other
$Cu(tbmp)_2(ClO_4)_2$	d.green	—	38.43 (38.95)	4.84 (4.96)	4.48 (4.60)		165		ϕNO_2: 28
$Cu(tbmp)_2(BF_4)_2$	d.green	149-150	40.05 (40.05)	5.04 (5.16)	4.67 (4.68)		170		ϕNO_2: 30
$Cu(tbmp)_2Cl_2$	lime	89-90	48.32 (48.17)	6.08 (6.16)	5.64 (5.55)		22	65	ϕNO_2: 4 H_2O:211 EtOH:16
$Cu(tbmp)_2Br_2$	green	91-93	40.99 (41.07)	5.16 (5.30)	4.78 (4.87)		36	73	
$[Cu(tbmp)_2Cl]BF_4$	green	112-113	43.80 (43.32)	5.51 (5.56)	5.12 (4.85)		86	101	
$[Cu(tbmp)_2Br]BF_4$	lime	123-124	40.52 (40.61)	5.10 (5.16)	4.73 (4.65)	Br, 13.48 (13.97)	92	100	

NOTES: - molar conductivities at 25 °C :

	1:1	2:1
Nitromethane	(70-90),	(150-170).
Methanol	(100-130),	(210-250).
Nitrobenzene	(20-30)	
Ethanol	(60-80)	
Water		(210-250)

- d = dark

CHAPTER 3

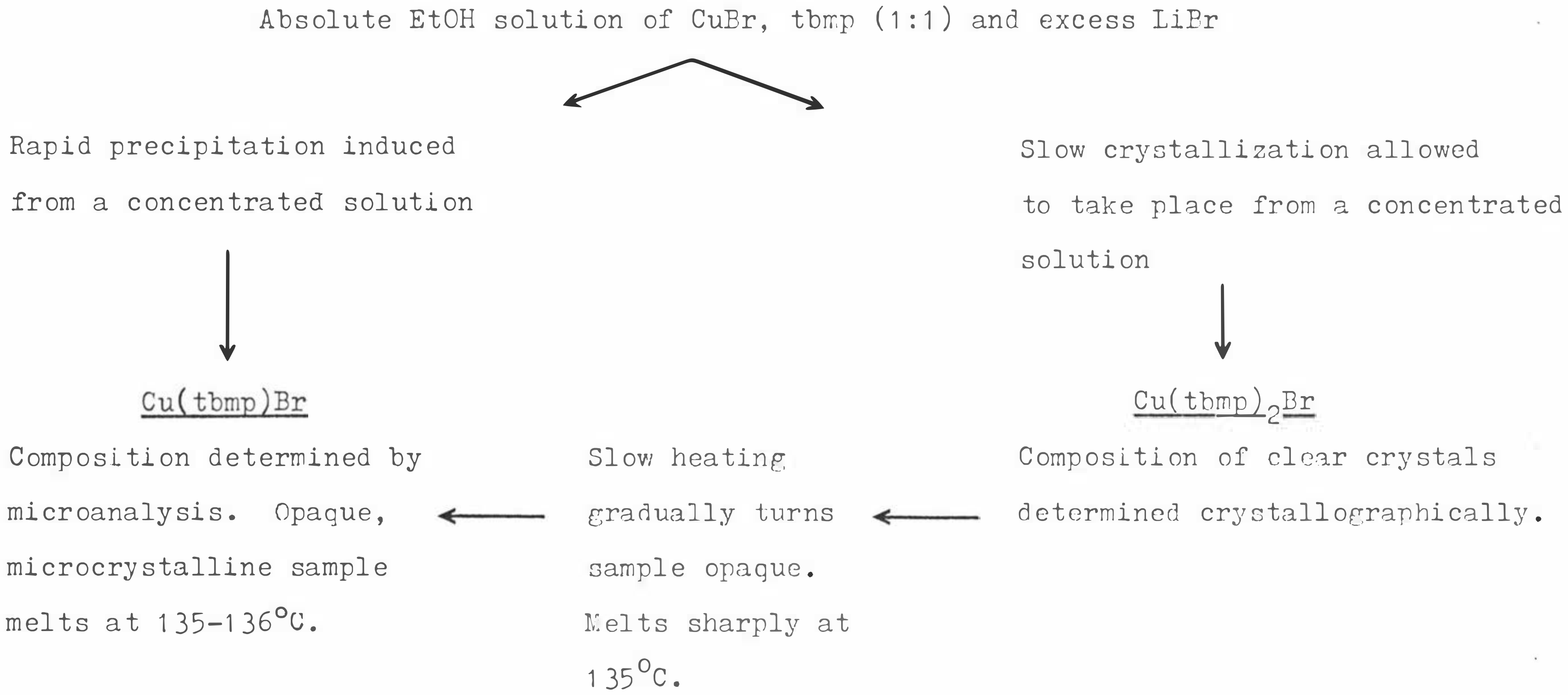
COPPER(I) COMPLEXES
OF
2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE
AND THE
2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINIUM CATION

The Cu(I) complexes $Cu(tbmp)_nBr$ (n=1 or 2) and $[Cu(tbmpH)X_2]_2$ ($X = Cl^-$, Br^-), where tbmpH is the 2-(3,3-dimethyl-2-thiabutyl)pyridinium cation, were characterized in these studies. The spectroscopic properties of the distorted tetrahedral $Cu(tbmp)_2Br$ and $[Cu(tbmpH)Br_2]_2$ complexes, can be interpreted with reference to their crystal structures. Although the structural nature of Cu(tbmp)Br is uncertain, $[Cu(tbmpH)Cl_2]_2$ probably has a structure which is similar to that of the bromide analogue.

Various attempts were made to isolate complexes such as $Cu(tbmp)_nCl$ and $Cu(tbmp)_2BF_4$, but these were unsuccessful.

FIGURE 14a

Relationships Between Cu(tbmp)Br and Cu(tbmp)$_2$Br



Absolute EtOH solution of CuBr, tbmp (1:1) and excess LiBr

Rapid precipitation induced from a concentrated solution

Slow crystallization allowed to take place from a concentrated solution

Cu(tbmp)Br

Composition determined by microanalysis. Opaque, microcrystalline sample melts at 135-136°C.

Slow heating gradually turns sample opaque. Melts sharply at 135°C.

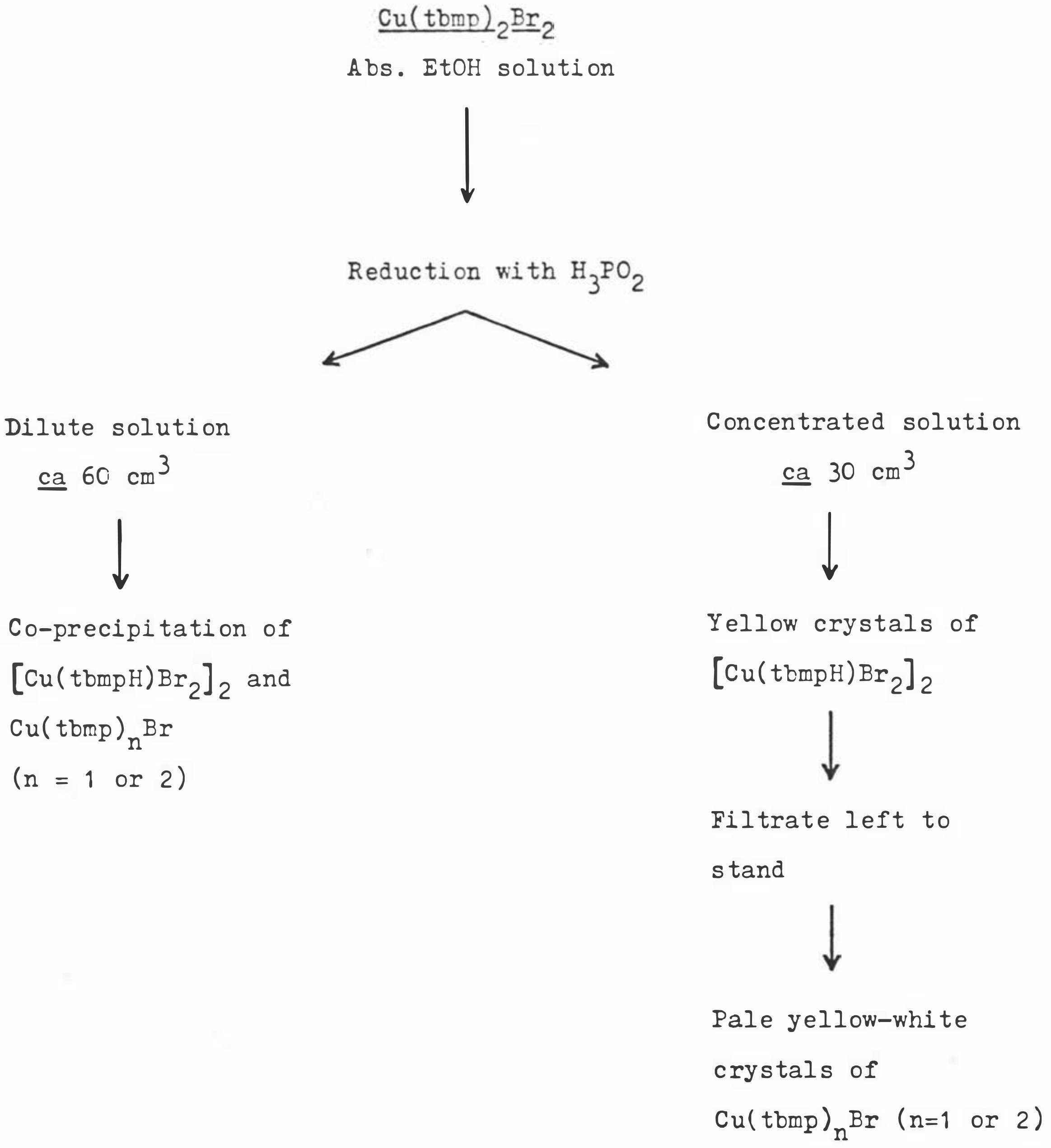
Cu(tbmp)$_2$Br

Composition of clear crystals determined crystallographically.

FIGURE 14b

Relationships Between $[Cu(tbmpH)Br_2]_2$ and $Cu(tbmp)_nBr$

$(n = 1,2)$



3.1 THE CHEMISTRY OF $Cu(tbmp)_2Br$, $Cu(tbmp)Br$ and $[Cu(tbmpH)Br_2]_2$

$Cu(tbmp)Br$ and $[Cu(tbmpH)Br_2]_2$ were prepared and analysed (see SYNTHESES) during the initial experimental work on the Cu(I) complexes of tbmp. $[Cu(tbmpH)Cl_2]_2$, which is quite susceptible to oxidation, was also prepared.

i) Relationships Between $Cu(tbmp)Br$ and $Cu(tbmp)_2Br$

For the crystallographic work, some clear almost colourless crystals were slowly grown in solutions that were similar to those from which $Cu(tbmp)Br$ was originally prepared (see SYNTHESES). These crystals were thought to be $Cu(tbmp)Br$. but subsequent investigations indicated that the crystals were $Cu(tbmp)_2Br$. This was confirmed when the crystal structure (see 3.2) was solved. If a crystal of $Cu(tbmp)_2Br$ is crushed and then slowly heated, a slow conversion to $Cu(tbmp)Br$ appears to occur. The relationships between $Cu(tbmp)Br$ and $Cu(tbmp)_2Br$ that are apparent from these studies, are illustrated in Figure 14a.

ii) Relationships Between $[Cu(tbmpH)Br_2]_2$ and $Cu(tbmp)_nBr$ ($n = 1$ or 2)

Yellow crystals of $[Cu(tbmpH)Br_2]_2$ can be prepared by reducing a concentrated absolute ethanol solution of $Cu(tbmp)_2Br_2$ (prepared <u>in situ</u>) with several drops of hypophosphorous acid (H_3PO_2). It also became apparent that at least two complexes can be isolated from the reduced solutions. The second complex , which precipitates as pale yellow-white crystals, appears to be either $Cu(tbmp)Br$ or $Cu(tbmp)_2Br$. These crystals are identified as $Cu(tbmp)_nBr$ (where $n = 1$ or 2) in Figure 14b, which summarizes the observations that were made during these investigations.

3.2 CRYSTAL STRUCTURE OF BROMO-BIS[2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE]COPPER(I)

The experimental method that was followed in the elucidation of this structure, is outlined at the end of this Chapter. The observed and calculated structure factors can be found in the Appendices.

DESCRIPTION

In this discrete Cu(tbmp)$_2$Br monomer, one tbmp ligand is chelated while the second is monodentate, binding via the sulphur atom, only. The Cu(I) ion is thus bound by a terminal bromine, two thioether sulphur atoms and the pyridyl nitrogen of the chelated tbmp ligand, in a distorted tetrahedral environment (Figure 15).

The non-coordinated pyridyl nitrogen of the monodentate tbmp ligand does not participate in any bonding interactions within the molecule, or with any of the other molecules in the unit cell. There are no intermolecular contacts of less than 3.5 Å.

The important structural details for this complex are presented in Table 15a.

DISCUSSION

One of the features of the Cu(I) geometry, is the small S2-Cu-N2 chelate-bite angle [85.4(3)°] which imposes a rather distorted environment on the Cu(I) ion (Table 15a). This observation is typical of the constraints that are imposed on Cu(I) complexes by the chelate-ligand effect.[10]

The remaining angles that are subtended at the Cu(I) centre are normal and range from 109.1(1)° to 120.7(1)°.

The dihedral angle* (w) is 88.5°, close to the expected value of 90° for a tetrahedral complex.[39]

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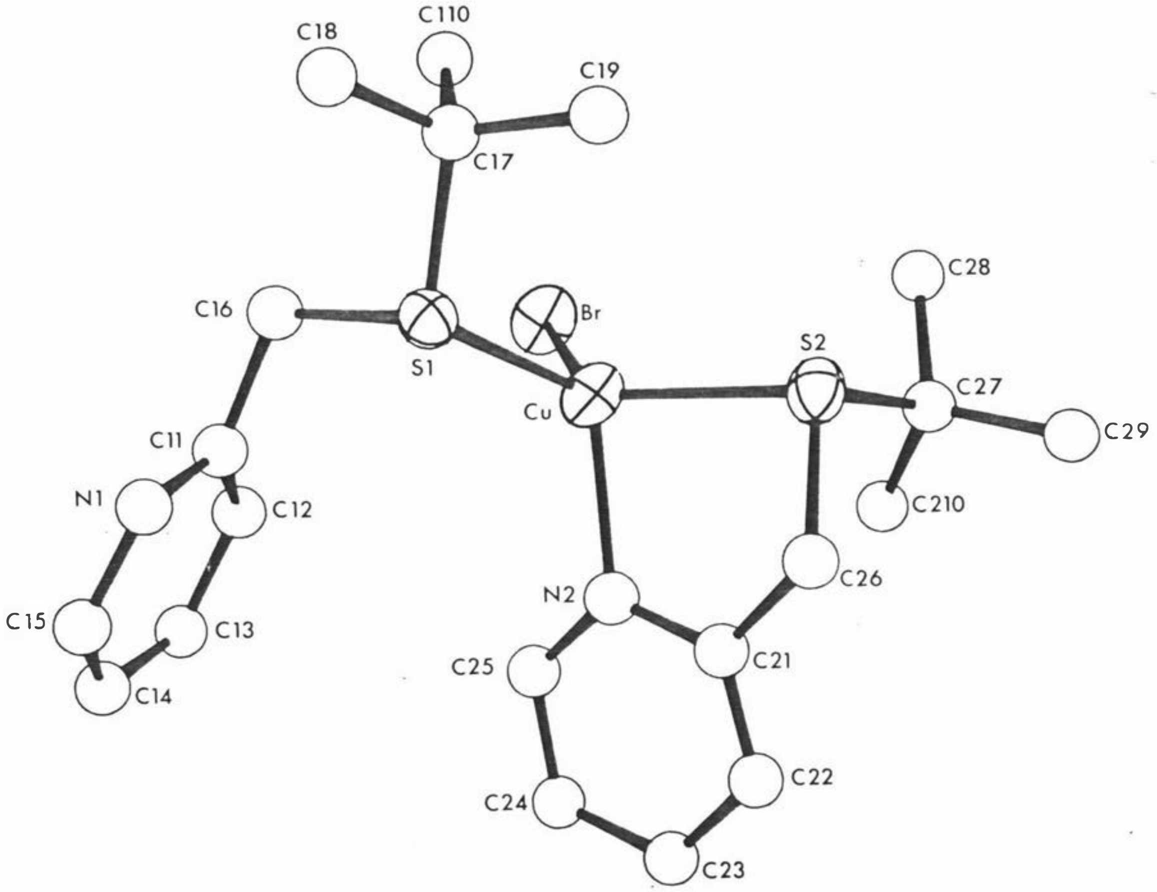
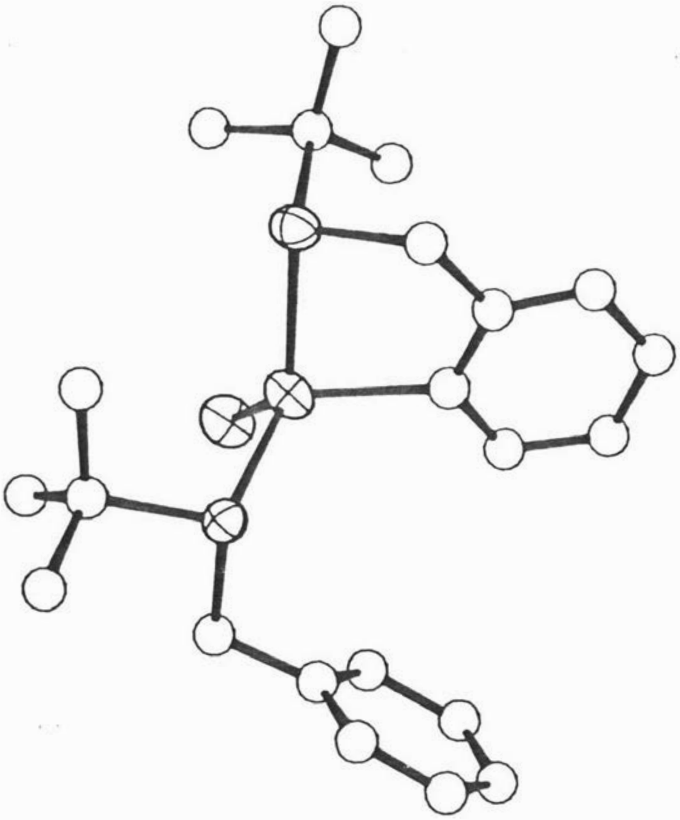
* w is defined by the planes through Cu, S2, N2 and Cu, S1, Br respectively. See end of Chapter for equations.

FIGURE 15

Structure of Cu(tbmp)$_2$Br





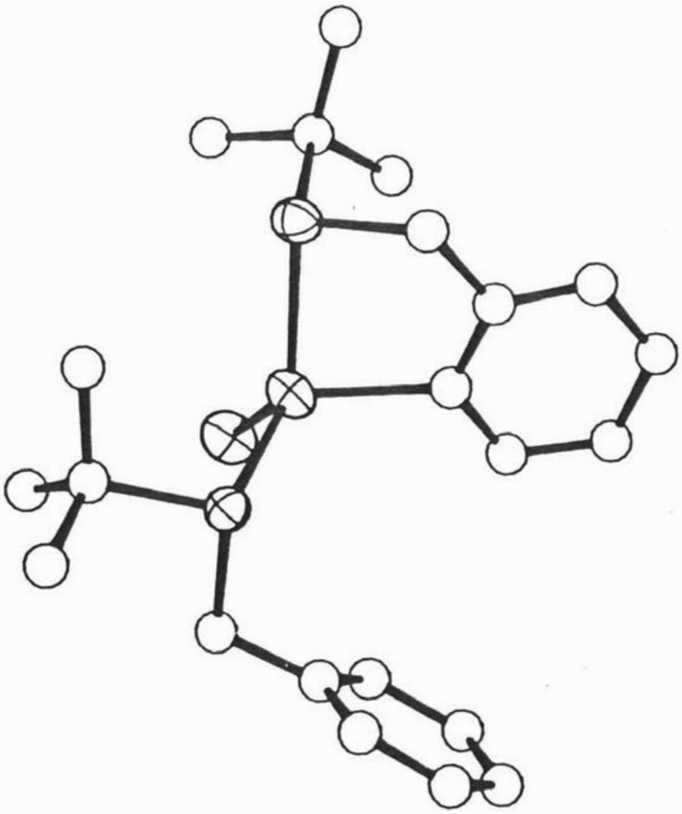


TABLE 15a

STRUCTURAL DETAILS FOR Cu(tbmp)$_2$Br

FROM ATOM	TO ATOM	DISTANCE/Å	FROM ATOM	TO ATOM	DISTANCE/Å
Cu	Br	2.426(2)	C12	C13	1.42(2)
Cu	S1	2.304(3)	C13	C14	1.37(2)
Cu	S2	2.358(4)	C14	C15	1.34(2)
Cu	N2	2.11(1)	C17	C18	1.56(2)
S1	C16	1.85(1)	C17	C19	1.53(2)
S1	C17	1.86(1)	C17	C110	1.56(2)
S2	C26	1.85(1)	C21	C22	1.37(2)
S2	C27	1.87(1)	C21	C26	1.53(2)
N1	C11	1.34(1)	C22	C23	1.40(2)
N1	C15	1.35(2)	C23	C24	1.43(2)
N2	C21	1.35(1)	C24	C25	1.42(2)
N2	C25	1.34(1)	C27	C28	1.56(2)
C11	C12	1.37(2)	C27	C29	1.54(2)
C11	C16	1.52(2)	C27	C210	1.57(2)

ANGLE	DEGREES	ANGLE	DEGREES
Br-Cu-S1	109.1(1)	C14-C15-N1	124(1)
Br-Cu-S2	120.7(1)	C11-C16-S1	108.6(9)
Br-Cu-N2	112.9(3)	C18-C17-C19	113(1)
S1-Cu-S2	115.0(1)	C18-C17-C110	109(1)
S1-Cu-N2	111.7(3)	S1-C17-C18	108.4(8)
S2-Cu-N2	85.4(3)	S1-C17-C19	105.9(9)
Cu-S1-C16	105.4(4)	S1-C17-C110	110.3(8)
Cu-S1-C17	111.2(4)	C19-C17-C110	110(1)
C16-S1-C17	100.3(6)	N2-C21-C22	123(1)
Cu-S2-C26	93.9(4)	N2-C21-C26	118(1)
Cu-S2-C27	113.7(4)	C22-C21-C26	119(1)
C26-S2-C27	104.7(6)	C21-C22-C23	119(1)
C11-N1-C15	118(1)	C22-C23-C24	120(1)
Cu-N2-C21	117.0(8)	C23-C24-C25	117(1)
Cu-N2-C25	122.8(9)	C24-C25-N2	122(1)
C21-N2-C25	120(1)	C21-C26-S2	112.1(9)
N1-C11-C12	121(1)	S2-C27-C28	102.6(9)
N1-C11-C16	118(1)	S2-C27-C29	109.4(9)
C12-C11-C16	121(1)	S2-C27-C210	111.5(9)
C11-C12-C13	119(1)	C28-C27-C29	112(1)
C12-C13-C14	118(1)	C28-C27-C210	110(1)
C13-C14-C15	119(2)	C29-C27-C210	111(1)

NOTE: - estimated standard deviations are in parentheses.

TABLE 15b

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR Cu(tbmp)$_2$Br

ATOM	x/a	y/b	z/c	B/Å^2
Br	0.7910(1)	0.2391(2)	-0.0623(1)	
Cu	0.7603(1)	0.4504(2)	0.0260(1)	
S1	0.7245(2)	0.3606(4)	0.1540(2)	
S2	0.6826(2)	0.6546(4)	-0.0405(2)	
N1	0.8823(7)	0.279(1)	0.3092(8)	5.16
N2	0.8550(6)	0.608(1)	0.0532(6)	3.00
C11	0.8694(7)	0.233(1)	0.2250(8)	3.18
C12	0.9318(8)	0.219(1)	0.1799(8)	4.15
C13	1.0114(9)	0.252(2)	0.224(1)	5.95
C14	1.023(1)	0.295(2)	0.311(1)	5.97
C15	0.959(1)	0.306(2)	0.350(1)	5.54
C16	0.7848(7)	0.188(1)	0.1820(7)	3.24
C17	0.6217(7)	0.279(1)	0.1316(7)	3.07
C18	0.6015(9)	0.221(2)	0.2209(9)	5.31
C19	0.5658(9)	0.407(2)	0.0908(9)	5.28
C110	0.6174(8)	0.144(2)	0.0652(9)	4.87
C21	0.8357(7)	0.755(1)	0.0399(7)	2.88
C22	0.8916(8)	0.867(2)	0.0443(8)	3.91
C23	0.9731(9)	0.829(2)	0.0651(9)	5.13
C24	0.9958(8)	0.674(2)	0.0787(8)	4.61
C25	0.9324(8)	0.568(2)	0.0724(8)	4.12
C26	0.7469(8)	0.798(1)	0.0247(8)	3.66
C27	0.6935(8)	0.690(2)	-0.1574(8)	4.10
C28	0.6445(8)	0.558(2)	-0.2083(9)	4.97
C29	0.6571(9)	0.845(2)	-0.1871(9)	4.96
C210	0.7835(9)	0.680(2)	-0.1686(9)	4.81

- estimated standard deviations are in parentheses.

TABLE 15c

ANISOTROPIC THERMAL PARAMETERS FOR Cu(tbmp)$_2$Br

ATOM	B11	B22	B33	B12	B13	B23
Br	0.0048	0.0114	0.0040	0.0003	0.0014	-0.0006
Cu	0.0037	0.0095	0.0042	-0.0003	0.0011	0.0009
S1	0.0028	0.0093	0.0029	-0.0002	0.0002	0.0000
S2	0.0030	0.0116	0.0038	0.0004	0.0010	0.0015

Some bondlength data for Cu(I) complexes of thioether and substituted pyridyl ligands is presented with the data for $\mathrm{Cu(tbmp)_2Br}$ and $\mathrm{[Cu(tbmpH)Br_2]_2}$ (see 3.3) in Table 16.

It can be seen that the Cu(I)-S2 bond (2.358(4) Å) is slightly longer than the mean of the Cu(I)-S bonds (2.312(3) Å) of other thioether complexes. This may be the result of the constraints that are imposed by the planar and therefore rigid, N2, C21, C26 backbone of the chelated ligand. This suggestion is supported by two observations. The first is, that the Cu(I)-S bondlengths of the monodentate tbmp (2.304(3) Å) and $\mathrm{tbmpH^+}$ ligands (2.276(2) Å) in this complex and $\mathrm{[Cu(tbmpH)Br_2]_2}$ respectively (mean, 2.290 (3) Å), are significantly shorter than the Cu(I)-S2 bond. The second observation comes from a comparison of the Cu(I)-S (thioether) bonding in other five-membered chelate-ring systems such as those in $\mathrm{Cu(dto)_2BF_4}$[10]. In this complex, the mean Cu(I)-S bond (2.303(5) Å) is also significantly shorter than the Cu(I)-S2 bond of $\mathrm{Cu(tbmp)_2Br}$.

Even though chelation may have some affect on the Cu(I)-S2 bonding, it is still shorter than the predicted Cu(I)-S single-bond length of 2.39 Å (if the Cu(I) covalent radius is taken as being about 1.35 Å[22]). These observations imply that there may be π-components in the respective Cu(I)-S1 and Cu(I)-S2 bonds of $\mathrm{Cu(tbmp)_2Br}$, thus supporting the conclusions that have been reached from other crystallographic studies of Cu(I)-S bonding[10].

The Cu(I)-N2 bond (2.11(1) Å) is slightly longer than in the Cu(I) complexes of bipyridine, pyridine and

TABLE 16

Cu(I)-S(thioether) AND Cu(I)-N(pyridyl) BOND DATA

COMPLEX	Cu(I)-S	Cu(I)-N	REFERENCE
$Cu(tbmp)_2Br$	2.331(4)	2.11(1)	This Work
$[Cu(tbmpH)Br_2]_2$	2.276(2)		This Work
$[Cu(dth)Cl]_n$	2.339(2)		108
$[Cu(dto)_2]BF_4$	2.303(5)		10
$Cu(14\text{-}ane\text{-}S_4)ClO_4$	2.317(4)		7
$Cu(pdto)PF_6$	2.345(1)	2.042(5)	11
$Cu(py_2S_2)_2ClO_4$	2.417(3) ϕ	2.02(1)	109
$Cu(py_2Et_2S_2)_2ClO_4$	2.322(1) ϕ	2.029(1)	110
$Cu(bipy)_2ClO_4$		2.01(2)	111
$Cu(pea)^+$	2.295(1)	2.000(3)	112
$Cu(py)_4^+$		2.05(1)	113

NOTES: - mean bondlengths (Å) have been given where more than one Cu(I)-L bond is involved,

ϕ Cu-SS(disulphide) bonds.

substituted pyridine ligands (ca 2.00(2) - 2.042(5) Å, Table 16,) being close to the predicted Cu(I)-N single-bond length of about 2.09 Å (taking the single-bond covalent radius of N as 0.74 Å [22]). This again may arise from the same constraints that give rise to the slight lengthening of the Cu(I)-S2 bond (above).

The puckered nature of the five-membered chelate ring is illustrated by the deviation of the S2 atom [0.743(3) Å] from the mean least-squares plane that is defined by Cu, N2, C21 and C26. The latter atoms are coplanar as expected.

Equation of Plane: $0.2181X - 0.0082Y - 0.9759Z = 2.3519$

ATOMS IN PLANE	DEVIATIONS FROM PLANE (Å)				
Cu,N2,C21,C26	Cu	N2	C21	C26	S2
	0.023(2)	-0.056(9)	0.07(1)	-0.03(1)	0.743(3)

3.3 CRYSTAL STRUCTURE OF BIS[DIBROMO(1-H-2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE)]-COPPER(I)

The crystal structure of $[Cu(tbmpH)Br_2]_2$ was determined by Dr K.L. Brown [114] , using crystals that were prepared as described at the end of this Chapter.

DESCRIPTION

The two distorted tetrahedral Cu(I) centres of this centrosymmetric dimer are bridged by two bromide ions with the two remaining coordinating positions of each Cu(I) ion being occupied by a terminal bromide ion and a sulphur-bound, 2-(3,3-dimethyl-2-thiabutyl)pyridinium cation (Figure 16).

Relevant structural details for $[Cu(tbmpH)Br_2]_2$ are presented in Table 17.

FIGURE 16

Structure of $[Cu(tbmpH)Br_2]_2$

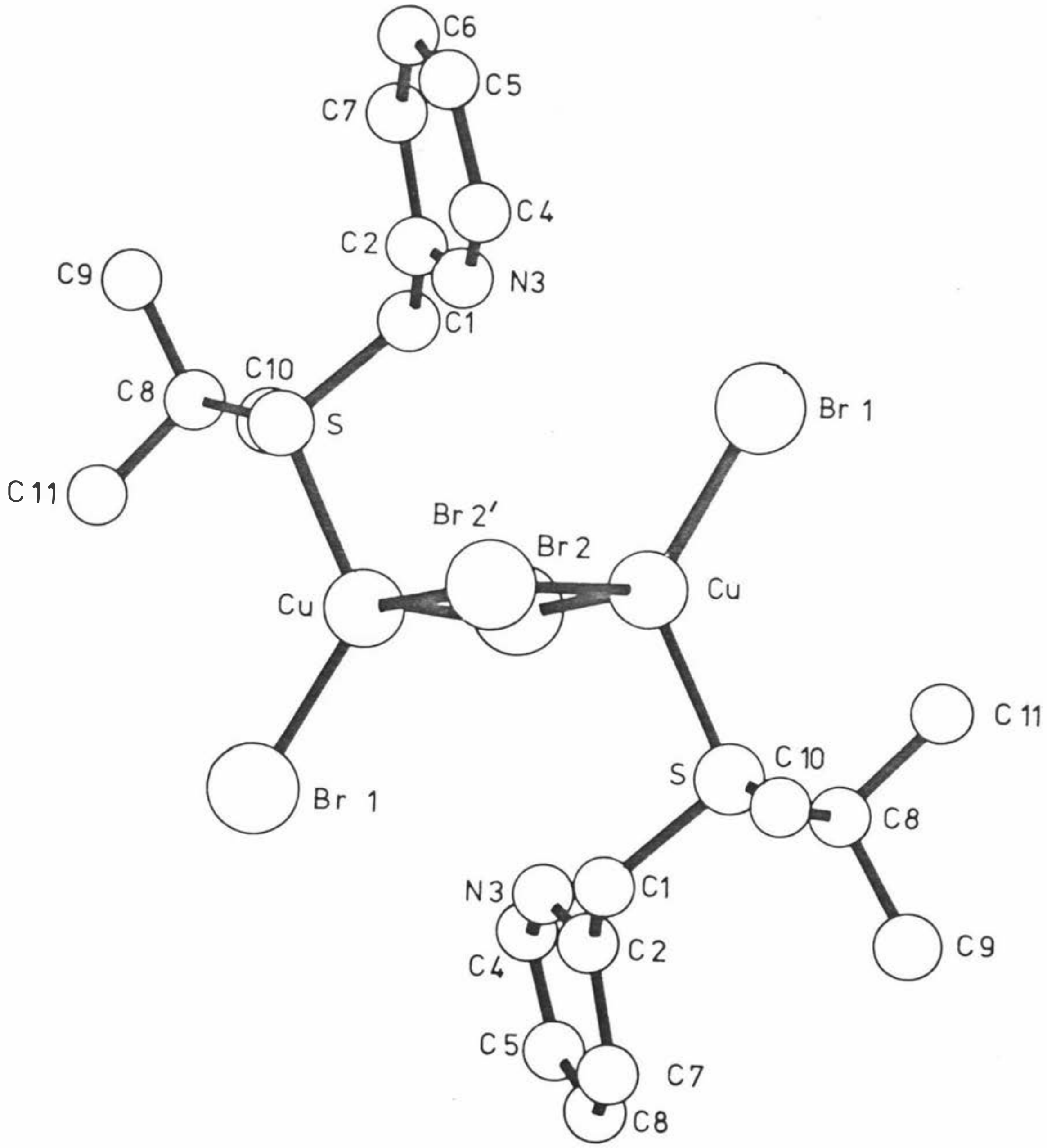


TABLE 17

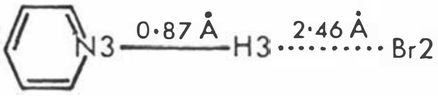
STRUCTURAL DETAILS FOR $[Cu(tbmpH)Br_2]_2$

FROM ATOM	TO ATOM	DISTANCE/Å	FROM ATOM	TO ATOM	DISTANCE/Å
Cu	Cu′	3.18	N3	H3	0.87
Cu	Br1	2.363(1)	N3	C4	1.32(1)
Cu	Br2	2.621(1)	C4	C5	1.35(1)
Cu	Br2′	2.573(1)	C5	C6	1.39(1)
Cu	S	2.276(2)	C6	C7	1.36(1)
S	C1	1.840(8)	C7	C2	1.38(1)
S	C8	1.844(7)	C8	C9	1.53(1)
C1	C2	1.47(1)	C8	C10	1.51(1)
C2	N3	1.33(1)	C8	C11	1.54(1)

ANGLE	DEGREES	ANGLE	DEGREES
Br1-Cu-Br2	110.9(1)	N3-C2-C7	117.1(7)
Br1-Cu-Br2′	109.3(1)	C2-N3-C4	124.0(7)
Br1-Cu-S	126.2(1)	N3-C4-C5	120.4(8)
Br2-Cu-Br2′	104.4(1)	C4-C5-C6	117.8(8)
Br2-Cu-S	97.2(1)	C5-C6-C7	120.3(8)
Br2′-Cu-S	106.5(1)	C6-C7-C2	120.3(8)
Cu-Br2-Cu′	75.6(1)	S-C8-C9	108.8(6)
Cu-S-C1	106.3(3)	S-C8-C10	111.8(6)
Cu-S-C8	114.1(2)	S-C8-C11	102.2(5)
C1-S-C8	104.2(4)	C9-C8-C10	112.7(7)
S-C1-C2	109.8(5)	C9-C8-C11	110.0(7)
C1-C2-N3	117.7(6)	C10-C8-C11	110.8(7)
C1-C2-C7	125.2(7)		

DISCUSSION

The closest intermolecular contact is between the pyridinium proton (H3) and the Br2 atom of an adjacent molecule ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), as shown below.



where N3------Br2 is 3.30 Å and N3-Br2-H3 is 4.74°. Both the length of this contact and its geometry (i.e. almost linear N3——H3----Br2 interactions) suggest that there is a significant degree of H3----Br2 hydrogen bonding. The N3----Br2 contact (van der Waals distance is 3.45 Å [22]) may even be short enough for direct overlap of nitrogen and bromine orbitals as suggested for the structure of [4-methylpyridinium]$^+$[ϕ_3PZnBr$_3$]$^-$.[115] In this latter complex, the Br----N contact is 3.2 Å, while Br--H—N is 120°. Weak NH----Br hydrogen bonding has been described for complexes such as Bisthiourea Pyridinium Bromide[116] (N----Br = 3.47 Å, N-H-Br = 144°) and [4-EtpyH]$^+$[FeBr$_4$]$^-$ [117] (N----Br = 3.32 Å, N-H-Br = 154°).

The N3-H3----Br2 interaction in [Cu(tbmpH)Br$_2$]$_2$ could thus be described as being quite strong.

The Cu-Br2-Cu bridging angle for this complex (75.6(1)) is significantly smaller than the analogous bridging angles (83.0(1)-100.4(1)°) of dibromo-bridged Cu(II) dimers (see Chapter 1). The reason for this appears to be the greater Br2-Cu-Br2′ angle that is imposed by the tetrahedral geometry of the Cu(I) ions. As a consequence of these effects, the Cu(I)----Cu(I) separation (3.18 Å) is significantly shorter than the shortest Cu(II)----Cu(II) separation (3.570(3) Å) thus far observed in the analogous Cu(II) complexes.[19] It is interesting to note that the Cu(I)----Cu(I) separation is only 0.5 Å greater than the sum (2.70 Å) of the tetrahedral Cu(I) covalent radii.[22]

COMPARISONS BETWEEN Cu(tbmp)$_2$Br AND [Cu(tbmpH)Br$_2$]$_2$

It is apparent that the terminal Cu(I)-Br bond (2.426(2) Å) and the Cu(I)-S1 bond (2.304(3) Å, S1 belonging to the monodentate tbmp ligand) of Cu(tbmp)$_2$Br are slightly longer than the corresponding Cu(I)-L bonds (2.276(2) Å) of [Cu(tbmpH)Br$_2$]$_2$. The weak interactions between Cu(I) and the bridging bromide ions in the latter complex, probably allow stronger interactions between Cu(I) and its other ligands; namely the terminal bromide ion (Br1) and the sulphur atom of tbmpH$^+$. Similar phenomena have been previously described for other Cu(I) complexes.[108,118]

3.4 INFRARED SPECTRA

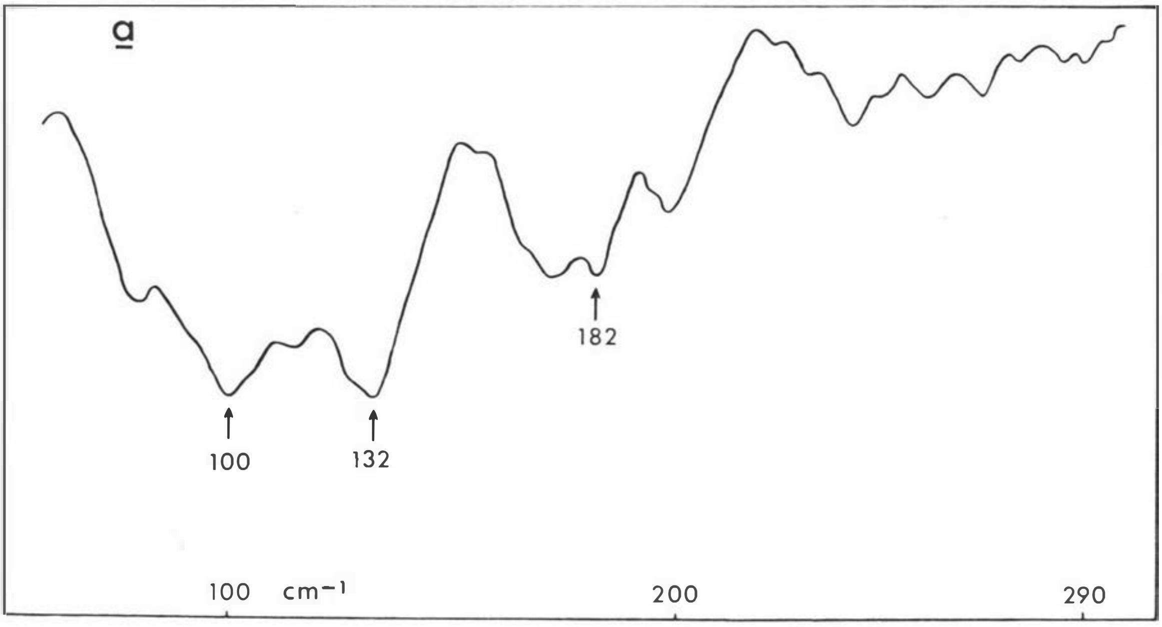
i) Far-Infrared

Some crystallographically correlated far-infrared data and data for complexes whose structures are inferred from other studies, is presented in Table 18a together with the data for Cu(tbmp)Br and [Cu(tbmpH)X$_2$]$_2$ (X=Cl$^-$, Br$^-$). There is a paucity of crystallographically correlated data for Cu(I) complexes that contain bromide ligands, although inferences can usually be drawn on the basis of other spectroscopic measurements.

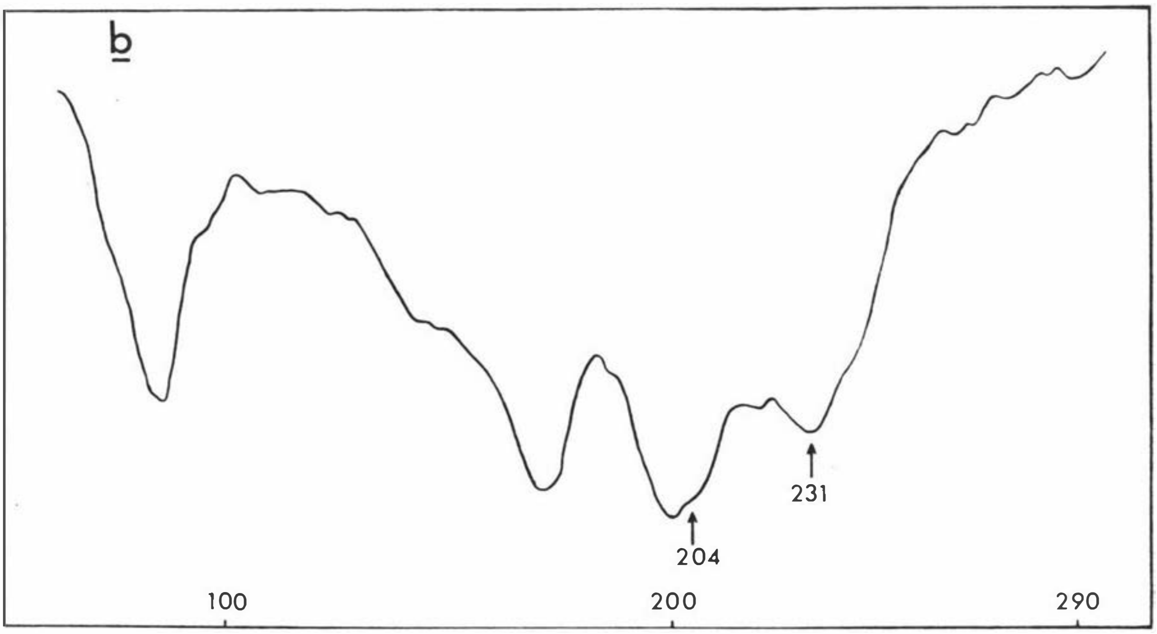
[Cu(tbmpH)Br$_2$]$_2$: The ν(Cu-Br) absorptions at 132 and 100 cm^{-1} are at very low energy (Figure 17a) but they are consistent with the long Cu(I) to bridging-bromine bonds that are found in the crystal structure of this

FIGURE 17

IR Spectra - Cu(I) Complexes and Pyridinium Salts

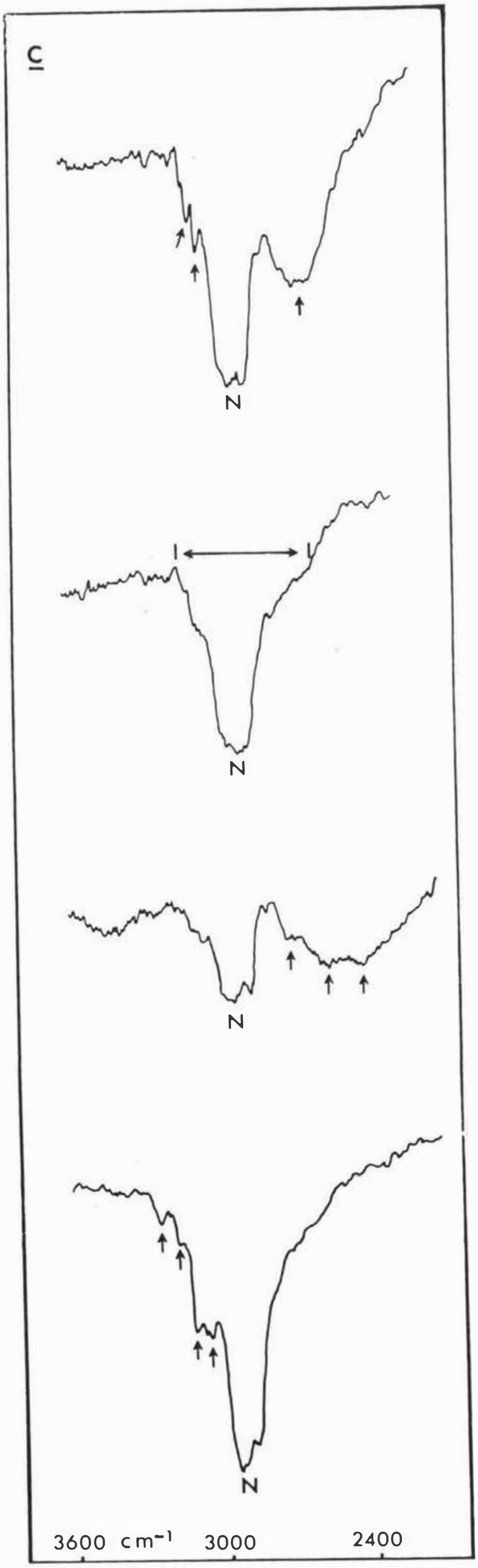


17a Far-IR : $[Cu(tbmpH)Br_2]_2$
ν(Cu-Br) absorptions are shown.



17b Far-IR : $[Cu(tbmpH)Cl_2]_2$
ν(Cu-Cl) absorptions are shown.

17c $\nu(N^+-H)$ Absorptions



$[Cu(tbmpH)Cl_2]_2$

$[Cu(tbmpH)Br_2]_2$

(tbmpH)Br

(tbmpH)PF_6

(N = Nujol absorption)

TABLE 18a

FAR-IR DATA, Cu(I) COMPLEXES

COMPLEX	ν(Cu-X)/cm^{-1}	STRUCTURE	REFERENCES IR data	 X-ray
X = Cl				
$[Cu(Me_3PS)Cl]_3$	299	Terminal Cl	119,120	121
	275			
CuCl(dth)	271	Terminal Cl	82	108
(CuCl)tal-i-C_3H_7	194	Bridging Cl	122	n.a.
$(CuCl)C_8H_8\ _2$	254,222	Bridging Cl	123	124
$[Cu(tbmpH)Cl_2]_2$	204	Bridging Cl	This work	n.a.
	231	Terminal Cl		
X = Br				
$(CuBr)_2(DPPA)_3$	202	Terminal Br	125	n.a.
$[Cu(Me_3PS)Br]_n$	176	Bridging Br	119	n.a.
(CuBr)tal-CH_3	152	Bridging Br	122	n.a.
CuBr[dth]	169,152	Bridging Br	82	n.a.
$[Cu(tbmpH)Br_2]_2$	182	Terminal Br	This work	This work
	132,100	Bridging Br		
Cu(tbmp)Br	182	Unassigned	This work	n.a.

NOTES: - n.a. = not available

- spectra (this work) recorded for paraffin mulls, at room temperature.

TABLE 18b

GENERAL IR DATA, Cu(I) COMPLEXES

COMPLEX	ν(pyridyl ring)/cm^{-1}
$[Cu(tbmpH)Cl_2]_2$	1618(s), 1531(m)
$[Cu(tbmpH)Br_2]_2$	1634(m), 1616(m), 1536(w)
Cu(tbmp)Br	1595(s), 1567(m)

NOTE: - spectra recorded for Nujol mulls.

complex. The absorptions are relatively strong and their assignment is supported by their non-appearance in the spectrum of $[Cu(tbmpH)Cl_2]_2$ (Figure 17b). The terminal ν(Cu-Br) absorption is tentatively assigned at 182 cm^{-1}.

$[Cu(tbmpH)Cl_2]_2$: The ν(Cu-Cl) absorption at ca 204 cm^{-1} is consistent with bridging chloride (Figure 17b), by analogy with the data that is presented in Table 18a. The absorption at 231 cm^{-1} can probably be assigned as being due to terminal Cu-Cl stretching as there are no other bands in this spectrum that can be assigned as such. However, it should be noted that 231 cm^{-1} is also within the range (ca 194 - ca 254 cm^{-1}) observed for bridging ν(Cu-Cl) frequencies.

Cu(tbmp)Br: A ν(Cu-Br) absorption is tentatively assigned at 182 cm^{-1}. It is not possible to confidently assign the absorption as arising from either terminal or bridging Cu-Br bonding, when the assignments for $[Cu(tbmpH)Br_2]_2$ are compared with those for other Cu(I) complexes, (Table 18a).

ii) General Infrared

$\nu(N^+—H)$ Absorptions: The broad absorptions between 2400 and 3200 cm^{-1} in the mull spectra of the $[Cu(tbmpH)X_2]_2$ complexes (Figure 17c), are good evidence for the pyridyl nitrogen having been protonated. Similar absorptions, their frequencies depending on the degree of hydrogen bonding in the salts, were reported by Nuttall et al[126], who assigned them as the symmetrical $\nu(N^+—H)$ modes for a series of pyridinium salts. For $[Cu(tbmpH)Br_2]_2$, the broad absorption(s) occurs at higher frequencies than in a sample of $(tbmpH)^+Br^-$ that was prepared for comparison (Figure 17c). This observation suggests that the $N^+—H-----Br$ hydrogen bonding interactions are less[98] in $[Cu(tbmpH)Br_2]_2$ than in $(tbmpH)^+Br^-$.

1700-1500 cm^{-1} Absorptions: In the Cu(I) complexes where tbmp has been protonated (i.e. $[Cu(tbmpH)X_2]_2$), the blue-shifts in the higher frequency ring stretching absorption (Table 18b) are generally greater (up to 25 cm^{-1}) than those which occur (up to 19 cm^{-1}) in the M(II) complexes (M=Cu, Ni, Co) of tbmp (Tables 13c and 24).

Gill *et al*[99] were able to show that the absorptions at about 1600 cm^{-1} and 1540 cm^{-1} in the spectra of pyridinium salts are due to N-H deformation and combination modes. On the basis of these results, the medium-weak absorption at about 1532 cm^{-1} in the spectra of $[Cu(tbmpH)X_2]_2$ and the $(tbmpH)^+X^-$ salts ($X = Br^-$, PF_6^-), is probably one of these modes. The second mode has not been resolved in these spectra.

3.5 ELECTRONIC SPECTRA

Although the electronic spectra of the yellow Cu(I) complexes of disulphide ligands such as py_2S_2 and $(Me_2N)_2Et_2S_2$ (see Table 19) have been discussed by Seff *et al*,[109,127] the yellow dimer $[Cu(tbmpH)Br_2]_2$, is the first coloured Cu(I) complex of a sulphur-coordinated thioether ligand, to be crystallographically characterized. It is probable that $[Cu(tbmpH)Cl_2]_2$ has a structure similar to that of the bromide complex as its reflectance spectrum is similar. Its far-infrared spectrum is not inconsistent with this proposal, either.

TABLE 19

ELECTRONIC SPECTRA, Cu(I) COMPLEXES

COMPLEX	STATE	C.T. MAXIMA (nm)	REFERENCE
Cu(tbmp)Br	CH_2Cl_2	ca 355(sh)	This work
$[Cu(tbmpH)Cl_2]_2$	CH_2Cl_2	ca 350(sh) 435(ϵ=128)	This work
	Refl.	ca 370(sh) † ca 412(sh) †	
$[Cu(tbmpH)Br_2]_2$	Refl.	ca 375(sh) † ca 415(sh) †	This work
$Cu(tbmq)_2ClO_4$	Refl.	378 475	This work
$[Cu(py_2S_2)_2]ClO_4$	Nujol mull	335(sh) φ	109
$[Cu((Me_2N)_2Et_2S_2)]_2$	Nujol mull	293 φ	127

NOTES: † maxima disappear in methanol,

φ assigned as red-shifted disulphide absorption.

The visible spectra of the Cu(I) complexes that are being studied in this thesis, are compared with those of the disulphide ligand complexes in Table 19.

Higher Energy Maxima

The absorption at about 365 ± 10 nm is common to the reflectance spectra of all of the Cu(I) complexes of tbmp, $tbmpH^+$ and tbmq (see Chapter 6). It is probably too high in energy to involve Cu(I)⟶ π*(N) charge transfer (if the complexes of tbmp and tbmq contain chelated ligands) and the lack of major variations in the energy of this maximum (on changing the anion) suggests that it can not be assigned to Cu(I)⟶ X^- charge transfer. These observations are consistent with Cu(I)⟶ S charge transfer being responsible for the ca 365 nm absorption, as Cu(I)-thioether interactions probably occur in all of these complexes.

Lower Energy Maxima

The second absorption (at about 414 nm) in the reflectance spectra of the $[Cu(tbmpH)X_2]_2$ dimers does not appear in the spectra of the Cu(I) complexes of tbmp and tbmq. This implies that this absorption is not likely to arise from Cu(I)⟶ S charge transfer and because the reflectance spectra of the dimers are almost identical it can not be due to a Cu(I)⟶ X^- transition. The very short and almost linear Br^------H—N^+ interaction that is described in 3.3, is consistent with this interaction having appreciable covalent bonding character. This would facilitate Cu(I)⟶ Br---⟶H⟶ N^+ charge transfer. The 414 nm absorption is thus assigned as being due to charge transfer from the d-orbitals of Cu(I), to the π^*-orbitals of the pyridinium ring, via the Br-----H —N$^+$ "bridge". The positive charge on the pyridinium ring would thus be partially neutralised by this charge transfer and would also enhance it.

3.6 REACTION OF $[Cu(tbmpH)Cl_2]_2$ WITH Ph_4AsCl

The $[Cu(tbmpH)X_2]_2$ complexes are both 1:1 electrolytes in nitromethane and methanol (based on the M.W of one $Cu(tbmpH)X_2$ "monomer") and their electronic spectra in methanol (both complexes have an absorption at 305 nm, Table 19) show that they do not retain their solid state structures in this solvent. This conclusion is supported by the isolation of $[Ph_4As]CuCl_2$ from a methanol solution of $[Cu(tbmpH)Cl_2]_2$ and Ph_4AsCl (see Appendices). There are at least two ways in which $[Cu(tbmpH)Cl_2]_2$ (and $[Cu(tbmpH)Br_2]_2$) can break down in solution and both are consistent with the above observations:

i) the complexes can break down to give the CuX_2^- and $tbmpH^+$ ion pairs, or

ii) complete decomposition can occur to yield solvated Cu(I), $tbmpH^+$ and two halide ions. This possibility is favoured in hydrogen bonding solvents.[128]

EXPERIMENTAL

DETERMINATION OF STRUCTURE OF Cu(tbmp)$_2$Br

i) General

The approximate unit cell dimensions of the almost colourless crystals of Cu(tbmp)$_2$Br were determined by preliminary oscillation, Weissenberg and precession photography. The crystals were prepared as described in 3.1. The space group P2$_1$/n was established from the systematic absences in the Weissenberg and precession photographs. Accurate cell dimensions were calculated after a crystal fragment had been aligned on a four-circle X-ray diffractometer. The least-squares analysis of the positions of twelve general reflections was used to define the crystal orientation.

TABLE 20a

CRYSTAL DATA FOR Cu(tbmp)$_2$Br

M.W.	506.03 g.
Crystal System	Monoclinic
Space Group	P2$_1$/n
Cell Dimensions	a = 16.927(3) Å
	b = 8.867(1) β = 100.61(1)°
	c = 15.371(2)
Cell Volume	U = 2268 Å^3
Density	$D_m^\dagger$ = 1.482 g. cm^{-3}
	D_{calc} = 1.482 g. cm^{-3}(Z=4)
Radiation	Mo-Kα
μ(Mo-Kα)	45.7 cm^{-1}

NOTE: † Determined by flotation method.
Measured in NaI/EtOH/H$_2$O.

ii) Data Collection and Reduction

A crystal fragment with maximum dimensions of about 0.02 x 0.02 x 0.02 cm was mounted about its b axis for the data collection on a computer controlled Hilger and Watts four-circle X-ray diffractometer.

TABLE 20b

DATA COLLECTION FOR Cu(tbmp)$_2$Br

λ(Mo-Kα)	0.7107 Å
Background Count Time	20 s. each side
Counting Steps	80
Counting Time/Step	1 s.
Standard Reflections	(7,3,0);(1,3,7);(1,5,-1)

The data was collected from the $0^{\circ} < \theta < 26^{\circ}$ shell for the hkl and hk$\bar{l}$ reflections; the three standard reflections, which were checked after every 100 reflections, revealed no systematic intensity changes. After merging, the 4485 measurements were reduced to 4251 independent reflections, of which 2032 had intensities greater than 2σ. The usual Lorentz and polarization corrections were made, but absorption corrections were not applied to the data.

iii) Structure Solution and Refinement

An electron density map, phased on the bromine and copper atoms, was calculated after the coordinates of these two atoms had been determined from a Patterson vector map. The atoms were given arbitrary isotropic temperature factors of 3.5 Å^2 for the structure factor calculation. This map revealed the positions of another sixteen atoms and the remaining eight atoms were found after a second electron density map, phased on all of the previously located atoms, had been calculated.

The structure was refined using the full-matrix least-squares program, CUCLS.[74] The least squares refinement was carried out on F, with the quantity $\sum w(|F_o| - |F_c|)^2$ being minimised and the weight (w) being $4(F_o)^2/[\sigma(F_o)^2]^2$. The conventional reliability index R, converged at 0.093 after six cycles of refinement for which all of the atoms were given isotropic temperature factors. Anisotropic temperature factors were then given to the bromine, copper and sulphur atoms and another three refinement cycles were carried out. Refinement converged at R = 0.072 for the 2032 reflections where $|F_c|^2 \geqslant 2.0\,\sigma_{|F_o|}^2$. The final weighted R factor $R' = \sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2$ was 0.078. Anomalous dispersion corrections were applied to the bromine and copper atoms for the final cycle of refinement, but these did not affect R. The values of $\Delta f'$ and $\Delta f''$ were taken from Reference 290 and they were assumed to be constant for all values of θ.

A difference map which was calculated after the refinement had converged, revealed the possible locations of some of the hydrogen atoms but these have not been included in any structure factor calculations and no attempts have been made to calculate the positions of the remaining hydrogen atoms.

The anisotropic atoms have the following RMS components of thermal displacement along the principal axes, R:

ATOM	R = 1	R = 2	R = 3
Br	0.1965 (Å)	0.2213	0.2619
Cu	0.1827	0.2201	0.2339
S1	0.1787	0.1917	0.2067
S2	0.1832	0.2013	0.2373

TABLE 20c

MEAN LEAST-SQUARES PLANE EQUATIONS

ATOMS IN PLANE	EQUATION
Br, Cu, S1	$-0.8873X-0.0376Y-0.4597Z = -11.6836$
Cu, S2, N2	$0.4331X-0.2161Y-0.8751Z = 4.3347$
Br, Cu, S2	$0.8743X+0.4631Y-0.1454Z = 12.9794$
Cu, S1, N2	$-0.6707X+0.7411Y-0.0305Z = -5.6344$
N2, C21-25	$0.1932X-0.1081Y-0.9752Z = 1.4006$
N1, C11-15	$-0.0610X+0.9551Y-0.2898Z = 0.1373$

SYNTHESES

Bis[Dichloro(1-H-2-(3,3-dimethyl-2-thiabutyl)pyridine)copper(I)]

1 mmole of $Cu(tbmp)_2Cl_2$ was prepared in Abs.EtOH and precipitated by the addition of ether. The solid was filtered, dissolved in about 150 cm^3 of warm Abs.EtOH and then hypophosphorous acid (ca 1 cm^3) was added to the solution. The resulting pale yellow solution was concentrated to about 5 cm^3 and cooled. The yellow crystals that grew were filtered and washed with Abs.EtOH then ether. The complex has to be sealed *in vacuo* for prolonged storage.

YIELD: 0.245 g (77%)

Bis[Dibromo(1-H-2-(3,3-dimethyl-2-thiabutyl)pyridine)copper(I)]

A few drops of hypophosphorous acid were added to a warm EtOH solution of 1 mmole of $Cu(tbmp)_2Br_2$ (prepared *in situ*). The reduced solution was filtered, concentrated and cooled to crystallize the yellow, air-stable complex.

YIELD: 0.200 g. (49%)

Bromo[2-(3,3-dimethyl-2-thiabutyl)pyridine]copper(I)

1 mmole of anhydrous CuBr (0.143 g.) was dissolved in an Abs.EtOH solution of excess LiBr. The syrupy solution was vacuum filtered and 1 mmole of ligand (0.182 g.) in Abs.EtOH was added to give a light yellow solution. This was concentrated *in vacuo*, cooled and "scratched" to precipitate the almost colourless crystals.

YIELD: 0.243 g. (75%)

Bromo-bis[2-(3,3-dimethyl-2-thiabutyl)pyridine]copper(I)

These crystals can be isolated if a solution of 1 mmole of anhydrous CuBr, excess LiBr and 1 mmole of tbmp (i.e. the solution is similar to those used for preparation of Cu(tbmp)Br) is allowed to stand at 4 °C for a couple of days. The crystals were filtered and washed with Abs.EtOH.

TABLE 21

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/%				CONDUCTIVITY/ohm^{-1}mol.$^{-1}$ cm^2	
			C	H	N	Other	CH_3NO_2	MeOH
$[Cu(tbmpH)Cl_2]_2$	yellow	123-125	37.92	5.09	4.42	Cl, 22.38	92	115
			(37.94)	(5.23)	(4.26)	(22.45)		
$[Cu(tbmpH)Br_2]_2$	yellow	138-140	29.61	3.98	3.45		84	123
			(29.95)	(4.21)	(3.26)			
Cu(tbmp)Br	v.pale	137-138	36.98	4.66	4.31	Br, 24.61	31	35
			(37.16)	(4.63)	(4.55)	(24.69)		

NOTES: - molar conductivities at 25 °C: Nitromethane 1:1 (70-90),
Methanol (100-130)

- v = very

CHAPTER 4

BIS[2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE] COBALT(II) AND NICKEL(II) COMPLEXES

The synthesis and isolation of the $M(tbmp)_2X_2$ complexes ($M=Co(II)$, $Ni(II)$; $X=Cl^-$, Br^-) is similar to that of the analogous Cu(II) complexes (Chapter 2) and likewise, they appear to have distorted cis-octahedral structures in the solid state. In the presence of perchlorate anions, the bis-complexes are isolated with either one or two water molecules in the M(II) coordination sphere, depending on whether or not the drying reagent TEOF (triethylorthoformate), is added to the reaction. The reflectance spectra of $[M(tbmp)_2(H_2O)_2](ClO_4)_2$ and $[M(tbmp)_2H_2O.ClO_4]ClO_4$ are not inconsistent with these complexes also having distorted cis-octahedral structures.

In non-ligating solvents, only $Co(tbmp)_2Cl_2$ and $Co(tbmp)_2Br_2$ are sufficiently soluble to enable their electronic spectra to be measured and it is evident that tetrahedral species are predominant in solvents of this type. Although all of the complexes are soluble in methanol, they probably undergo extensive solvation.

4.1 ELECTRONIC SPECTRA

Three spin-allowed electronic transitions are expected for the high spin octahedral complexes of Co(II) and Ni(II).[129]

For most complexes, spin-orbit coupling, which is only optically important for the T_{1g} and T_{2g} states[42], and lower than O_h symmetry, lead to a splitting of the octahedral field states. With Co(II) complexes, spin-forbidden transitions to doublet states may also complicate the spectra.

FIGURE 18

SPIN-ALLOWED TRANSITIONS FOR OCTAHEDRAL Co(II) and Ni(II)

Co(II)*		Ni(II)*
$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	↑	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
$^4T_{1g}(F) \longrightarrow {}^4A_{2g}$		$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$
$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$		$^3A_{2g} \longrightarrow {}^3T_{2g}$

Increasing Energy

* Reference: 129

* Reference: 129, 130

COBALT (II) COMPLEXES

i) Reflectance

The spectra appear to be consistent with those of other six-coordinate $CoN_2S_2X_2$ complexes although in general, a greater number of absorptions are observed for each tbmp complex (Table 22a). Some of these absorptions in the visible region may arise from doublet transitions that have been enhanced by mixing with spin-allowed transitions or the $^4T_{1g}(P)$ level may have been split by low symmetry ligand fields.[131] Although in principle, the main near-infrared absorption can be assigned to the $^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ transition and the main visible absorption can be assigned to the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition,[43] the wide range and multiplicity of the absorptions for these

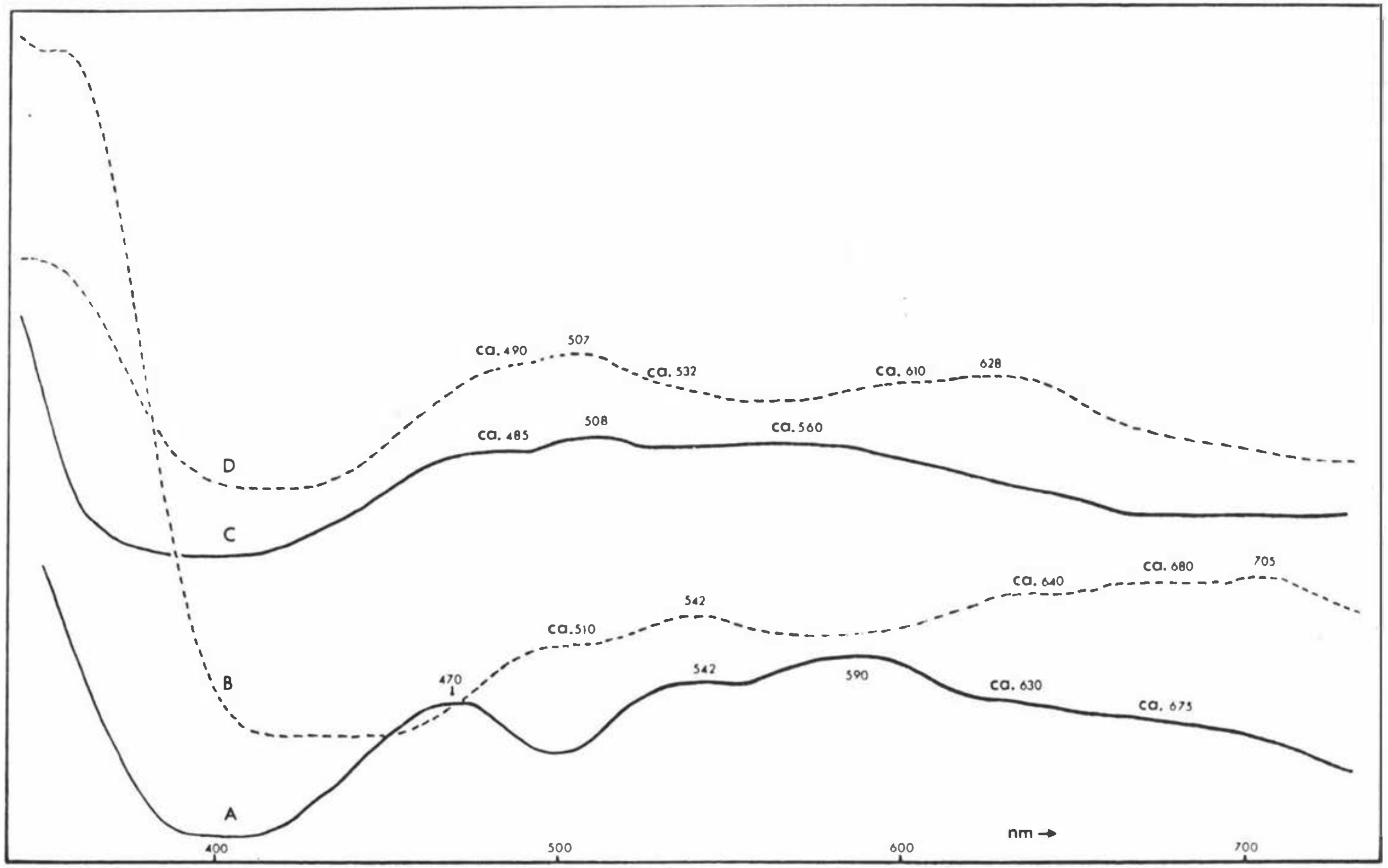
$Co(tbmp)_2X_2$ complexes present some difficulties in making specific assignments. Only two of the three spin-allowed absorptions are normally observed for tetragonal Co(II) complexes as the weak $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ two-electron transition is often obscured by the nearby $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition.[131] No attempt has been made to assign the two-electron transition in these spectra.

It is apparent from the spectra (Figure 19a) that the centre of gravity of the visible region maxima moves to lower energy in the order $Co(tbmp)_2Cl_2 > Co(tbmp)_2Br_2$ as expected from the spectrochemical series.[42] The unassigned absorptions at about 610(sh) and 628nm for $[Co(tbmp)_2.ClO_4.H_2O]ClO_4$, move to higher energy (560nm) when another water molecule coordinates to give $[Co(tbmp)_2.2H_2O](ClO_4)_2$. It is probable then, that some of the unassigned transitions in Table22a are spin-forbidden quartet ⟶ doublet transitions as these too, are expected to move to higher energy when the ligand-field strength is increased.[131]

In complexes that are known or thought to exhibit distorted cis-octahedral symmetry, the near-infrared absorptions are split into at least two components while the remaining absorptions are similar to those of trans-tetragonal Co(II) complexes.[43] The electronic spectral data for the crystallographically characterized cis-octahedral complexes, $Co[(CH_3)_3PO]_2(NO_3)_2$ and $Co(Hpymt)_2Cl_2$, is also presented in Table 22a. The latter complex exhibits weak Co—S bonding to give a cis-$CoN_2S_2Cl_2$ chromophore. A distinctive splitting of the lowest energy maximum (ca 1350nm) for the tbmp complexes is observed only for $[Co(tbmp)_2.2H_2O](ClO_4)_2$ (suggesting that it is distorted cis-octahedral) but this does not necessarily rule

FIGURE 19a

Electronic Spectra-$Co(tbmp)_2X_2$ Complexes (Reflectance)



$\underline{A}$ = $Co(tbmp)_2Cl_2$

$\underline{B}$ = $Co(tbmp)_2Br_2$

$\underline{C}$ = $[Co(tbmp)_2.2H_2O](ClO_4)_2$

$\underline{D}$ = $[Co(tbmp)_2.ClO_4.H_2O]ClO_4$

TABLE 22a

REFLECTANCE SPECTRA, Co(II) COMPLEXES

COMPLEX	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$	OTHER	REFERENCE
$Co(tbmp)_2Cl_2$	470,542,590	1330	ca630(sh),ca675(sh)970	This work
$Co(mmp)_2Cl_2$	465,540(sh),575			15
$Co(NSSN)Cl_2$	555	1300,1515		132
$Co(Hpymt)_2Cl_2$	580,640	1506,1808	950	133
$Co(tbmp)_2Br_2$	ca 510(sh),542		ca355(sh)†, ca640(sh), ca680(sh), 705	This work
$Co(mmp)_2Br_2$	490,530,615			15
$Co(NSSN)Br_2$	555	1315,1471		132
$Co(Hpymt)_2Br_2$	582,675	1710	870	133
$[Co(tbmp)_2.ClO_4.H_2O]ClO_4$	ca490(sh),507,ca532(sh)		ca610(sh),628,875	This work
$[Co(tbmp)_2.2H_2O](ClO_4)_2$	ca485(sh),508	ca1300(sh),1410	ca560(br),875	This work
ϕ $Co[(CH_3)_3PO]_2(NO_3)_2$	550,612(sh)	1310(asym)	835	134

NOTES:
- all maxima are nm.
- sh = shoulder; br = broad; asym = asymmetric

† the high intensity of this shoulder suggests that it is possibly a S ⟶ Co(II) C.T. maximum[135]

- all complexes are $CoN_2S_2X_2$ chromophores except ϕ
- $Co(NSSN)X_2$ complexes, also likely to have cis-octahedral structures

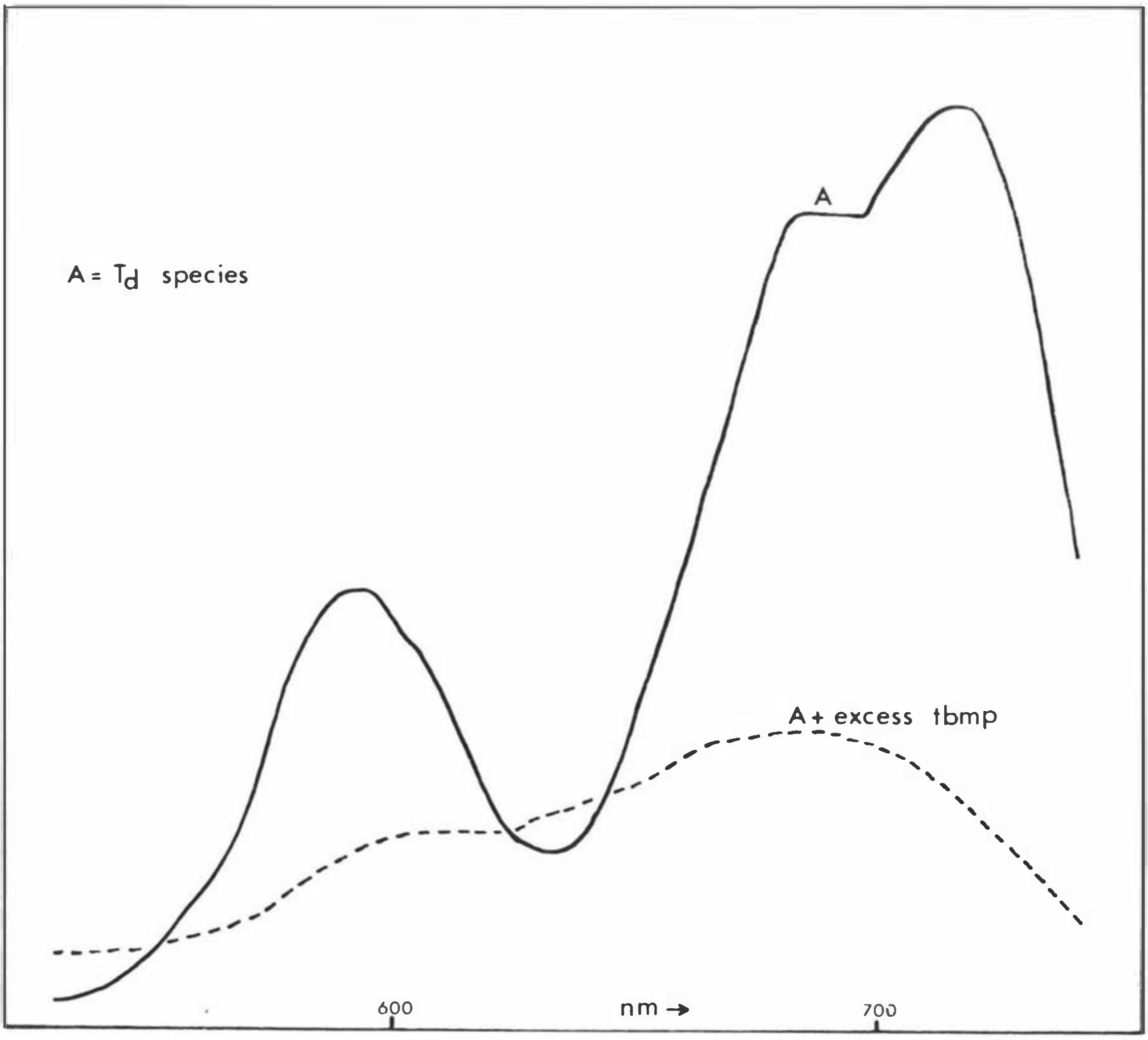
TABLE 22b

ELECTRONIC SPECTRA, Co(II) COMPLEXES IN MeOH

COMPLEX	ABSORPTION/nm	ϵ (l.mol.$^{-1}$cm^{-1})
$Co(tbmp)_2Cl_2$	535	11
	ca 660	1
$Co(tbmp)_2Br_2$	527	8
$Co(tbmp)_2(ClO_4)_2$	520	7
	ca 645	2

FIGURE 19b

Electronic Spectra - Tetrahedral $Co(tbmp)_2X_2$ Species



- spectra recorded in non-ligating solvents.

TABLE 22c

ELECTRONIC SPECTRA, TETRAHEDRAL Co(II) COMPLEXES

COMPLEX	LIGANDS	STATE	$^4A_2 \longrightarrow {}^4T_1(P)$/nm	REFERENCE
$Co(tbmp)_2Cl_2$	2N, $2Cl^-$?	CH_2Cl_2	565, 667, 712 ϕ (218)(301)(407)	This work
		ϕNO_2	564, <u>ca</u> 575, 662, 700, 708 (195) (328) (388)	
$Co(mmp)_2Cl_2$	2N, $2Cl^-$?	ϕNO_2	560, 610, 650, 680	15
Co(∝-pic)$_2Cl_2$	2N, $2Cl^-$	CH_2Cl_2	588, 625, 637	This work†
$Co(Me_3PS)_2Cl_2$	2S, $2Cl^-$	CH_2Cl_2	604, 659, 750	136
$Co(mmtq)Cl_2$	N, S, $2Cl^-$	Refl.	560, 660	14
$Co(tbmp)_2Br_2$	2N, $2Br^-$?	CH_2Cl_2	592, 690, 718 (262)(492)(560)	This work
* CoL'_2Br_2	2N, $2Br^-$	Refl.	586, 621, 636	137
$Co(Me_3PS)_2Br_2$	2S, $2Br^-$	CH_2Cl_2	631, 679, 756	136
$Co(mmtq)Br_2$	N, S, $2Br^-$	Refl.	580, 680	14

<u>NOTES</u>: - for tbmp complexes, extinction coefficients are in parentheses

ϕ also an absorption at 1375(ϵ =37) nm.

† sample prepared by method of Allan <u>et al</u>[138]

* L′ = 2-methylthio-3-methylimidazole.

out the assignment of distorted cis-octahedral geometries for the other Co(tbmp)$_2$X$_2$ complexes. Where X is chloride and bromide, the far-infrared spectra strongly support the assignment of distorted cis-octahedral symmetry to the complexes (see 4.2)

ii) Solution

Methanol: The spectra of the Co(tbmp)$_2$X$_2$ complexes (X=ClO$_4^-$, Cl$^-$, Br$^-$) (Table 22b) suggest that partial, if not complete, displacement of the ligands is occurring. The main absorption maximum of each of the pink solutions is quite weak and very close in energy to that of Co(II) in methanol.

Dichloromethane and Nitrobenzene: The spectra of the blue solutions that are formed by Co(tbmp)$_2$Cl$_2$ and Co(tbmp)$_2$Br$_2$ in these non-ligating solvents, are typical of tetrahedral Co(II) [129] (Table 22c and Figure 19b), but the nature of the species of these solutions is not readily apparent. The formation of species such as CoCl$_4^{2-}$ and $[\text{Co(tbmp)}_2]^{2+}$ can be ruled out by the non-electrolytic behaviour of Co(tbmp)$_2$Cl$_2$ in nitrobenzene (Λ = 2 ohm^{-1}mol.$^{-1}$cm^2). Co(tbmp)$_2$Br$_2$ appears to behave similarly. While some spectral changes occur on adding excess ligand (Figure 19b), the spectra remain strongly suggestive of tetrahedral Co(II) and this implies that if an equilibrium such as (i) exists, it must lie strongly in favour of Co(tbmp)$_2$X$_2$. The behaviour of these complexes is in contrast to that of the analogous Cu(II) complexes, which appear to dimerize in dichloromethane (see Chapter 2).

(i) $\text{Co(tbmp)}_2\text{X}_2 \rightleftharpoons \text{Co(tbmp)X}_2 + \text{tbmp}$

On the basis of these observations, it appears probable that the major species in these non-ligating solvents can be formulated as tetrahedral Co(tbmp)$_2$X$_2$, where both tbmp ligands are unidentate. Similar behaviour was reported for the related complex $Co(mmp)_2Cl_2$, where mmp is 2-methylthiomethylpyridine[15] and for this complex, it was suggested that both mmp ligands are bound via the pyridyl nitrogen only.

NICKEL (II) COMPLEXES

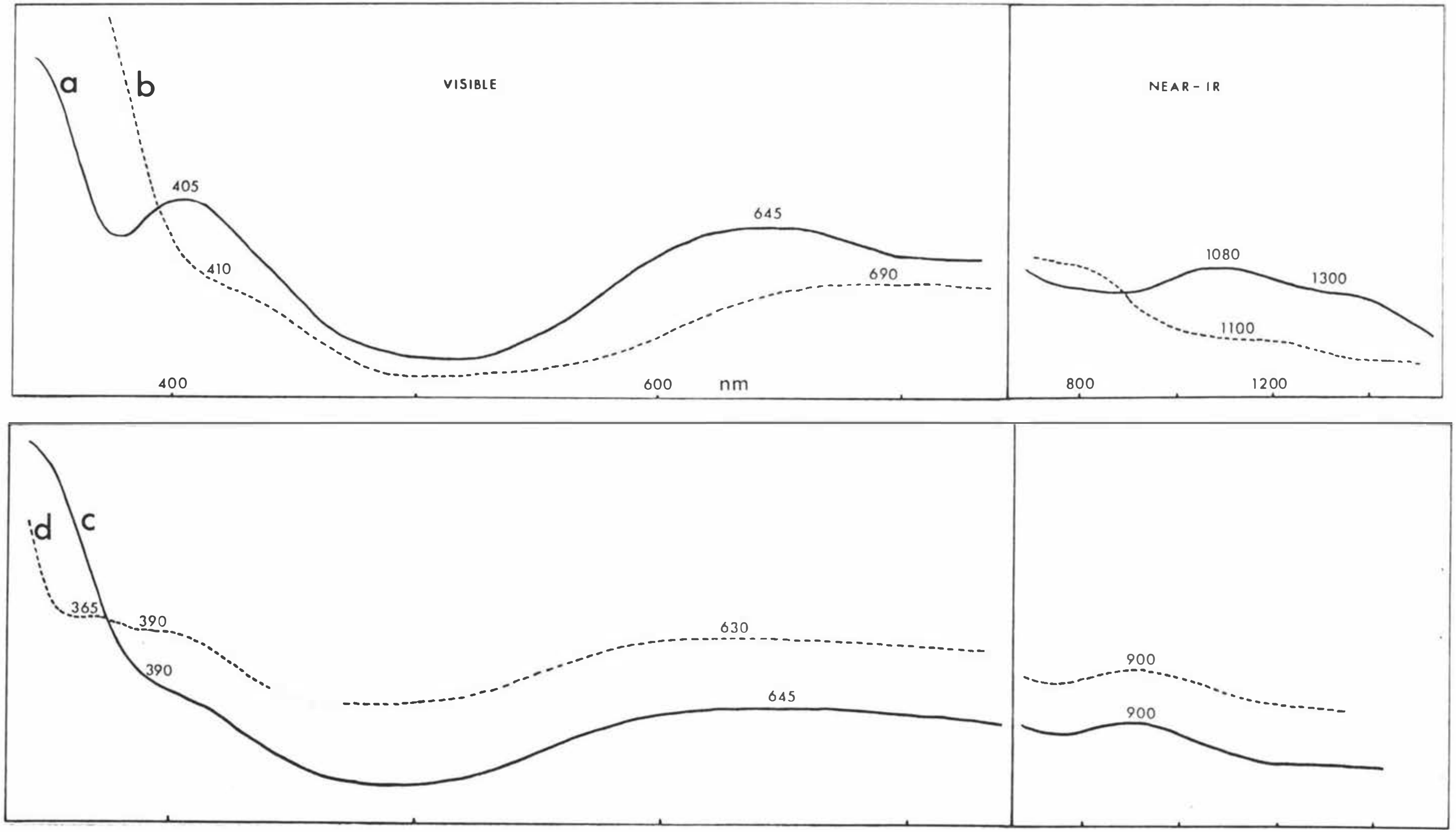
(i) Reflectance

The reflectance spectra are consistent with the complexes being six-coordinate $NiN_2S_2X_2$ chromophores and the tentatively assigned ligand field maxima are presented in Table 23a. Although the $Ni(tbmp)_2(ClO_4)_2.xH_2O$ (x=1,2) complexes do not exhibit any absorptions below 1000nm, this does not necessarily imply that they are square planar as the ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ transition can be found over a wide range of wave-lengths (770-1430nm) in distorted octahedral Ni(II) complexes.[43] The infrared spectra (see 4.2) of the $Ni(tbmp)_2(ClO_4)_2.xH_2O$ complexes suggest that the respective chromophores are $[Ni(tbmp)_2.ClO_4.H_2O]^+$ and $[Ni(tbmp)_2.2H_2O]^{2+}$. The reflectance spectra are not inconsistent with these structures. The spectra of the $Ni(tbmp)_2X_2$ ($X=Cl^-,Br^-$) complexes (Figure 20) and the $Ni(tbmp)_2(ClO_4)_2.xH_2O$ complexes do not show the marked splitting of the ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ maxima that characterizes trans-tetragonal Ni(II) complexes.[140] The electronic spectral evidence thus supports the far-infrared evidence (see 4.2) for the assignment of distorted cis-octahedral structures to these complexes.

It would be intuitively expected, from the similarities in their respective NS donor sets, that the relative ligand field strength of two tbmp ligands would be comparable in magnitude to the ligand field strength of quadradentate 1,8-bis(2-pyridyl)-3,6-dithiaoctane in its Ni(II) complexes. This expectation is confirmed by the estimates of the crystal field parameter Dq (Table 23b) for each of the complexes of these ligands. Hence Dq for $Ni(tbmp)_2Cl_2$ ($1142cm^{-1}$) is

FIGURE 20

Electronic Spectra - $Ni(tbmp)_2X_2$ Complexes (Reflectance)



a = $Ni(tbmp)_2Cl_2$

b = $Ni(tbmp)_2Br_2$

c = $[Ni(tbmp)_2.ClO_4.H_2O]ClO_4$

d = $[Ni(tbmp)_2.2H_2O](ClO_4)_2$

TABLE 23a

ELECTRONIC SPECTRA, $NiN_2S_2X_2$ COMPLEXES

COMPLEX	STATE	$^3A_{2g}\longrightarrow{}^3T_{1g}(P)$	$^3A_{2g}\longrightarrow{}^3T_{1g}(F)$	$^3A_{2g}\longrightarrow{}^3T_{2g}$	REFERENCE
$Ni(tbmp)_2Cl_2$	Refl.	405	645	1080, ca 1300(sh)	This work
	MeOH	415(9), [490(1)]	770(4)		
$NiACl_2$	Refl.	425	720	1205	139
$Ni(mmp)_2Cl_2$	Refl.		630, 730(sh)	1000(br)	15
$Ni(NSSN)Cl_2$	Refl.		633	1111	132
$Ni(tbmp)_2Br_2$	Refl.	ca 410(sh)	690	ca 1100(sh)	This work
	MeOH	410(8), [ca 465(2)]	780(2)		
$NiABr_2$	Refl.	425	725	1198	139
$Ni(mmp)_2Br_2$	Refl.		650, 750(sh)	1000(br)	15
$Ni(NSSN)Br_2$	Refl.		645	1136	132
$[Ni(tbmp)_2.ClO_4.H_2O]ClO_4$	Refl.	ca 390(sh)	645	900	This work
	MeOH	405(7)	755(3)		
$[Ni(tbmp)_2.2H_2O](ClO_4)_2$	Refl.	365(sh), 390(sh)	630	900	This work
$[NiA(H_2O)_2](ClO_4)_2$	Refl.	368	597		139

NOTES: - for tbmp complexes, extinction coefficients are in parentheses

- $Ni(NSSN)X_2$ complexes, also likely to have *cis*-octahedral structures.

[ ] could be "forbidden" $^3A_{2g}\longrightarrow{}^1A_{1g}$ transition[139]

TABLE 23b

ESTIMATED Dq AND B FOR Ni(II) COMPLEXES

COMPLEX	Dq/cm^{-1}	B/cm^{-1}
Ni(tbmp)$_2$Cl$_2$	1142	394
NiACl$_2$	1130	232
Ni(tbmp)$_2$Br$_2$	1168	253
NiABr$_2$	1180	218
[Ni(tbmp)$_2$.ClO$_4$.H$_2$O]ClO$_4$	1225	302
[Ni(tbmp)$_2$.2H$_2$O](ClO$_4$)$_2$	1266	294
[NiA(H$_2$O)$_2$](ClO$_4$)$_2$	1274	375

NOTE: - see Table 23a for reference to NiAX$_2$ complexes.

comparable in magnitude to Dq for $NiACl_2$ ($1130cm^{-1}$), where A is 1,8-bis(2-pyridyl)-3,6-dithiaoctane and similarly for the remaining pairs of analogous complexes. The electronic spectra are compared in Table 23a.

Dq(Δ_o=10Dq) and the Racah (interelectronic repulsion) parameter B, were estimated using Lever's graph procedure.[141]

(ii) Solution

The weak maxima that are observed for the $Ni(tbmp)_2X_2$ complexes in methanol, show that tetragonal species exist in this solvent. Where X is chloride and bromide, the complexes are 1:1 electrolytes and where X is perchlorate, they are 2:1 electrolytes in methanol and this implies that partial solvation can occur. Partial solvation and/or partial decomposition of the complexes is evident from the differences between the reflectance and methanol solution spectra (Table 23a). The complexes were insufficiently soluble to allow spectral studies in non-ligating solvents such as dichloromethane.

4.2 INFRARED SPECTRA

FAR-INFRARED (M(II)-halogen stretching)

The appearance of at least two ν(M-X) vibrations in the spectra (Table 24) of the $M(tbmp)_2X_2$ complexes (M=Co(II), Ni(II); $X=Cl^-$, Br^-) suggests that the complexes have distorted cis-octahedral structures[86] rather than the more common trans structures. In contrast to tetragonal Cu(II) complexes, Jahn-Teller distortions are not expected for tetragonal Ni(II) complexes[129] . This means that cis and trans ν(Ni-X) absorptions will be indistinguishable if the absorption frequencies alone are considered. Very little is known about the effects of Jahn-Teller distortion on tetragonal Co(II) complexes[129] and so it is not possible to predict what differences there will be, if any, between cis and trans ν(Co-X) absorption frequencies.

Co(II) Complexes

$Co(Hpymt)_2Cl_2$ (Hpymt = pyrimidine-2-thione) has been shown to have a cis-distorted octahedral structure for which the ν(Co-Cl) absorptions are found at 232 and 246(sh)cm^{-1}.[133] These are similar to those observed for $Co(tbmp)_2Cl_2$ (222, 249cm^{-1}) but for $Co(tbmp)_2Br_2$, the ν(Co-Br) frequencies (194, 210cm^{-1}) are slightly higher than those of $Co(Hpymt)_2Br_2$ (176, 188(sh)).[133] Trans-$Co(py)_4Cl_2$ has a single ν(Co-Cl) frequency at 230cm^{-1} but in contrast to tetragonal complexes, the ν(Co-X) frequencies of tetrahedral Co(II) complexes are substantially higher.[86]

Ni(II) Complexes

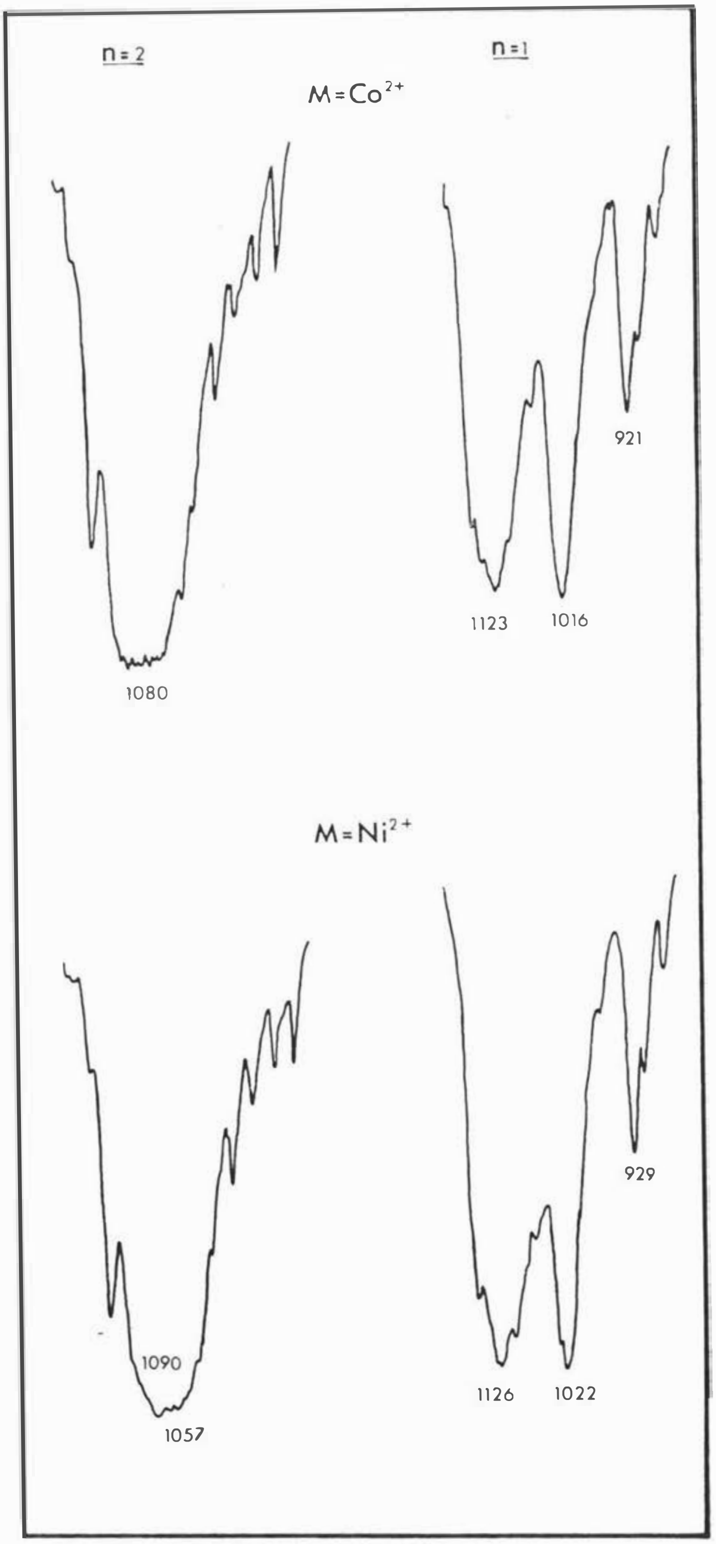
While the ν(Ni-Cl) frequencies (230, 253cm^{-2}) of $Ni(tbmp)_2Cl_2$ are similar to those assigned for trans-tetragonal complexes such as $Ni(3\text{-picoline})_4Cl_2$ (243cm^{-1})[142] and $Ni(py)_4Cl_2$ (246cm^{-1}),[86] both the ν(Ni-Cl) and ν(Ni-Br) frequencies of $Ni(tbmp)_2X_2$ ($X=Cl^-$, Br^-) are significantly lower than those of tetrahedral Ni(II) complexes.[86] As the latter also have two ν(Ni-X) absorptions, the $Ni(tbmp)_2X_2$ spectra are more consistent with the complexes having distorted cis-octahedral structures.

GENERAL INFRARED

(i) Anion coordination: It is probable that at least one of the perchlorate anions is semi-coordinated in $Co(tbmp)_2(ClO_4)_2.H_2O$ and $Ni(tbmp)_2(ClO_4)_2.H_2O$ as the splitting of the perchlorate ν_3 mode (see 2.3) is quite pronounced (Figure 21 , Table 24). However when a second water molecule is present, the ν_3 mode of $Co(tbmp)_2(ClO_4)_2.2H_2O$ is broad and unsplit and in

FIGURE 21

IR Spectra - ν_3 Modes, M(tbmp)$_2$(ClO$_4$)$_2$.nH$_2$O Complexes



- spectra recorded for Nujol mulls; frequencies are cm^{-1}.

TABLE 24

INFRARED SPECTRA, Co(II) AND Ni(II) COMPLEXES

COMPLEX	ν(pyridyl ring)	$\nu_3(ClO_4^-)$	$\nu_1(ClO_4^-)$	ν(M-X): ($X=Cl^-, Br^-$)
$Co(tbmp)_2Cl_2$	1605(s), 1571(w)			222, 249
$Co(tbmp)_2Br_2$	1607(s), 1571(m)			192, 228
$[Co(tbmp)_2.ClO_4.H_2O]ClO_4$		1123(vs), 1016(vs)	921(m)	
† $[Co(tbmp)_2.2H_2O](ClO_4)_2$		<u>ca</u> 1080(br)		
$Ni(tbmp)_2Cl_2$	1605(s), 1571(w)			230, 253
$Ni(tbmp)_2Br_2$	1608(s), 1573(m)			194, 210
$[Ni(tbmp)_2.ClO_4.H_2O]ClO_4$	1611(s), 1576(w)	1126(vs), 1022(vs)	929(m)	
ϕ $[Ni(tbmp)_2.2H_2O](ClO_4)_2$	1611(s), 1578(w)	1090(vs), 1057(vs)		

NOTES:
- all spectra recorded for mulls; frequencies are cm^{-1}
- s = strong; m = medium; w = weak; v = very; br = broad
- ν(pyridyl ring) for uncoordinated tbmp at 1593(s), 1570(m) cm^{-1}
- ionic ClO_4^-; ν_3 at ca 1100 cm^{-1}, ν_1 at ca 930 cm^{-1}.

† prepared by leaving $[Co(tbmp)_2.ClO_4.H_2O]ClO_4$ exposed to air

ϕ $\nu_3(ClO_4^-)$ only weakly split (see text)

$Ni(tbmp)_2(ClO_4).2H_2O$ it is weakly split. The weak splitting of the ν_3 absorption may result from hydrogen bonding effects, which can also lower the symmetry of the anion.[143] It is more likely that the water molecules are bound to Ni(II) in the latter complex, rather than the weakly coordinating perchlorate anions.

(ii) Ring Stretching Modes: Similar trends in the shifts of the higher frequency pyridyl ring-stretching mode are observed for the Co(II) and Ni(II) complexes of tbmp when they are compared with the Cu(II) complexes that were discussed in Chapter 2. Coordination of the pyridine ring has resulted in a blue-shift of this frequency for each of the complexes (Table 24).

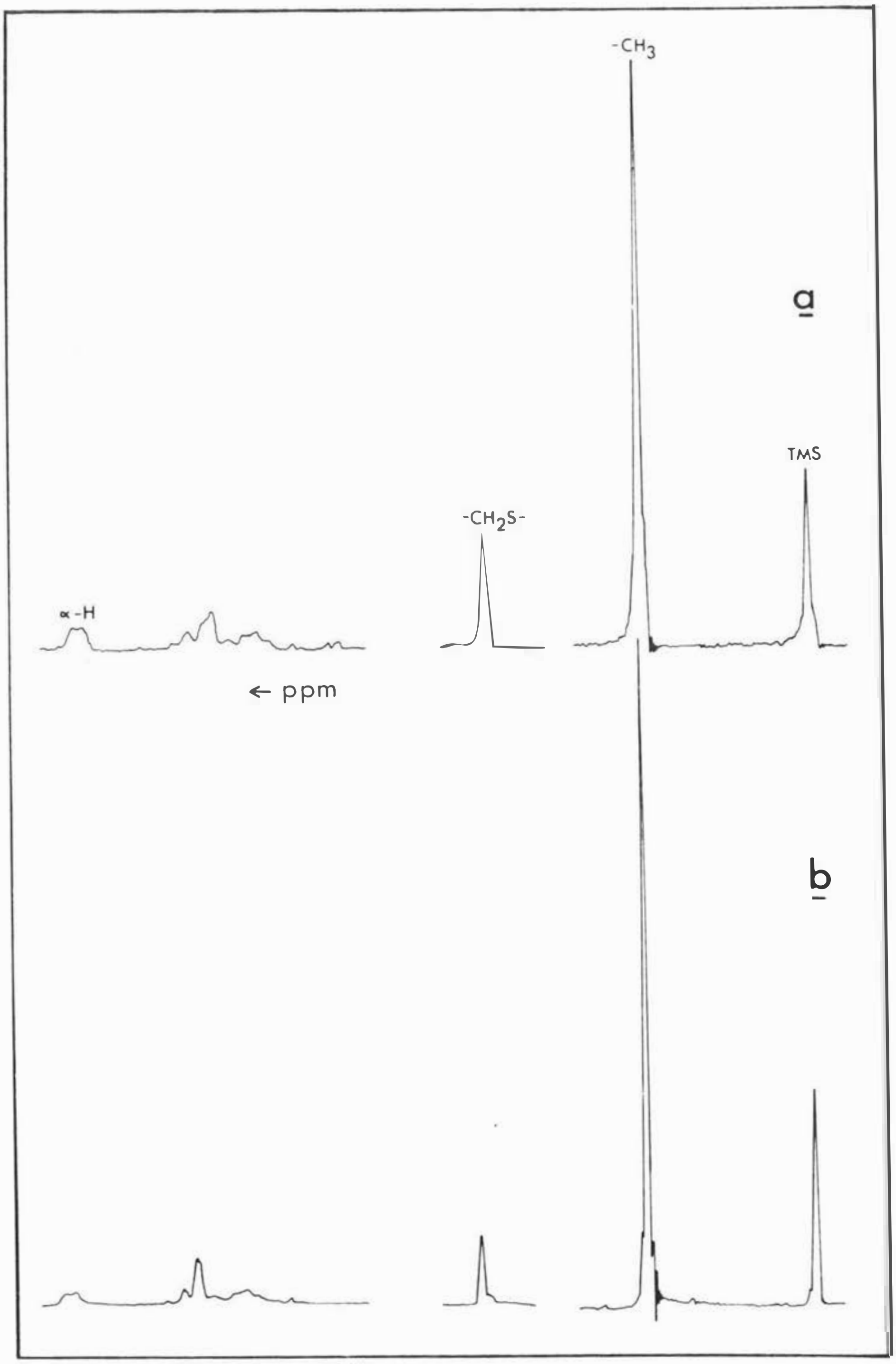
4.3 PARAMAGNETIC ^1H nmr LINE BROADENING EXPERIMENT

This experiment was carried out in a manner similar to that of the experiment that was discussed in Chapter 2 (see 2.6).

The effect of adding Co(II) to tbmp is illustrated in Figure 22. The paramagnetic broadening of the α-proton and methylene protons' resonances is not as dramatic as it is in the presence of Cu(II) and this can be attributed to the shorter relaxation time of Co(II) compared to Cu(II). Line broadening effects thus decrease in the order Cu(II) $>$ Co(II) $\gg$ Ni(II).[144] With Co(II), the heights of the α-proton and methylene protons' resonances are reduced while the TMS and methyl proton peaks are slightly enhanced. The former resonances also shift slightly downfield (ca 0.05 ppm). It is possible that the changes in the methylene protons' resonance are due solely to Co(II)-pyridyl interactions (see Chapter 2) and so while it can be confidently concluded that Co(II) exchange is taking place at the pyridyl nitrogen of tbmp, similar conclusions can not be drawn about exchange at the thioether sulphur.

FIGURE 22

^{1}H nmr - Addition of Co(II) to tbmp (in CH_2Cl_2)



a - tbmp in absence of Co(II)

b - tbmp in presence of Co(II) [1.2×10^{-3} mol.l.$^{-1}$]

SYNTHESES

Some general comments that relate to all of these syntheses can be found in the experimental section of the Appendices.

Perchloratoaquobis[2-(3,3-dimethyl-2-thiabutyl)pyridine] cobalt(II)perchlorate.

A pink solution results from the addition of 1 mmole of $Co(ClO_4)_2$ (0.258 g.) (plus a few drops of triethylorthoformate) to 2 mmole of ligand (0.363 g.). The mauve complex was isolated after concentrating the solution and cooling it.

YIELD: 0.144 g. (23%)

Dichlorobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]cobalt(II)

The addition of 1 mmole of $CoCl_2.6H_2O$ (0.238 g.) to 2 mmole of ligand (0.363 g.) gave a deep blue solution which was concentrated to precipitate the mauve complex.

YIELD: 0.312 g. (63%)

Dibromobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]cobalt(II)

$CoBr_2.6H_2O$ (0.5 mmole, 0.163 g.) was slowly added to 1 mmole of the ligand (0.181 g.) to give a deep blue-purple solution. This was cooled to give a mauve precipitate and a second crop was isolated from the filtrate.

YIELD: 0.173 g. (59%)

Perchloratoaquobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]nickel(II) perchlorate.

A solution of 1 mmole of $Ni(ClO_4)_2.6H_2O$ (plus triethylorthoformate) was added to 2 mmole of ligand to give a pale blue-green solution. The pale green complex was isolated after the solution had been reduced in volume and cooled.

YIELD: 0.121 g. (19%)

Diaquobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]nickel(II) perchlorate.

A pale blue solution resulted from 1 mmole of $Ni(ClO_4)_2.6H_2O$ (0.366 g.) being added to 2 mmole of ligand. The solution was concentrated and "scratched" to precipitate the pale blue complex. It was then filtered off and washed with Abs. EtOH and then ether.

YIELD: 0.250 g. (40%)

Dichlorobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]nickel(II)

1 mmole of $NiCl_2.6H_2O$ (0.238 g.) was added to 2 mmole of the ligand to give a pale green solution. A pale blue-green complex precipitated from this solution when it was concentrated in vacuo.

YIELD: 0.320 g. (65%)

Dibromobis[2-(3,3-dimethyl-2-thiabutyl)pyridine]nickel(II)

$NiBr_2.3H_2O$ (0.5 mmole, 0.136 g.) was added to 1 mmole (0.181 g.) of the ligand to give a green solution. Green crystals began to appear while the Ni(II) was being added. The solution was cooled and "scratched" to induce further crystallization.

YIELD: 0.212 g. (73%)

TABLE 25

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/%			CONDUCTIVITY/ohm^{-1}mol.$^{-1}$cm^2		
			C	H	N	CH_3NO_2	MeOH	Other
$Co(tbmp)_2(ClO_4)_2.H_2O$	mauve	-	37.62 (37.56)	5.05 (5.04)	4.39 (4.36)	168		
$Co(tbmp)_2Cl_2$	mauve	152-155	48.78 (48.82)	6.14 (6.22)	5.69 (5.70)	22	126	ØNO$_2$: 2
$Co(tbmp)_2Br_2$	mauve	148-150	41.32 (41.18)	5.20 (5.24)	4.82 (4.74)	26	138	
$Ni(tbmp)_2(ClO_4)_2.2H_2O$	p.blue	-	36.60 (36.72)	5.22 (5.47)	4.27 (4.03)	168		
$Ni(tbmp)_2(ClO_4)_2.H_2O$	p.green	-	37.64 (37.61)	5.05 (5.20)	4.39 (4.15)	169		
$Ni(tbmp)_2Cl_2$	p.blue/green	212-213	48.80 (48.68)	6.14 (6.24)	5.69 (5.53)	7	138	
$Ni(tbmp)_2Br_2$	p.green	191-193	41.33 (41.36)	5.20 (5.30)	4.82 (4.76)	20	145	

NOTES: - molar conductivities at 25°C :

Nitromethane	1:1 (70-90),	2:1 (150-170)
Methanol	(100-130),	(210-250)
Nitrobenzene	(20-30)	

- p = pale

CHAPTER 5

M(II) COMPLEXES OF 2-ETHYLTHIOETHYLAMINE (M(II) = Cu(II)) AND 2-METHYLTHIO-2-IMIDAZOLINE (M(II) = Cu(II), Co(II))

Cu(II) Complexes: The reactions of 2-ethylthioethylamine (etea) yield Cu(etea)X_2 ($X=Cl^-$, Br^-) and $Cu(etea)_2X_2$ ($X=BF_4^-$, ClO_4^-, Cl^-, Br^-). The former group appear to be tetragonal polymeric while in the latter group, the far-infrared spectra of $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$ indicate that the anions are bound trans to each other. Where X is ClO_4^- or BF_4^-, the reflectance spectra suggest that the coordinated sulphur atoms are cis to each other, however in solution, they are probably trans.

$[Cu(etea)_2Cl]BF_4$ can be isolated from the 1:1 reaction of LiCl with $Cu(etea)_2(BF_4)_2$ if care is taken to ensure that the co-precipitation of $Cu(etea)_nCl_2$ (n=1 or 2) and $Cu(etea)_2(BF_4)_2$ does not take place. Its structure is probably similar to that of the other bis-complexes in the solid state, but in CH_2Cl_2 it is probably tetragonal pyramidal.

Polymerization problems were usually encountered in the reactions of 2-methylthio-2-imidazoline (mti) and the isolation of the $Cu(mti)_4X_2$ ($X=BF_4^-$, Cl^-, Br^-) complexes was quite difficult. $Cu(mti)_4(BF_4)_2$ and $Cu(mti)_4Cl_2$ appear to be trans-tetragonal while the electronic spectral evidence suggests that $Cu(mti)_4Br_2$ may be cis-octahedral.

Co(II) Complexes: In the reaction of mti with $CoCl_2.6H_2O$, $Co(mti)_3Cl_2$ was isolated and this probably has a distorted tetrahedral structure in which one mti molecule remains uncoordinated. $Co(mti)_4(ClO_4)_2$ could not be isolated and a sample of "$Co(mti)_4(B\O_4)_2$" that was prepared, was impure.

TABLE 26

SUMMARY OF RESULTS-$Cu(etea)_nX_2$ COMPLEXES (n = 1,2)

COMPLEX	STATE	STRUCTURE	PHYSICAL TECHNIQUE
$Cu(etea)_2X_2$	solid	tetrag. $Cu(etea)_2X_2$	electronic, infrared
($X=BF_4^-$, ClO_4^-)	CH_2Cl_2 (rm.temp.)	$[Cu(etea)_2]^{2+}$	electronic
	MeOH (rm.temp.,77K)	$[Cu(etea)_2(MeOH)_2]^{2+}$	electronic, esr
($X=Cl^-$, Br^-)	solid	tetragonal	electronic, far-IR
	CH_2Cl_2(rm.temp.,77K)	tetrag. $Cu(etea)_2X_2$	electronic, esr
	MeOH (rm.temp.)	$[Cu(etea)_2X.MeOH]^+$	electronic,conductivity
	(77K)	trig.bipyr. $[Cu(etea)_2X]^+$	esr
$[Cu(etea)_2Cl]BF_4$	solid	tetragonal	electronic, infrared
	CH_2Cl_2(rm.temp.,77K)	tetrag.pyr. $[Cu(etea)_2Cl]^+$	electronic, esr
	MeOH (rm.temp.)	$[Cu(etea)_2Cl.MeOH]^+$	electronic, conductivity
	(77K)	$[Cu(etea)_2Cl.MeOH]^+$ and trig.bipyr. $Cu(etea)_2Cl^+$	esr
$Cu(etea)X_2$	solid	tetrag. polymeric	electronic, far-IR
($X=Cl^-$, Br^-)	MeOH (rm.temp.)	polymeric structure broken up	electronic, conductivity
	(77K)	major species is $Cu(MeOH)_n^{2+}$ (n=4 or 6) (where $X=Br^-$, minor species is trig.bipyr.)	esr

5.1 ELECTRONIC SPECTRA

Where possible, tentative assignments have been made for these complexes and these are presented with the spectra, in Tables 27a and 27b. The assignments have been based on comparisons made within each series of complexes and according to the work of other authors.

A) LIGAND FIELD TRANSITIONS

2-ETHYLTHIOETHYLAMINE COMPLEXES

i) $Cu(etea)_2(ClO_4)_2$ and $Cu(etea)_2(BF_4)_2$

The reflectance ligand field maxima are consistent with the anions being weakly trans-coordinated in a manner similar to that of the complex $Cu(NH_2CH_2CH_2SCH_3)_2(ClO_4)_2$, which has been characterized crystallographically[33] and spectroscopically[47]. The maxima are virtually unchanged in dichloromethane solution.

In methanol, the red-shifts of the ligand field maxima suggest that methanol is binding[145] and the predominant species is probably $[Cu(etea)_2(MeOH)_2]^{2+}$ for both anions.

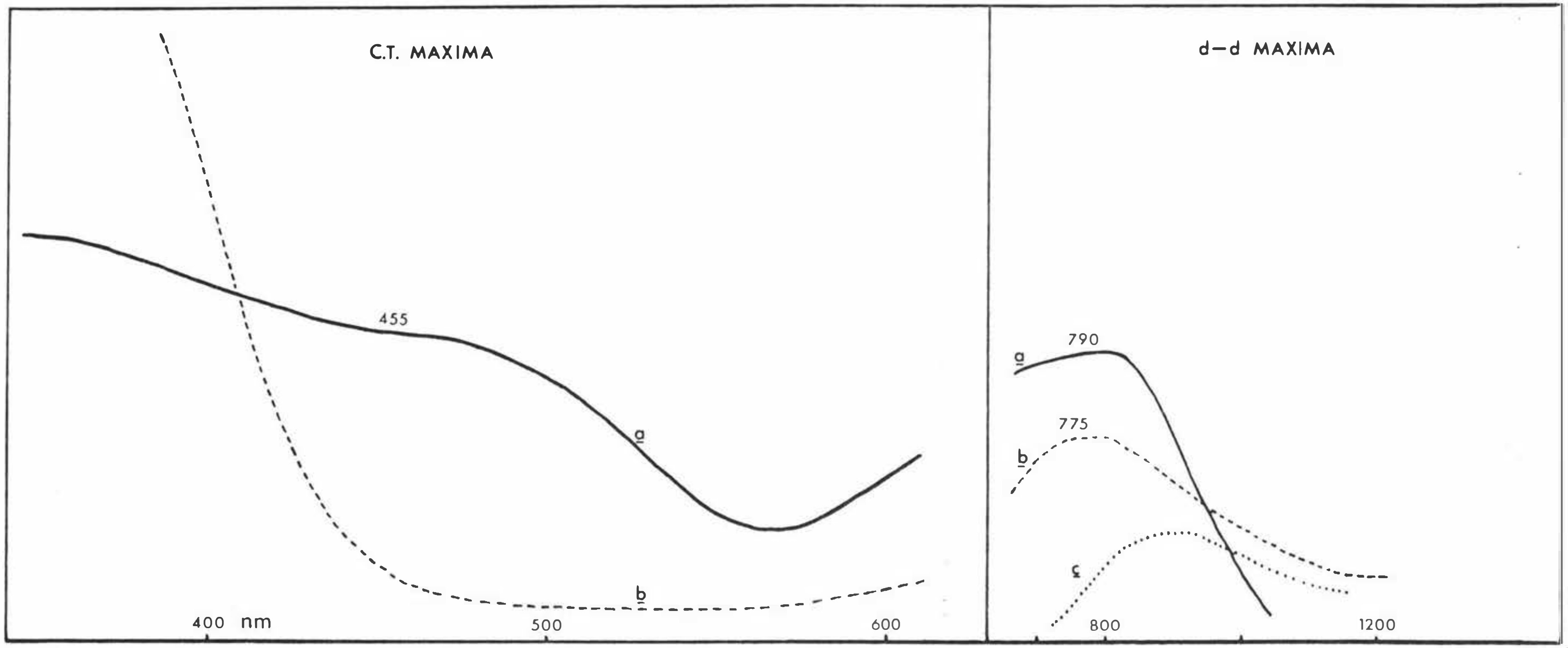
ii) $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$

The ligand field maxima are red-shifted in relation to the spectra of $Cu(etea)_2(ClO_4)_2$ and $Cu(etea)_2(BF_4)_2$ and a low energy shoulder appears in the reflectance spectra. Both effects are consistent with the complexes having trans-tetragonal structures[90,145] where the anions occupy the axial coordination positions. This conclusion is supported by the far-infrared spectra.

These structures appear to be retained in dichloromethane but in methanol the 1:1 electrolytic nature of the complexes (Table 31) suggests that they may exist as the trans-tetragonal

FIGURE 23

Electronic Spectra - Cu(etea)Br$_2$



a = Reflectance

b = MeOH solution

c = CuBr$_2$ in MeOH

TABLE 27a

ELECTRONIC SPECTRA, etea COMPLEXES

COMPLEX	REFLECTANCE	ASSIGNMENT	CH_2Cl_2(ε)	ASSIGNMENT	MeOH(ε)	ASSIGNMENT	OTHER
Cu(etea)$_2$(ClO$_4$)$_2$			250	σ(N)→Cu(II)	249(2148)	σ(N)→Cu(II)	
	355	σ(S)→Cu(II)	345	σ(S)→Cu(II)	313(2893)†		
	ca 385(sh)	σ(S)→Cu(II)			385(1818)	σ(S)→Cu(II)	
	537†	LF	560	LF	627(124)	LF	
Cu(etea)$_2$(BF$_4$)$_2$			250	σ(N)→Cu(II)	251(2304)	σ(N)→Cu(II)	
	360	σ(S)→Cu(II)	341	σ(S)→Cu(II)	313(3213)†		
	ca 390(sh)	σ(S)→Cu(II)			386(2128)	σ(S)→Cu(II)	
	535(br)†	LF	560	LF	627(123)	LF	
Cu(etea)$_2$Cl$_2$			ca 254(4246)	σ(N)→Cu(II)	253(2436)	σ(N)→Cu(II)	Abs.EtOH
			283(6825)	apical Cl$^-$→Cu(II)			275(3430)†
			ca 320(sh)		316(2800)†		
	ca 370(br)	σ(S)→Cu(II)			375(1945)	σ(S)→Cu(II)	352(2678)†
	688	LF	750(238)†	LF	705(288)†	LF	720(br;314)
	ca 1120(sh)	LF					
Cu(etea)$_2$Br$_2$			265	σ(N)→Cu(II)	251(2352)	σ(N)→Cu(II)	
			327	apical Br$^-$→Cu(II)	313(br;2978)		
	405†		ca 360(sh)	σ(S)→Cu(II)	375(sh;1451)	σ(S)→Cu(II)	
	647	LF	750†	LF	715(385)	LF	
	ca 850(sh)	LF					
[Cu(etea)$_2$Cl]BF$_4$			255(3182)	σ(N)→Cu(II)	252(2549)	σ(N)→Cu(II)	
			281(3606)	apical Cl$^-$→Cu(II)	314(3062)†		
	ca 385(br)	σ(S)→Cu(II)	350(3348)	σ(S)→Cu(II)	385(1903)	σ(S)→Cu(II)	
	ca 680(br)	LF	720(262)†	LF	690(110)†	LF	
	812	LF					
Cu(etea)Cl$_2$	360†	mixed			ca 357(990)		CH_3NO_2
	770†	LF			760(137)†	LF	775(262)†
Cu(etea)Br$_2$	ca 455(sh)	Br$^-$→Cu(II)			ca 340(br)		ca 460(sh)
	790†	LF			775(215)	LF	750(463)†
Cu(etea)$_2$SO$_4$					260(2202)	σ(N)→Cu(II)	
					326(3121)		
	700	LF			665(137)	LF	

NOTES: - all maxima are nm; extinction coefficients (l.mol.$^{-1}$cm^{-1}) are in parentheses,

- sh = shoulder; br = broad; LF = Ligand Field

† asymmetric maxima, implying a second, unresolved maximum,

- omission of extinction coefficients implies either partial solubility or the resolution is not good enough to enable accurate calculation.

$[Cu(etea)_2X.MeOH]^+$ species. The electronic spectra at room temperature (in methanol) are consistent with this proposal.

iii) $[Cu(etea)_2Cl]BF_4$

The reflectance spectrum suggests that this complex has a trans-tetragonal structure and this is in agreement with the infrared spectra. (see 5.3)

In dichloromethane, the form of the ligand field absorption envelope implies that the $[Cu(etea)_2Cl]^+$ chromophore has a square pyramidal structure (see Chapter 2) but in methanol, the similarity of the entire spectrum with that of $Cu(etea)_2Cl_2$ in this solvent implicates the presence of a $[Cu(etea)_2Cl.MeOH]^+$ species.

iv) $Cu(etea)Cl_2$ and $Cu(etea)Br_2$

In the reflectance spectra, the ligand field maxima lie at energies between those reported for the tetragonal polymeric $CuenX_2$ (en = ethylenediamine)[72] and $CudtoX_2$ (dto = 3,6-dithiaoctane)[82] complexes. It is probable that the $Cu(etea)X_2$ complexes are also tetragonal polymers and this suggestion is supported by the relatively insoluble nature of these complexes.

The differences between the spectra in methanol and the reflectance spectra indicate that the polymeric structure is being broken on dissolution. If one of the species in solution is $[Cu(MeOH)_n]^{2+}$ (as indicated by the esr spectra at 77K), there should be an absorption at 900-912nm. However, such a peak is not at all obvious (Figure 23).

In nitromethane, a $Br^- \longrightarrow Cu(II)$ charge transfer absorption can be assigned for $Cu(etea)Br_2$ and this indicates that the polymeric structure is not being completely broken up as in methanol.

TABLE 27b

ELECTRONIC SPECTRA, mti COMPLEXES

COMPLEX	REFLECTANCE	ASSIGNMENT	ACETONE	ASSIGNMENT	CH_2Cl_2	ASSIGNMENT	OTHER	
							EtOH	CH_3NO_2
$Cu(mti)_4(BF_4)_2$	492	$\sigma(S)\rightarrow Cu(II)$					ca370(sh)	
	830	LF	665(78)				620(84)	663(98)
$Cu(mti)_4Cl_2$					287	apical $Cl^-\rightarrow Cu(II)$	EtOH	CH_3NO_2
	367	$\sigma(N_{Im})\rightarrow Cu(II)$	427(1055)	$\sigma(N_{Im})\rightarrow Cu(II)$	418	$\sigma(N_{Im})\rightarrow Cu(II)$	383(1243)	
	675(br)	LF	825(150)	LF	ca850(br)	LF	670(30)	815(51)
$Cu(mti)_4Br_2$	ca 405(sh)	$\sigma(N_{Im})\rightarrow Cu(II)$	ca 415(sh)	$\sigma(N_{Im})\rightarrow Cu(II)$				
	475	$Br^-\longrightarrow Cu(II)$	ca 450(sh)	$Br^-\longrightarrow Cu(II)$	450	$Br^-\longrightarrow Cu(II)$		
	770	LF	820	LF	780	LF		

NOTES: - see Table 27a.

TABLE 27c

ELECTRONIC SPECTRA, $Co(mti)_3Cl_2$

STATE	$^4A_2\rightarrow{}^4T_1(P)$/nm	$^4A_2\rightarrow{}^4T_1(F)$/nm	OTHER/nm
Refl.	585, 620, 640	1100, ca 1350(sh), ca 1457(sh)	ca 370(sh), ca 480(br,sh)
CH_2Cl_2	603, ca 638(sh), 655		ca 375(sh), ca 470(sh)

NOTE: - complex only partially soluble in CH_2Cl_2

2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

i) Cu(mti)$_4$(BF$_4$)$_2$

The ligand field maxima at 830 nm in the reflectance spectrum (Table 27b) suggests that there is little tetragonal distortion[44] in this complex, compared to complexes such as Cu(benzimidazole)$_4$(ClO$_4$)$_2$ (526, 641(sh) nm)[145] and Cu(DMIZ)$_4$(BF$_4$)$_2$ (526 nm), where DMIZ is 1,2-dimethylimidazole.[146]

On dissolution in acetone, ethanol and nitromethane the ligand field maxima undergo a blue-shift to energies that are consistent with the presence of a trans-tetragonal $[\mathrm{Cu(mti)_4(solvent)_n}]^{2+}$ species.

ii) Cu(mti)$_4$Cl$_2$ and Cu(mti)$_4$Br$_2$

The reflectance spectra suggest that these complexes have six-coordinate geometries.

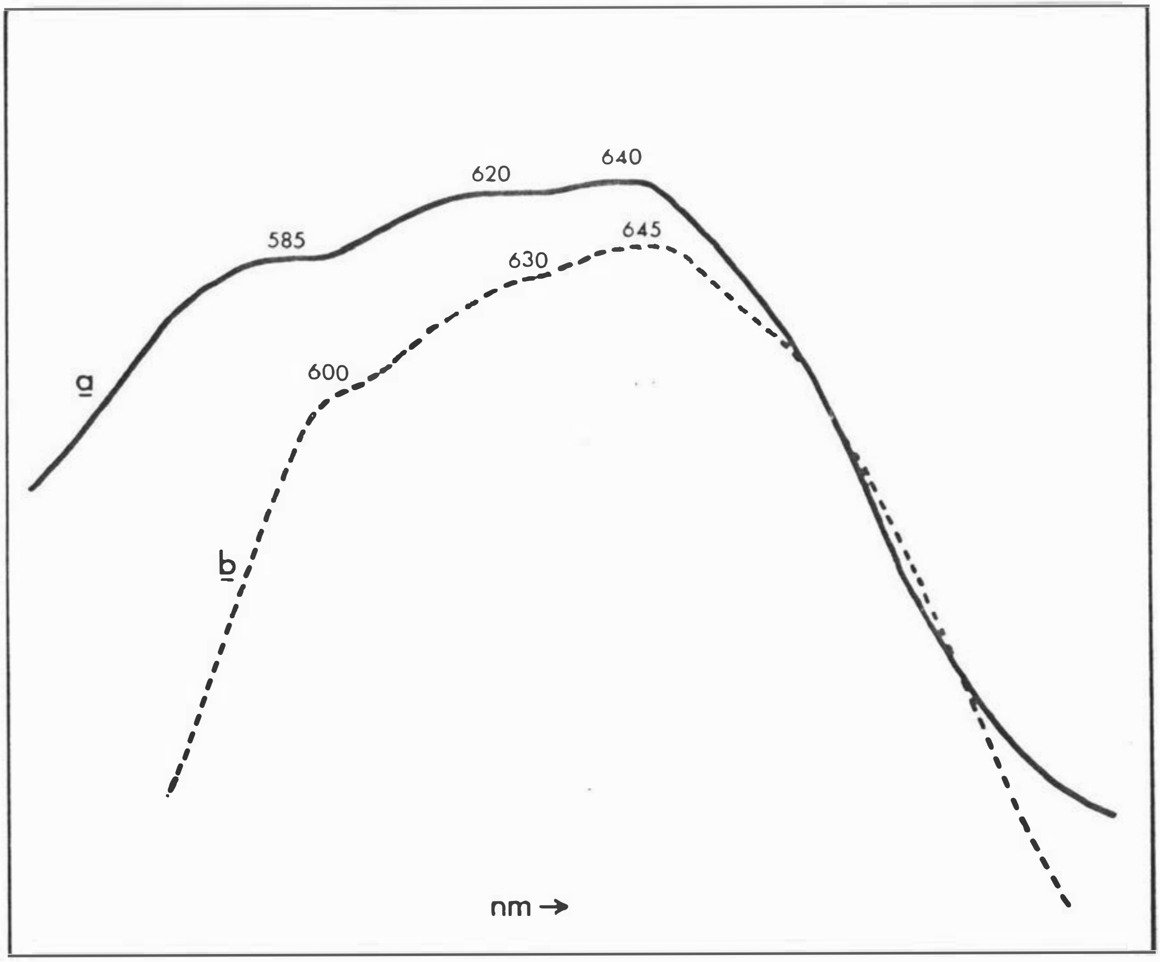
The conductivities of these complexes (Table 31) show that some dissociation is occurring on dissolution and the electronic spectra also undergo some changes. However it appears that the six-coordinate structure is probably being retained although there may be some differences in the degree of tetragonal distortion in Cu(mti)$_4$Cl$_2$, in going from the solid state to solution.

iii) Co(mti)$_3$Cl$_2$

The two spin-allowed transitions of tetrahedral Co(II) ($^4A_2 \longrightarrow {}^4T_1(F)$ and $^4A_2 \longrightarrow {}^4T_1(P)$) appear as intense, multicomponent absorptions in the near infrared and visible regions respectively.[43,129] The absorption maxima for Co(mti)$_3$Cl$_2$ are typical of such spectra (Figure 24) with quartet $\longrightarrow$ doublet transitions being responsible for the multiple absorptions on the higher energy side of the main

FIGURE 24

Electronic Spectra - $Co(mti)_3Cl_2$ and $Co(\alpha\text{-pic})_2Cl_2$

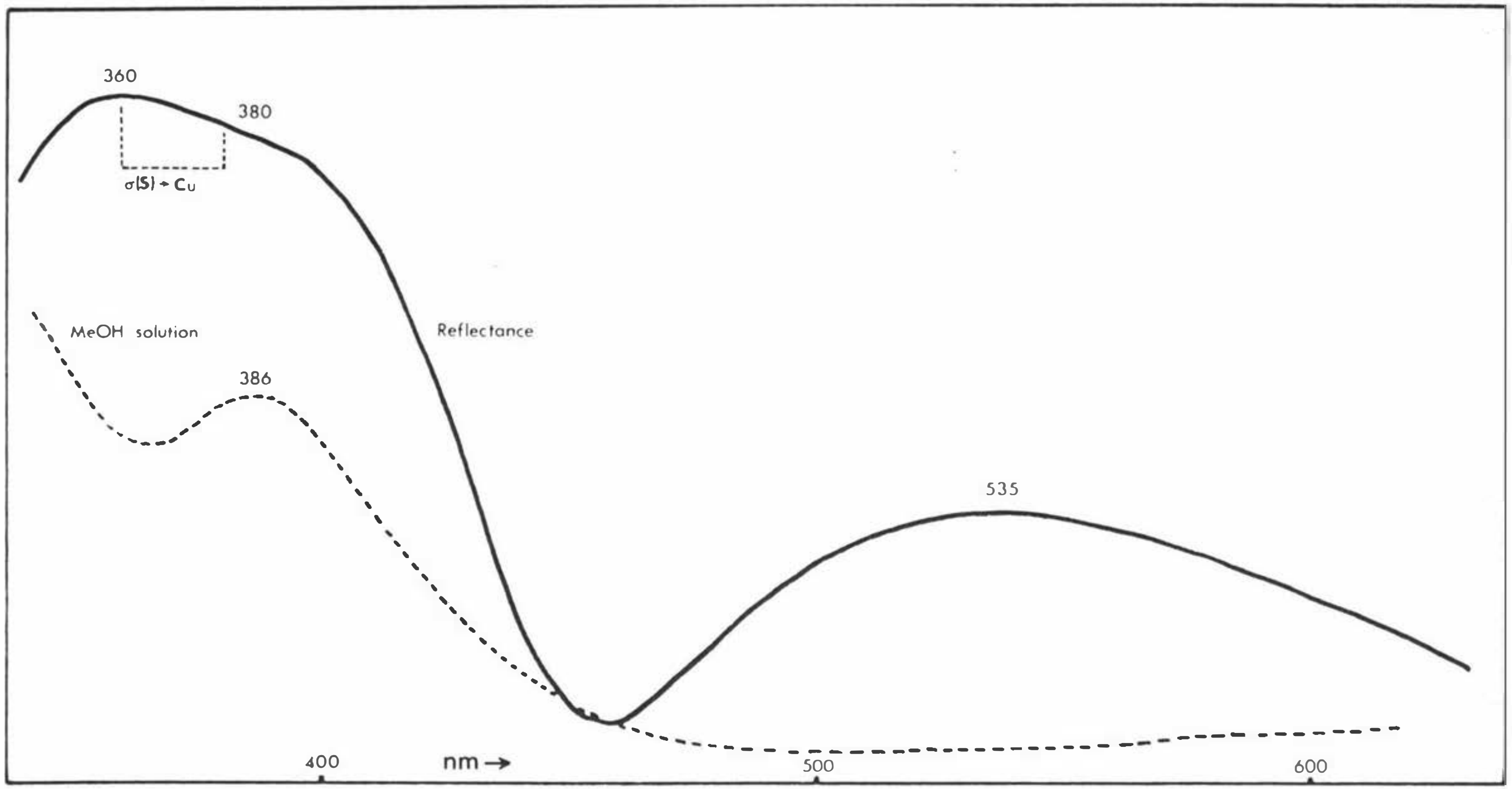


a = $Co(mti)_3Cl_2$ (reflectance)

b = $Co(\alpha\text{-pic})_2Cl_2$ (reflectance)

FIGURE 25a

Electronic Spectra - $Cu(etea)_2(BF_4)_2$



- only one σ(S)→Cu(II) C.T. absorption is observed in MeOH solution (386 nm).

transitions. The spectral assignments are given in Table 27c.

Similarities between the spectrum of Co(mti)$_3$Cl$_2$ and the spectra of tetrahedral CoN$_2$Cl$_2$ complexes such as Co(α-picoline)$_2$Cl$_2$ (Figure 24) and CoI$'_2$Cl$_2$, where I$'$ is 2-methylthio-3-methylimidazole,[137] suggest that only two of the mti ligands are bound to Co(II) in Co(mti)$_3$Cl$_2$. It appears then, that this complex has a distorted tetrahedral CoN$_2$Cl$_2$ chromophore.

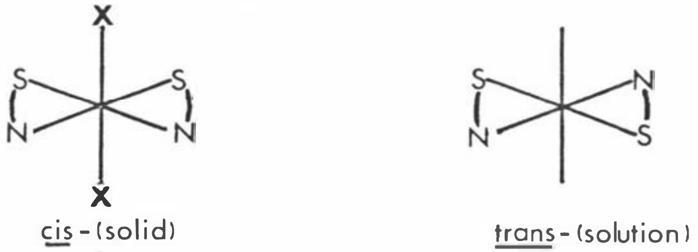
B) CHARGE TRANSFER TRANSITIONS

2-ETHYLTHIOETHYLAMINE COMPLEXES

i) Cu(etea)$_2$(ClO$_4$)$_2$ and Cu(etea)$_2$(BF$_4$)$_2$

Two σ(S) ⟶ Cu(II) charge transfer absorptions appear in the reflectance spectra (Table 27a, Figure 25a) but in solution, only one absorption is observed for each complex. By analogy with the Cu(tbmp)$_2$X$_2$ complexes (Chapter 2) and those discussed by other workers,[60,80] the spectra suggest that the sulphur atoms are cis with respect to each other in the solid state but rearrange in solution to form the trans-structure (Figure 25b).

Figure 25b



The σ(N) ⟶ Cu(II) charge transfer absorptions agree with the assignments that have been made for other Cu(II) complexes containing coordinated primary amines.[47,274,275]

ii) Cu(etea)$_2$Cl$_2$ and Cu(etea)$_2$Br$_2$

In dichloromethane, the assignment of apical

X^- → Cu(II) charge transfer absorptions is in agreement with the work of Schugar et al[47] and with the results of the far-infrared spectra. Schugar et al assigned apical X^- → Cu(II) absorptions for the ethylenediamine complexes $[Cu(en)_2X.H_2O]X$ where the apical ligation by X^- has been demonstrated crystallographically.[89,91,97]

The single $\sigma(S) \rightarrow$ Cu(II) charge transfer absorption in the spectrum of $Cu(etea)_2Br_2$ (dichloromethane) is consistent with a trans ligand arrangement.

iii) $[Cu(etea)_2Cl]BF_4$

The apical $Cl^- \rightarrow$ Cu(II) charge transfer absorption (dichloromethane solution) at 281 nm is very close in energy to the same transitions in $[Cu(Me_2NCH_2CH_2NMe_2).2Cl]_2$ (ca 275 nm)[47] $[Cu(en)_2.Cl.H_2O]Cl$ (ca 280 nm)[47] and $Cu(etea)_2Cl_2$ (283 nm, see above). The electronic spectrum is in agreement with the interpretation of the far-infrared spectrum for $[Cu(etea)_2Cl]BF_4$ (see 5.3).

The $\sigma(N) \rightarrow$ Cu(II) and $\sigma(S) \rightarrow$ Cu(II) charge transfer absorptions are consistent with the assignments for the other etea complexes in solution.

2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

i) $Cu(mti)_4(BF_4)_2$

In the reflectance spectrum, the assignment of the absorption of 492 nm as a $\sigma(S) \rightarrow$ Cu(II) charge transfer transition is supported by the disappearance of this absorption in nitromethane, acetone and ethanol solutions. There is also an accompanying colour change as the almost black crystals dissolve to give green/yellow solutions. The infrared spectra (see 5.3) are consistent with all four ligands binding via one of the heterocyclic nitrogen atoms and they also rule out the possibility of strong BF_4^--Cu(II) interactions which could account for the low tetragonal distortion suggested by the ligand field maxima. Strong axial interactions would be achieved by chelating two of the ligands to give the Cu(II) ion a *trans*-N_4S_2 environment.

(ii) $Cu(mti)_4Cl_2$ and $Cu(mti)_4Br_2$

For $Cu(mti)_4Cl_2$ in dichloromethane, the absorption at 287nm is consistent with apical ligation by the chloride ions but for $Cu(mti)_4Br_2$ the low energy $Br^- \longrightarrow Cu(II)$ charge transfer absorption (450nm) implies that the Br —— Cu bonding is non-axial (see Chapter 1). Hence $Cu(mti)_4Cl_2$ probably has a *trans*-tetragonal structure while $Cu(mti)_4Br_2$ may have a distorted *cis*-octahedral structure.

Few assignments of imidazole nitrogen ⟶ Cu(II) charge transfer absorptions have been made in the literature[147] but the assignments presented in Table 27b are in general agreement with the observations of Freedman *et al*[147] and the assignments for $Cu(mmbi)_4(BF_4)_2.2H_2O$ (mmbi=2-methylmercapto-benzimidazole) and $Cu(bi)_4(ClO_4)_2$ (bi=benzimidazole).[148]

From these studies it is apparent that $N_{Im} \rightarrow Cu(II)$ charge transfer absorptions will be found in the range from *ca* 330nm to 385nm in the solid state.

C) ELECTRONIC SPECTRA AT 90K

The only complexes that did not decompose in 20% Glycerol/MeOH were $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$. The spectra and their assignments are presented in Table 27d.

TABLE 27d

ELECTRONIC SPECTRA OF etea COMPLEXES AT 90K

COMPLEX	ABSORPTION	($l.mol.^{-1}cm^{-1}$)	ASSIGNMENT
$Cu(etea)_2Cl_2$	366	1101	$\sigma(S) \longrightarrow Cu(II)$
	650(br)	122	LF
$Cu(etea)_2Br_2$	366	1129	$\sigma(S) \longrightarrow Cu(II)$
	ca 680(br)	138	LF

NOTE:- extinction coefficients are approximate.

There are no absorptions in the visible region that can be assigned as $X^- \longrightarrow$ Cu(II) charge transfer absorptions and this supports the suggestion from other spectroscopic data that the halogens are axially coordinated.

The ligand field maxima are broad and it is not possible to determine whether there are any shoulders on the main absorptions which would support the esr evidence for the existence of trigonal bipyramidal species at these temperatures (see 5.2).

5.2 ELECTRON SPIN RESONANCE SPECTRA

The g and A parameters for the Cu(II) complexes of 2-ethylthioethylamine and 2-methylthio-2-imidazoline are presented in Tables 28a and 28b respectively. All of the spectra were recorded at 77K.

2-ETHYLTHIOETHYLAMINE COMPLEXES

i) $Cu(etea)_2(ClO_4)_2$

In acetone and methanol at 77K, $g_{\parallel}$ and $|A_{\parallel}|$ are consistent with the proposed trans-tetragonal structure for this complex and $Cu(etea)_2(BF_4)_2$ (see 5.1). However, it is probable that the species that give rise to these spectra are either $[Cu(etea)_2]^{2+}$ or a solvated species such as $[Cu(etea)_2(solvent)_2]^{2+}$.

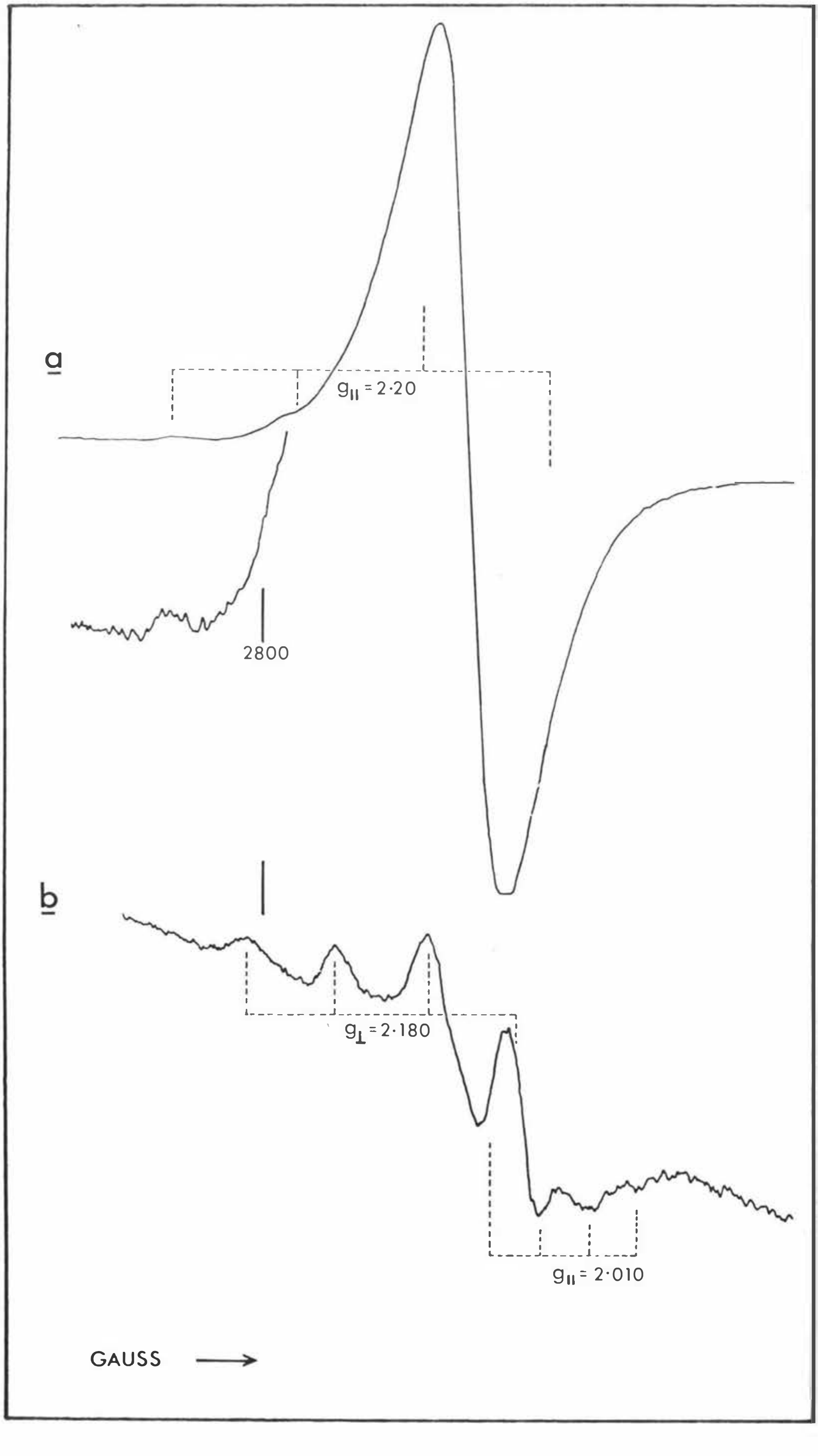
ii) $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$

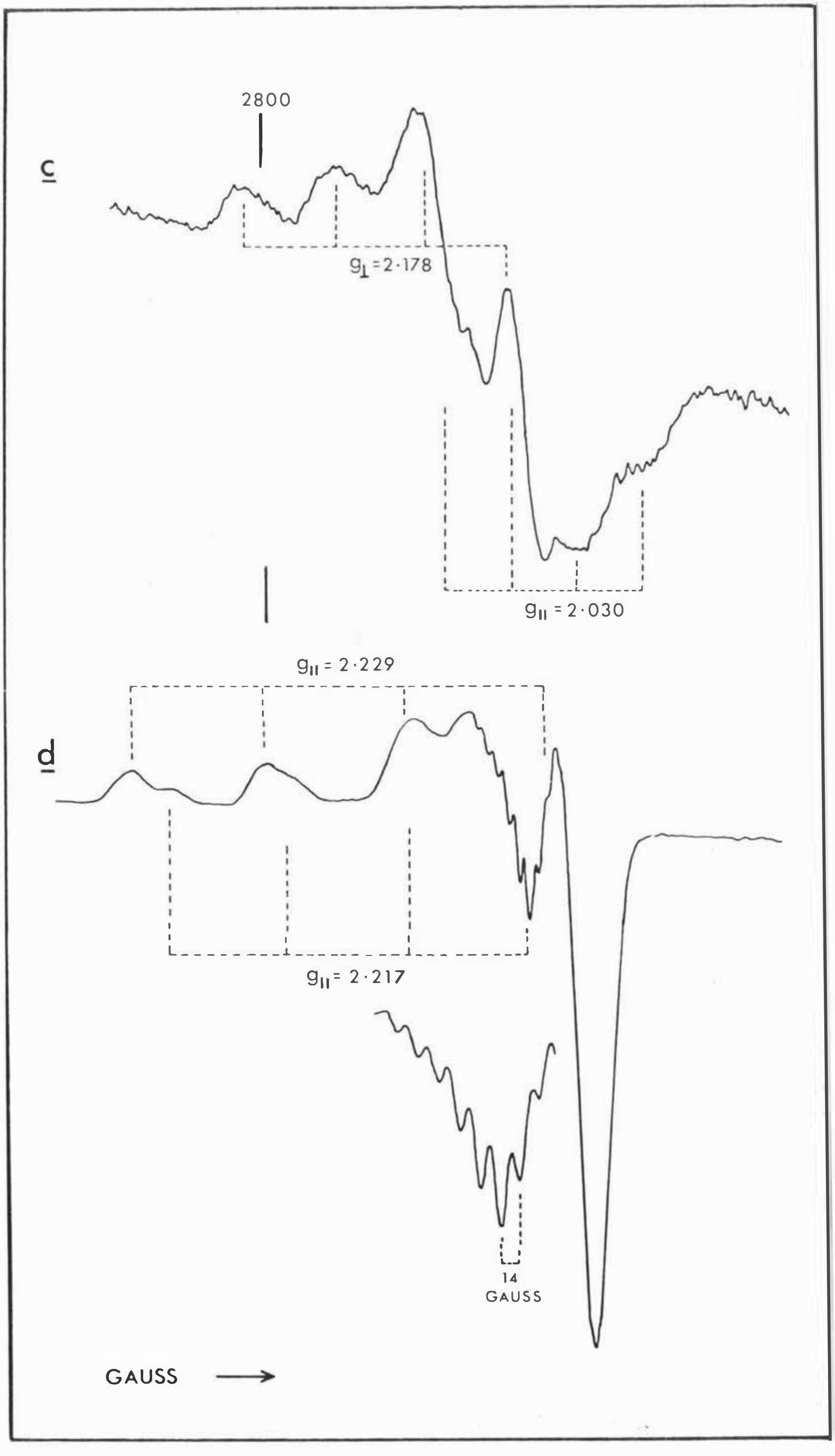
Dichloromethane: The spectrum of $Cu(etea)_2Cl_2$ is in agreement with the proposed trans-tetragonal structure, $|A_{\parallel}|$ having a typical tetragonal value and the spectrum is normal (Figure 26).

Methanol and 20% Glycerol/methanol: The spectra (Figure 26) strongly suggest that these complexes adopt distorted five-coordinate structures (probably trigonal bipyramidal) at 77K. The lowest g value approaches the

FIGURE 26

ESR Spectra - Cu(etea)$_n$X$_2$ Complexes (at 77K)




2800
c
$g_\perp = 2 \cdot 178$
$g_\parallel = 2 \cdot 030$
$g_\parallel = 2 \cdot 229$
d
$g_\parallel = 2 \cdot 217$
14
GAUSS
GAUSS →

Key to Figure 26

a - Cu(etea)$_2$Cl$_2$ in dichloromethane

b - Cu(etea)$_2$Cl$_2$ in 20% Glycerol/MeOH

c - Cu(etea)$_2$Br$_2$ in 20% Glycerol/MeOH

d - Cu(etea)$_2$Br$_2$ (+ excess etea) in methanol

e - [Cu(etea)$_2$Cl]BF$_4$ in nitromethane

f - [Cu(etea)$_2$Cl]BF$_4$ in methanol (2nd species is poorly resolved)

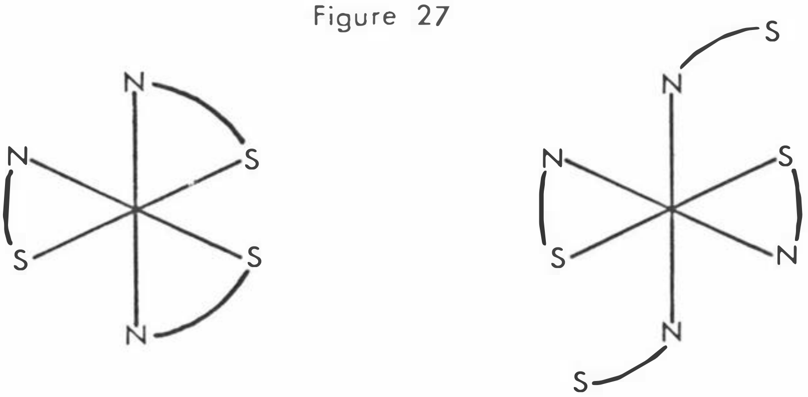
g - Cu(etea)Br$_2$ in methanol

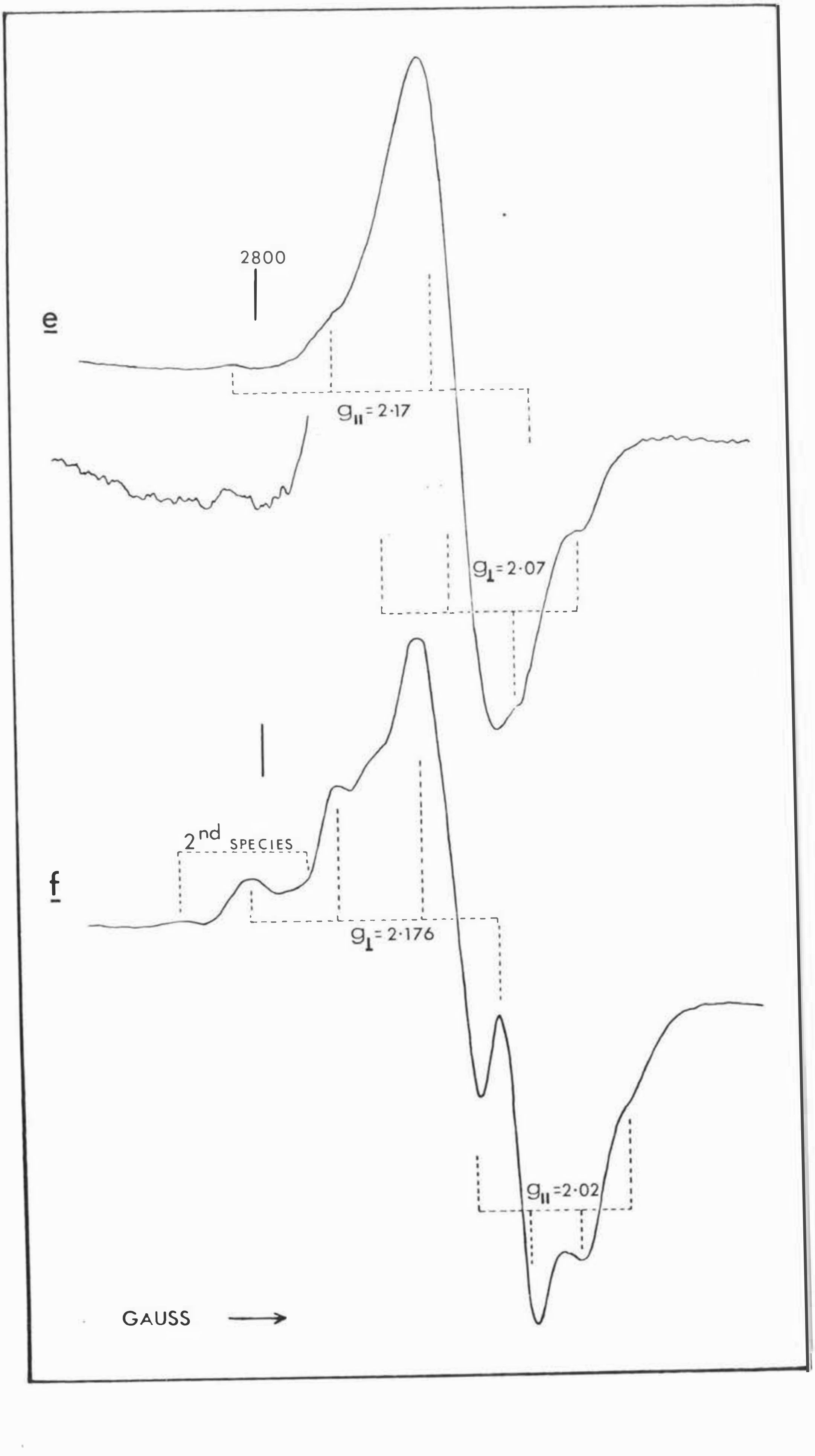
h - Cu(II) in methanol

FIGURE 27

Cu(II) Species Formed in Presence of Excess etea

Figure 27




2800
e
$g_{\parallel} = 2{\cdot}17$
$g_{\perp} = 2{\cdot}07$
f
2nd SPECIES
$g_{\perp} = 2{\cdot}176$
$g_{\parallel} = 2{\cdot}02$
GAUSS →

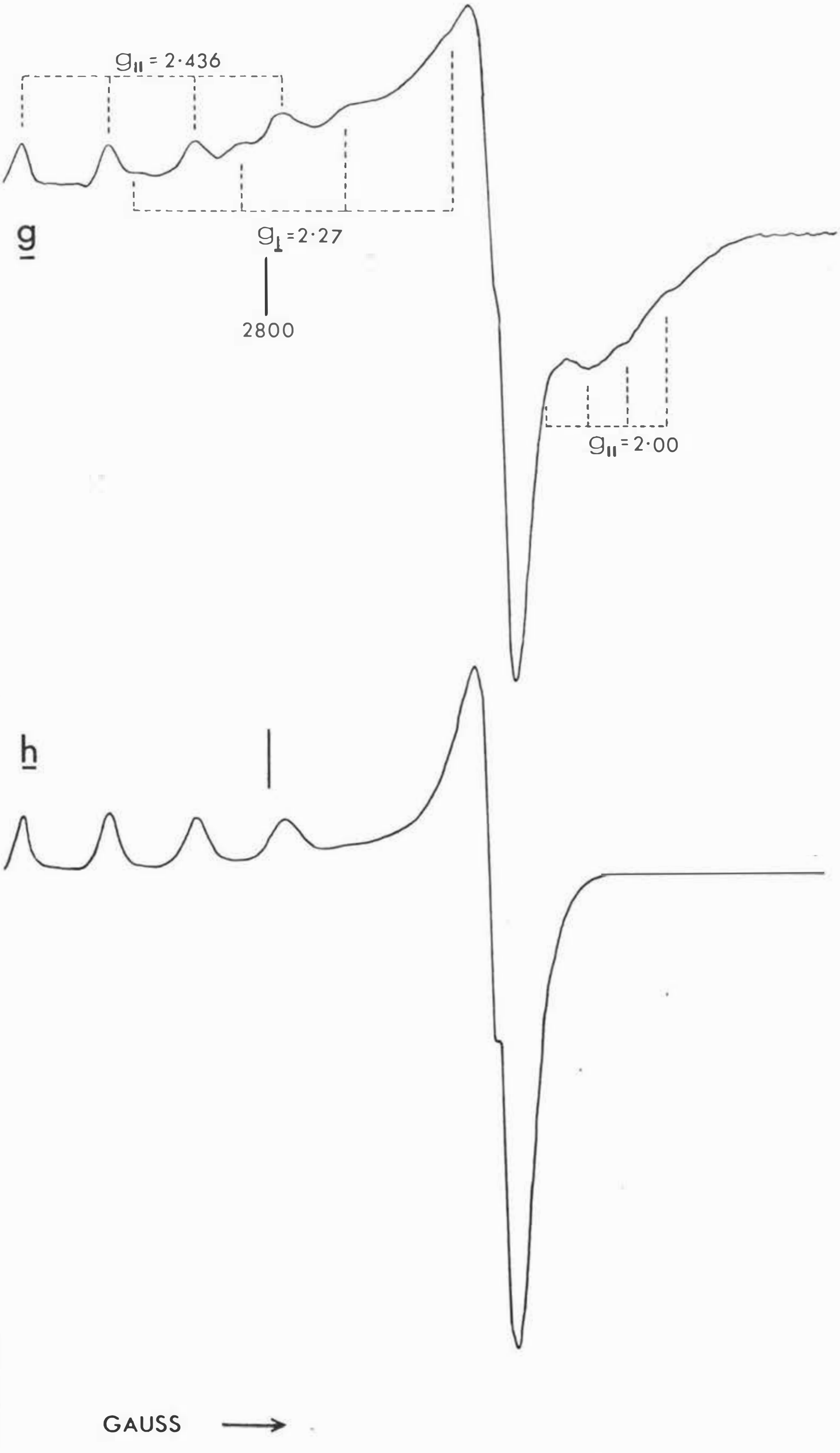

$g_{\parallel} = 2{\cdot}436$
g
$g_{\perp} = 2{\cdot}27$
2800
$g_{\parallel} = 2{\cdot}00$
h
GAUSS

TABLE 28a

ESR SPECTRA, etea COMPLEXES

COMPLEX	SOLVENT	$g_{\parallel}$	$10^4\|A_{\parallel}\|$	$g_{\perp}$	$10^4\|A_{\perp}\|$	g_{iso}
$Cu(etea)_2(ClO_4)_2$	MeOH	2.187	151			
	+ excess I a)	2.220	197			
	b)	2.210	170			
	Acetone	2.169	154			
$Cu(etea)_2Cl_2$	MeOH	*ca*2.02	*ca*71	2.172	122	
	+ excess I a)	2.224	193			
	b)	2.216	170			
	Glyc/MeOH	2.010	65	2.180	127	
	CH_2Cl_2	*ca*2.20	*ca*175			
	CH_3NO_2					2.084
$Cu(etea)_2Br_2$	MeOH	*ca*2.02	*ca*90	*ca*2.18	*ca*114	
	+ excess I a)	2.229	190			
	b)	2.217	166			
	Glyc/MeOH	2.030	83	2.178	127	
$[Cu(etea)_2Cl]BF_4$	MeOH a)	*ca*2.02	*ca*71	2.176	127	
	b)	*ca*2.20	*ca*184			
	+ excess I a)	2.231	193			
	b)	2.206	175			
	CH_3NO_2	*ca*2.17	*ca*142	*ca*2.07	*ca*92	
	Acetone					2.095
	CH_2Cl_2	*ca*2.27	*ca*85	2.095		
$Cu(etea)Cl_2$	MeOH a)	2.430	125			
	b)	2.372	133			
$Cu(etea)Br_2$	MeOH a)	2.436	125			
	b)	*ca*2.00	*ca*47	*ca*2.27	*ca*146	

NOTES: - units of $|A_{\parallel}|$ and $|A_{\perp}|$ are cm^{-1}
- iso = isotropic
- all spectra were recorded at 77K
- Glyc./MeOH = 20% glycerol/methanol

TABLE 28b

ESR SPECTRA, mti COMPLEXES

COMPLEX	SOLVENT	$g_{\parallel}$	$10^4\|A_{\parallel}\|$	$g_{\perp}$	$^{14}N_{shfs}$	g_{iso}
$Cu(mti)_4(BF_4)_2$	Acetone	2.253	184	*ca*2.05		
	CH_3NO_2	2.251	187	*ca*2.03	16($g_{\parallel}$);16($g_{\perp}$)	
	EtOH	2.259	181	2.051	14($g_{\parallel}$);17($g_{\perp}$)	
$Cu(mti)_4Cl_2$	Acetone					2.115
	CH_3NO_2	2.246	186			
	EtOH	2.265	175	*ca*2.05	17($g_{\perp}$)	
	MeOH a)	2.269	178		14-17($g_{\perp}$)	
	b)	2.276	131			
$Cu(mti)_4Br_2$	Acetone	*ca*2.25	*ca*184		16($g_{\perp}$)	
	CH_3NO_2	*ca*2.23	*ca*188			

NOTES: - units of $|A_{\parallel}|$ are cm^{-1},
- iso = isotropic; shfs = superhyperfine splitting
- units of $^{14}N_{shfs}$ are Gauss,
- all spectra were recorded at 77K.
- region in which $^{14}N_{shfs}$ lines are observed is indicated in parentheses.

theoretical value of 2.00 required for trigonal bipyramidal complexes (d_{z^2} ground state) and the |A| values are similar to those normally observed for this type of complex.[64,65,67] Trigonal bipyramidal complexes are also typified by their "reversed" spectra and the spectra of $Cu(etea)_2Cl_2$ and $Cu(etea)_2Br_2$ fulfil this requirement (see Chapter 1).

On the basis of these observations and the 1:1 electrolytic behaviour (Table 31) of the complexes in methanol, the spectra are assigned to the trigonal bipyramidal $[Cu(etea)_2X]^+$ ($X=Cl^-$, Br^-) species.

iii) $[Cu(etea)_2Cl]BF_4$

Dichloromethane and Nitromethane: An intermediate distorted five-coordinate structure is probably responsible for the spectra (Figure 26) although the high field region is not as diffuse as has been reported for other intermediate five-coordinate complexes[64]. Hence the $[Cu(etea)_2Cl]^+$ chromophore may have more tetragonal pyramidal character than trigonal bipyramidal character.

Methanol: Two species are present, the major one probably being trigonal bipyramidal $[Cu(etea)_2Cl]^+$ as its peaks (Figure 26) are superimposable on the spectrum of $Cu(etea)_2Cl_2$ in this solvent. The minor species ($|A| \sim 180$ Gauss) may be tetragonal $[Cu(etea)_2Cl.MeOH]^+$, as the semi-coordinated nature of the BF_4^- anion in the solid state (see 5.4) suggests that the sixth coordination site of $[Cu(etea)_2Cl]^+$ is relatively open and would allow solvation.

iv) $Cu(etea)Cl_2$ and $Cu(etea)Br_2$

In methanol, the major species in the spectrum of each complex corresponds exactly to the major species in the spectra of $CuCl_2.2H_2O$ and $Cu(ClO_4)_2.6H_2O$ under the same conditions (Figure 26). This implies that the polymeric $Cu(etea)X_2$ complexes are being broken up on dissolution, with $Cu(MeCN)_n^{2+}$ (n=4 or 6) being the major contributor to the spectra. Where X is bromide, the minor species that is formed probably has a trigonal bipyramidal geometry as its lowest g value is approximately 2.00 and the hyperfine splitting on the high-field side of the spectrum is very small (ca 47 x 10^{-4} cm^{-1}). The nature of the minor species where X is chloride, is not readily apparent.

v) Addition of Excess Ligand to $Cu(etea)_2X_2$ and $[Cu(etea)_2Cl]BF_4$

In methanol, two species are formed on adding excess ligand to any of the $Cu(etea)_2X_2$ complexes ($X=ClO_4^-$, Cl^-, Br^-) or to $[Cu(etea)_2Cl]BF_4$. The spectra (Figure 26) and the $g_{\parallel}$ and $|A_{\parallel}|$ values, are consistent with both complexes having tetragonal structures. The deep blue solutions are also formed in other solvents. In dichloromethane at room temperature the d-d maximum is at 642nm (ϵ=139) and a $\sigma(S)\longrightarrow Cu(II)$ charge transfer absorption can be assigned at 341nm. A concentration dependent $\sigma(N)\longrightarrow Cu(II)$ charge transfer absorption can be assigned at about 250nm and this assignment is supported by the appearance of ^{14}N superhyperfine lines in the esr spectra (Figure 26).

The two most obvious types of complex that could be formed in the presence of excess ligand are shown in Figure 27 .

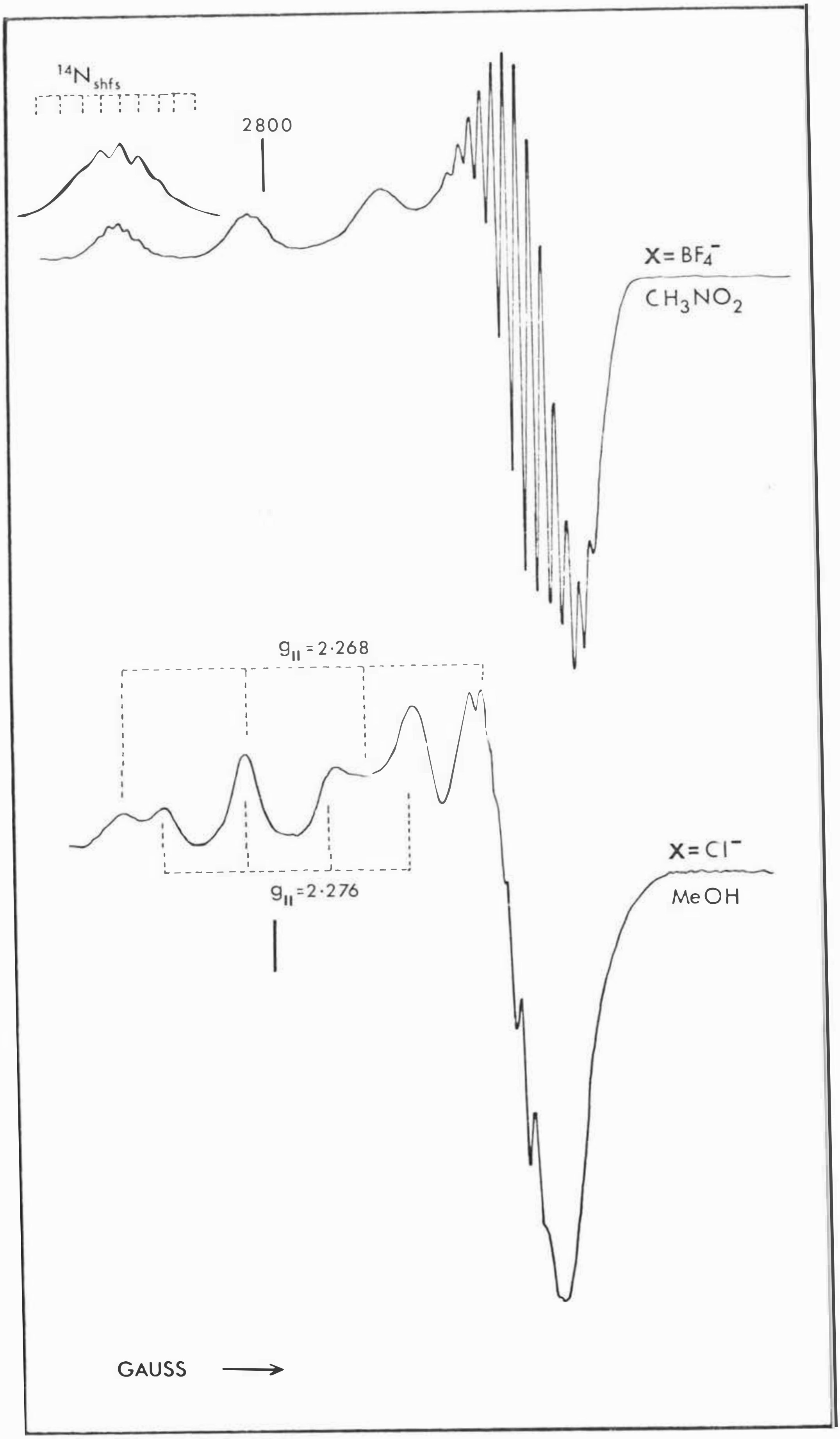
2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

i) $Cu(mti)_4(BF_4)_2$

In acetone, nitromethane and ethanol, $g_{\parallel}$, $g_{\perp}$ and $|A_{\parallel}|$ are normal for square planar CuN_4^{2+} or tetragonal CuN_4X_2

FIGURE 28

ESR Spectra - $Cu(mti)_4X_2$ Complexes (at 77K)



systems involving imidazole and substituted imidazole ligands.[146,149]

Nine ^{14}N superhyperfine lines are observed in the lowest-field copper hyperfine line (Figure 28) in a nitromethane glass. The intensity pattern of these lines is very similar to that which is calculated, in computer simulation studies, for Cu(II) in an environment of four equivalent nitrogens.[150] A similar superhyperfine structure was also reported for $Cu(DMIZ)_4Cl_2$, where DMIZ is 1,2-dimethylimidazole, in an ethylene glycol-H_2O glass.[146]

ii) $\underline{Cu(mti)_4Cl_2}$ and $\underline{Cu(mti)_4Br_2}$

The spectra are generally similar to those of $Cu(mti)_4(BF_4)_2$ although in nitromethane glasses the ^{14}N superhyperfine lines are not observed in $g_{\parallel}$. In the spectrum of $Cu(mti)_4Cl_2$ in methanol, two species of about equal concentration are observed (Figure 28). One of these ($|A_{\parallel}|$ =178 x $10^{-4}cm^{-1}$), is probably trans-tetragonal $Cu(mti)_4Cl_2$. The low $|A_{\parallel}|$ (131 x $10^{-4}cm^{-1}$) of the second species suggests that it may be either a tetragonal pyramidal complex such as $[Cu(mti)_4Cl]^+$ or a tetrahedrally distorted $Cu(mti)_4{}^{2+}$ chromophore.

5.3 FAR-INFRARED SPECTRA

2-ETHYLTHIOETHYLAMINE COMPLEXES

i) $\underline{Cu(etea)_2Cl_2}$ and $\underline{Cu(etea)_2Br_2}$

In an extensive study of a series of CuL_2X_2 complexes (where L is $R_2NCH_2CH_2NR'_2$), Lever and Mantovani[90] reported that the ν(Cu—X) frequencies were below 200cm^{-1} and were outside the range of the spectrometer that they used. On the basis of crystallographic and electronic spectra studies, these complexes have been assigned trans-tetragonal structures. As a general guide then, ν(Cu—X) absorptions will be found below

200cm^{-1} if the Cu(II)--X bonds are axial as in $[Cu(en)_2Cl.H_2O]Cl$ and $[Cu(en)_2Br.H_2O]Br$.[89,91,97]

The absorptions for $Cu(etea)_2Cl_2$ (182, 188cm^{-1}) and $Cu(etea)_2Br_2$ (163cm^{-1}) respectively (Table 29) are consistent with these complexes having trans-tetragonal structures similar to the ethylenediamine complexes. The two absorptions that are observed for $Cu(etea)_2Cl_2$, may be due to the symmetry of this complex being lower than D_{4h}. Only one absorption is expected for this symmetry.[86]

ii) $[Cu(etea)_2Cl]BF_4$

This complex appears to have an axial Cu—Cl bond as the ν(Cu—Cl) absorption frequency (ca 187(br)cm^{-1}) is very similar to the ν(Cu—Cl) frequencies for $Cu(etea)_2Cl_2$ (Table 29).

iii) $Cu(etea)Cl_2$ and $Cu(etea)Br_2$

These complexes have polymeric tetragonal structures similar to those of $Cu(en)X_2$ and $Cu(py)_2X_2$ for which far-infrared data has been reported (Table 13a). The ν(Cu——X) frequencies [$Cu(etea)Cl_2$; 254, 285cm^{-1} and $Cu(etea)Br_2$; 226 cm^{-1}] are also within the ranges [ν(Cu — Cl); 312—208cm^{-1} and ν(Cu-Br); 233— 187cm^{-1}] observed for other tetragonally distorted octahedral Cu(II) complexes.[72]

2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

i) $Cu(mti)_4Cl_2$

The most prominent absorptions (Table 29) occur at 142 and 286cm^{-1} but a satisfactory spectrum, with which comparisons could be made, was not obtained for $Cu(mti)_4Br_2$. The electronic spectrum of $Cu(mti)_4Cl_2$ in dichloromethane suggested that the Cu-Cl bonding is axial (see 5.1) and the far-infrared absorption at 142cm^{-1}, if it is a ν(Cu-Cl) absorption, would

TABLE 29

INFRARED SPECTRA, etea AND mti COMPLEXES

COMPLEX	ν(N-H)	ν(M-X)	ν(C=N)	$\nu_3(ClO_4^-/BF_4^-)$
$Cu(etea)_2(ClO_4)_2$	3317(s),3268(s),3140(w)			1097(s),1052(s)
$Cu(etea)_2(BF_4)_2$	3333(s),3282(s),3147(w)			1052(s),1020(s)
$Cu(etea)_2Cl_2$	3236(s),3210(s),3130(s)	182,189		
$Cu(etea)_2Br_2$	3220(s),3198(s),3113(s)	163		
$Cu(etea)Cl_2$	3277(s),3222(s),3143(s)	254,285		
$Cu(etea)Br_2$	3307(w),3252(m),3200(m),3132(m)	226(sh)		
$[Cu(etea)_2Cl]BF_4$	3342(s),3287(m),3217(s),3132(s)	_ca_ 187(br)		1100(s),1030(s)
$Cu(mti)_4(BF_4)_2$	3392(s)		1525(s)	1050(s),1033(s)
$Cu(mti)_4Cl_2$	3234(m)	142	1547(s)	
$Cu(mti)_4Br_2$	3444(w),3422(w),_ca_ 3247(m-br)		1526(s)	
$Co(mti)_3Cl_2$	_ca_ 3167(br)	310,318	1532(s)	

NOTES:
- all spectra recorded for mulls; frequencies are cm^{-1},
- ν(N-H) for etea: 3367(s-br),3304(s-br) [neat ligand] and 3380(s),3310(m), $CHCl_3$ solution
- ν(N-H) for mti: _ca_ 3093(br) [mull] and 3431(s) [$CHCl_3$ solution],
- ν(C=N) for mti: 1554(s) [mull],
- s = strong; m = medium; w = weak: br = broad,
- ionic ClO_4^- and BF_4^-, ν_3 at _ca_ 1100 cm^{-1}.

be consistent with this structure. The axial chloride ions must be very weakly bound if this assignment is correct, because the absorption is about 40cm^{-1} lower than in trans-tetragonal Cu(etea)$_2$Cl$_2$.

The absorption at 286cm^{-1} is consistent with it being a ν(Cu-N) absorption as these have been assigned in the region from about 242 to 292cm^{-1} in the Cu(II) complexes of 2-substituted imidazoles.[147]

ii) Co(mti)$_3$Cl$_2$

The two ν(Co-Cl) absorptions (310, 318cm^{-1}) that have been tentatively assigned (Table 29) agree with the proposal (5.1) that this complex has a distorted tetrahedral structure. The far-infrared spectra of tetrahedral CoN$_2$Cl$_2$ complexes have been thoroughly characterized.[86,137,142]

5.4 GENERAL INFRARED SPECTRA

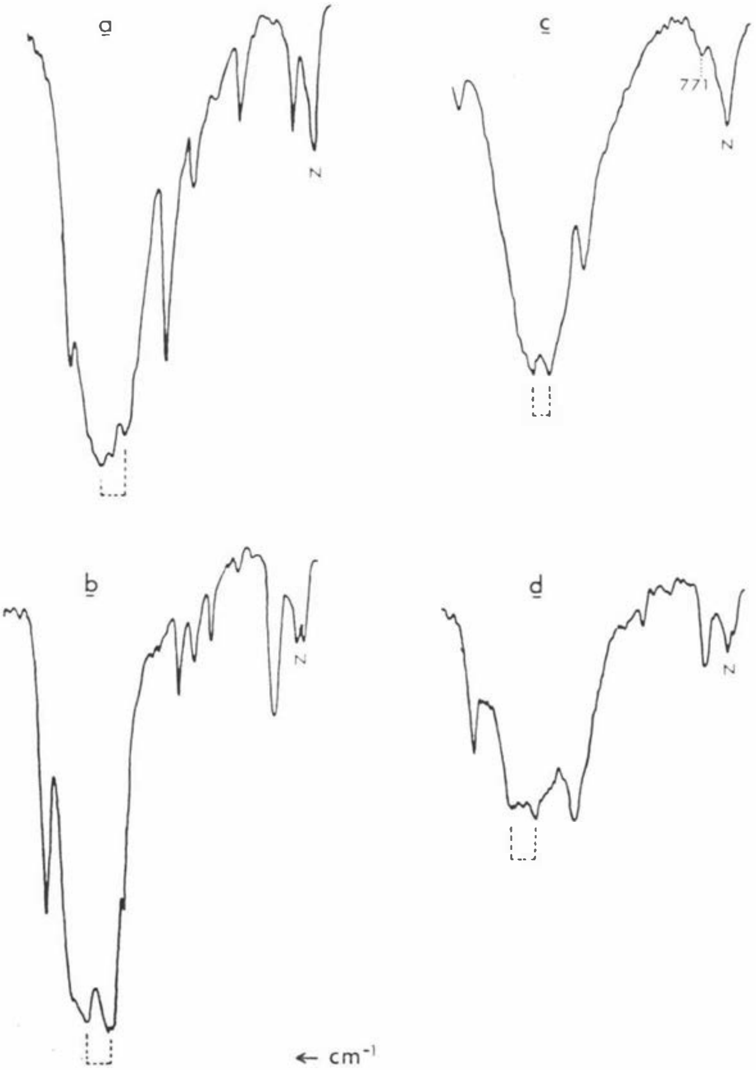
2-ETHYLTHIOETHYLAMINE COMPLEXES

i) Ligand Coordination: In contrast to the [M(CO)$_5$]$_2$etea (M=Cr, W) and M(CO)$_4$etea (M=Cr, Mo, W) complexes (Section II, Chapter 3), the ν(NH) absorptions of the Cu(II) complexes show significant shifts (Table 29) to lower frequencies on coordination. Up to four absorptions are observed, compared to the two absorptions (due to the symmetric and asymmetric ν(NH) vibrations[151]) in the spectra of the free ligand.

ii) Anion Coordination: The weak splitting of the perchlorate and tetrafluoroborate ν_3 modes in the spectra of Cu(etea)$_2$X$_2$ (X=ClO$_4^-$, BF$_4^-$) and [Cu(etea)$_2$Cl]BF$_4$ indicates that these anions are probably participating in weak, axial bonding in a manner analogous to Cu(en)$_2$(ClO$_4$)$_2$[91] and Cu(en)$_2$(BF$_4$)$_2$[91] .

FIGURE 29a

IR Spectra - ClO_4^- and BF_4^- ν_3 Modes



a = $Cu(etea)_2(ClO_4)_2$

b = $Cu(tbmp)_2(ClO_4)_2$

c = $Cu(mti)_4(BF_4)_2$

d = $Cu(tbmp)_2(BF_4)_2$

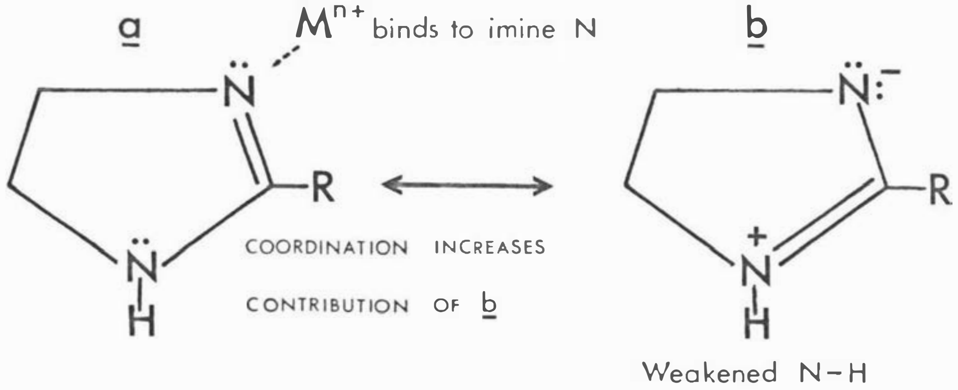
(N = Nujol absorption)

The splitting of the ν_3 mode in the spectra of the etea complexes is not as pronounced as in the spectra of $Cu(tbmp)_2(ClO_4)_2$ and $Cu(tbmp)_2(BF_4)_2$ (Figure 29a) and this suggests that in the latter complexes (Chapter 2), the Cu(II)---anion interactions are significantly stronger.

2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

i) ν(NH) Absorptions: In an early study of some metal complexes of 2-substituted imidazoline ligands (e.g. 2-(2-pyridyl)-2-imidazoline), Freiser et al[152] showed that the ν(NH) frequency decreases on ligand coordination to M^{2+}. Hence although the metal probably binds to the imine nitrogen,[152,153] a consideration of the two resonance structures for the imidazoline ligands, provides a mechanism by which the ν(NH) frequency can be lowered (Figure 29b).

FIGURE 29b



Hydrogen bonding effects in the solid state spectrum of uncomplexed mti, result in a substantial lowering of the ν(NH) absorption frequency compared to the spectrum in chloroform (Table 29). The ν(NH) absorption in the spectra of $Cu(mti)_4X_2$ ($X=BF_4^-$, Cl^-) is relatively sharp and this suggests that Cu(II)-ligand bonding and not hydrogen bonding, is responsible for the decrease in the ν(NH) frequencies on complexation. $Cu(mti)_4Br_2$ and $Co(mti)_3Cl_2$ have relatively broad ν(NH) absorptions. For the former complex, this may be due to its hygroscopic nature while for the latter complex, electronic and far-infrared spectroscopic investigations and conductivity measurements (Table 31) indicate that one of the mti ligands is uncomplexed.

ii) <u>ν(C=N) Absorptions</u>: By analogy with other Cu(II)-imine complexes such as those of the N-(2-thenylidene)alkylamine ligands[122], the ν(C=N) frequency should decrease on complexation to Cu(II) or Co(II). Although for $Cu(mti)_4Cl_2$ the decrease is not very significant (Table 29), the decreases in the spectra of the remaining complexes provide enough evidence to conclude that the ligand is binding via one of the heterocyclic nitrogen atoms. More specifically, it is probably binding via the imine nitrogen.[152,153]

iii) <u>Tetrafluoroborate Coordination in $Cu(mti)_4(BF_4)_2$</u>.

The BF_4^- ν_3 mode is weakly split (Figure 29a) and this may be interpreted as indicating that the anions are weakly coordinating. However, only a very weak absorption is found at about 771cm^{-1} where the ν_1 absorption is expected and this weak absorption is also found in the spectrum of $Cu(mti)_4Cl_2$. Other studies have shown that the ν_1 mode (<u>ca</u> 760cm^{-1}) should be of medium intensity if the BF_4^- anion is semi-coordinated[143,154]. These results suggest that the BF_4^- anions remain uncoordinated in $Cu(mti)_4(BF_4)_2$.

5.5 REACTIVITY STUDIES

These were designed to test the stability of etea and mti towards replacement by pyridine.

i) <u>Addition of Pyridine to $Cu(etea)_2(ClO_4)_2$</u>

<u>In Ethanol</u>: With a 1:1 ratio of pyridine to Cu(II), the electronic spectrum provided no evidence for five-coordinate

adduct formation as the d-d maximum at 585nm remains unchanged.

In Acetone: In the presence of excess pyridine the d-d maximum shifts from 570nm to 595nm and this implies that adduct formation may be taking place.

$$[Cu(etea)_2]^{2+} \xrightarrow{\text{excess py}} [Cu(etea)_2(py)_n]^{2+} \quad (n = 1 \text{ or } 2)$$

In Pyridine: The total replacement of etea from the Cu(II) coordination sphere is achieved on dissolving the perchlorate complex in pyridine. A mauve precipitate which was isolated from this reaction, was characteristic of $Cu(py)_4(ClO_4)_2$; its d-d maximum being at 585nm in the solid state.

NOTE: In ethanol and acetone, the ligand-field absorption of $[Cu(py)_4]^{2+}$ is at 700nm and 645nm respectively.

ii) Addition of pyridine to $Cu(mti)_4(BF_4)_2$

The changes in the energy of the d-d absorption (Abs.EtOH solution) on adding different ratios of pyridine, are shown in Table 30.

TABLE 30

Cu(II):pyridine	d-d maximum/nm
1:0	620 (green/yellow solution
1:1	622
1:2	624
1:4	625
1:large Excess	650 (blue/green solution)

In the presence of a large excess of pyridine, the shift to 650nm suggests that an adduct, such as $[Cu(mti)_4(py)_n]^{2+}$ (n = 1 or 2), is being formed. A green oil was isolated from this reaction, but it could not be crystallized.

iii) Discussion

The results of these experiments are similar to those involving the complexes of tbmp (Chapter 2) where the ligand was shown to be quite stable towards replacement by pyridine.

In the complexes of the chelated N--S ligands tbmp and etea, the presence of coordinated nitrogen appears to confer greater stability to the Cu(II)—S bonding as similar experiments have shown that the displacement of chelated dithioether ligands is readily achieved (see Chapter 2).

5.6 PARAMAGNETIC ^{1}H nmr LINE BROADENING EXPERIMENT

The principles that are involved were discussed in Chapter 2 (see 2.6).

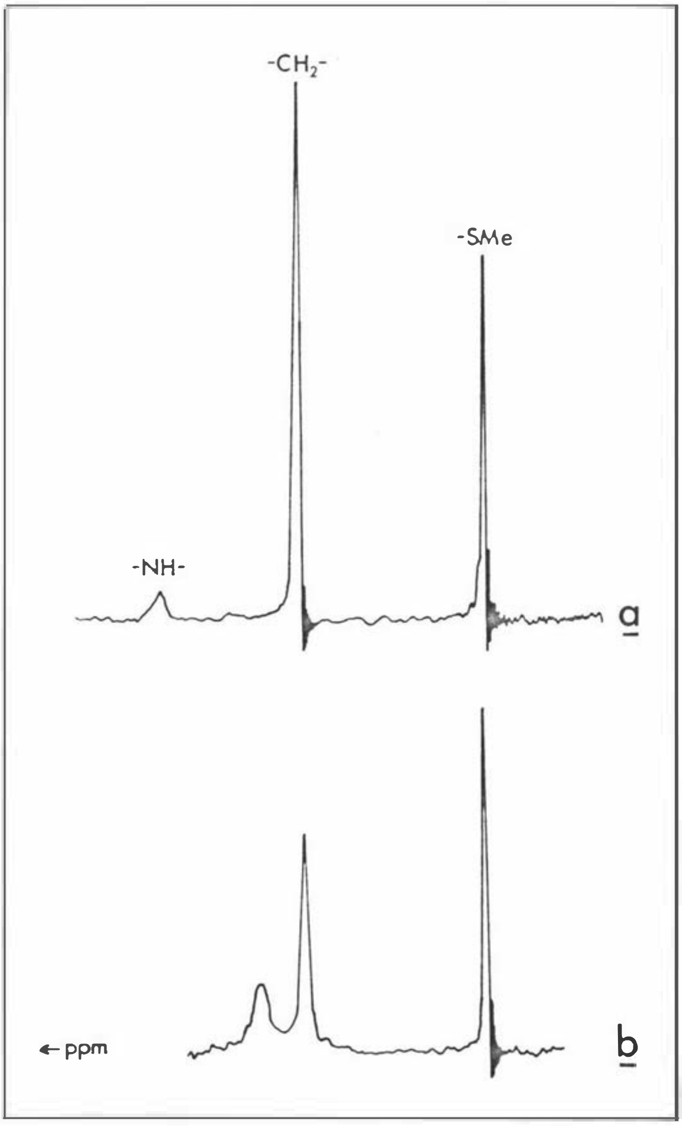
Cu(II) interactions with mti:

In Figure 30, it can be seen that the —NH— resonance increases in intensity with an increase in the concentration of Cu(II) and this implies that there is a decrease in the rate of exchange of the —NH— proton.[155] This resonance also shifts upfield and this may be due to decreasing hydrogen bonding effects in solution.

As there is no significant effect on the resonance of the —SMe protons and there is no broadening of the —NH— resonance, the results can be interpreted as meaning that the Cu(II) ions interact with the imine nitrogen under these conditions. In contrast to the spectra of the $M(CO)_5$mti complexes (M = Cr, Mo, W) (see Section II, Chapter 3), the $—CH_2—$ resonance is not split as a result of the Cu(II)--N interactions. This suggests that the rate of exchange of Cu(II) at the nitrogen binding site is too rapid for the $—CH_2CH_2—$ protons to be "seen" as being inequivalent on the nmr time scale.

FIGURE 30

^{1}H nmr - Addition of Cu(II) to mti (in $CDCl_3$)



a = mti in absence of Cu(II)

b - mti in presence of Cu(II) [8.9 x 10^{-4}mol.l.$^{-1}$]

SYNTHESES

Some general comments that relate to all of these syntheses can be found in the experimental section of the Appendices.

2-ETHYLTHIOETHYLAMINE COMPLEXES

Diperchloratobis(2-ethylthioethylamine)copper(II)

The addition of 1 mmole of $Cu(ClO_4)_2.6H_2O$ (0.370 g.) to a slight excess of ligand (0.220 g.) have an intense, deep blue solution. A purple precipitate appeared when almost all of the Cu(II) had been added.

YIELD: 0.298 g. (64%)

Ditetrafluoroboratobis(2-ethylthioethylamine)copper(II)

$Cu(etea)_2(BF_4)_2$ was isolated from an attempt to synthesize $Cu(etea)_4(BF_4)_2$. 1 mmole of $Cu(BF_4)_2.6H_2O$ (0.345 g.) was added to 4 mmole of the ligand (0.421 g.) to give an intense, deep blue solution. A blue oil was deposited after the solution had been concentrated and ether had been added to it. "Scratching" the oil gave a purple solid which was filtered and washed with Abs.EtOH and then ether.

YIELD: 0.150 g. (34%)

Bis(2-ethylthioethylamine)copper(II)sulphate

This complex was isolated from a qualitative attempt to synthesize $Cu(etea)_nSO_4$ (n= 3 or 4), in which some $CuSO_4.5H_2O$ was dissolved in neat ligand. The dark blue mixture was heated for about 1 minute and then ether was added to precipitate an oil. "Scratching" the oil induced solidification; the blue solid was filtered and then washed with Abs. EtOH and ether.

Dichlorobis(2-ethylthioethylamine)copper(II)

1 mmole of $CuCl_2.2H_2O$ (0.170 g.) was slowly added to an excess of the ligand ($>$ 0.210 g.) and the dark green solution was cooled. The precipitation of the blue complex was induced by "scratching" the flask.

YIELD: 0.200 g. (58%)

Dibromobis(2-ethylthioethylamine)copper(II)

The same procedure as for $Cu(etea)_2Cl_2$ was followed, using 1 mmole of $CuBr_2$ (0.223 g.). Dark green flakes precipitated from the solution after about 1 minute.

YIELD: 0.303 g. (70%)

Dichloro(2-ethylthioethylamine)copper(II)

$Cu(etea)Cl_2$ was prepared by the qualitative addition of etea to an excess of $CuCl_2.2H_2O$ in Abs. EtOH, to give a blue-green precipitate.

Dibromo(2-ethylthioethylamine)copper(II)

1 mmole of the ligand (0.105 g.) was slowly added to an excess of $CuBr_2$ ($>$ 0.223 g.) to give a fine, dark green precipitate. This was filtered off, washed with Abs. EtOH and air-dried.

YIELD: 0.118 g. (36%)

Chlorobis(2-ethylthioethylamine)copper(II)tetrafluoroborate

1 mmole of $Cu(etea)_2(BF_4)_2$ was prepared *in situ* using an excess of etea and the solution was filtered to remove a small quantity of light blue precipitate. Slightly less than 1 mmole of anhydrous LiCl ($<$ 0.042 g.) in Abs. EtOH/acetone was then added to this solution. The total volume at this stage should be about 50-60 cm^3 in order to avoid the precipitation of $Cu(etea)_2(BF_4)_2$ and $Cu(etea)_nCl_2$ (n= 1 or 2).

The resulting light blue solution was concentrated *in vacuo* cooled and "scratched" to induce the precipitation of impure $[Cu(etea)_2Cl]BF_4$. This was recrystallized from a minimum volume of hot Abs. EtOH.

YIELD: 0.104 g. (26%)

The filtrate yielded impure precipitates that contained dark blue $[Cu(etea)_2Cl]BF_4$ and what appeared to be $Cu(etea)Cl_2$ (green) and $Cu(etea)_2(BF_4)_2$ purple.

2-METHYLTHIO-2-IMIDAZOLINE COMPLEXES

N.B. For the preparation of the $Cu(mti)_4X_2$ complexes ($X = BF_4^-$, Cl^-, Br^-), it is essential to have the Cu(II): mti ratio as close to 1:4 as possible, otherwise large quantities of gelatinous precipitates will appear.

Tetrakis(2-methylthio-2-imidazoline)copper(II)tetrafluoroborate

1 mmole of $Cu(BF_4)_2.6H_2O$ (0.345 g.) was slowly added (while filtering) to a warm solution of 4 mmole of mti (0.464 g.)*. The solution was reduced in volume to about 1-2 cm^3 than set aside at 4°C. Large clumps of black crystals grew and these were filtered off and washed with Abs. EtOH and then sodium-dried ether.

YIELD: 0.361 g. (51%)

* It may be necessary to filter the brown-black solution at this point, to remove a dark green gelatinous precipitate.

NOTES: - forced precipitation with ether gave a complex that analysed as $Cu(mti)_4(BF_4)_2.xH_2O$ ($x = 1$ or 2),

- the crystals of $Cu(mti)_4BF_4)_2$ decompose over a period of several months.

Dichlorotetrakis(2-methylthio-2-imidazoline)copper(II)

As for $Cu(mti)_4(BF_4)_2$, the complex should be allowed to crystallize slowly from a concentrated solution.

The slow addition of 1 mmole of $CuCl_2.2H_2O$ (0.170 g.) to 4 mmole of mti (0.464 g.) gave a green-black solution that had to be filtered in order to remove a small quantity of a gold-coloured precipitate. The solution was reduced in volume and cooled for a prolonged period to yield the blue, hygroscopic complex.

An ether-forced precipitation gave a yield of 14%.

Dibromotetrakis(2-methylthio-2-imidazoline)copper(II)

1 mmole of $CuBr_2$ (0.223 g.) was slowly added to 4 mmole of mti (0.464 g.) and the green-black solution was filtered in order to remove a gelatinous precipitate. The solution was then concentrated *in vacuo* and cooled for 2 days before the large clumps of black crystals (that are blue when they are broken open) that resulted were filtered and washed with a minimum of cold Abs. EtOH.

YIELD: 0.266 g. (39%)

Dichlorotris(2-methylthio-2-imidazoline)cobalt(II)

$Co(mti)_3Cl_2$ was isolated from an attempt to synthesize $Co(mti)_4Cl_2$. A solution of 1 mmole of $CoCl_2.6H_2O$ (0.238 g.) (plus triethylorthoformate) was added to 4 mmole of mti (0.464 g.) to give a deep blue solution. This was concentrated and navy blue crystals were grown at 4°C. These were filtered and washed with a minimum volume of Abs. EtOH.

YIELD: 0.188 g. (39%)

TABLE 31

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/% C	H	N	Other	CONDUCTIVITY/ohm^{-1}mol^{-1}cm^{2} CH_3NO_2	MeCN	Other
$Cu(etea)_2(ClO_4)_2$	purple	-	20.76 (20.64)	4.79 (4.93)		Cl,15.32 (15.14)	127		
$Cu(etea)_2(BF_4)_2$	purple	175-177	21.47 (21.59)	4.95 (5.23)	6.26 (6.31)		150		
$Cu(etea)_2SO_4$	blue/green	178-180	26.69 (26.31)	6.16 (6.13)	7.78 (7.31)		Insol.		
$Cu(etea)_2Cl_2$	blue/green	114-116	27.86 (27.96)	6.43 (6.68)	8.13 (8.00)		21	109	EtOH: 24
$Cu(etea)_2Br_2$	d.green	115-118	22.15 (22.36)	5.11 (5.24)	6.46 (6.21)		39	116	
$Cu(etea)Cl_2$	blue/green	122-123	20.05 (20.32)	4.63 (4.76)		Cl,29.59 (29.25)	13		
$Cu(etea)Br_2$	d.green	109-111	14.62 (14.41)	3.37 (3.54)	4.26 (4.33)				
$[Cu(etea)_2Cl]BF_4$	blue	114-116	24.25 (23.73)	5.60 (5.53)	7.07 (6.78)		76	136	
$Cu(mti)_4(BF_4)_2$	black	119-121	27.38 (27.19)	4.59 (4.84)	15.97 (15.49)		177		ØNO_2: 51
$Cu(mti)_4Cl_2$	blue	114-116	32.07 (32.52)	5.38 (5.60)	18.70 (18.71)		64	144	Ac.: 20
$Cu(mti)_4Br_2$	black	101-103	27.92 (28.27)	4.69 (5.06)	16.29 (16.46)		90	144	Ac.: 36
$Co(mti)_3Cl_2$	navy blue	138-140	30.12 (30.01)	5.06 (5.49)	17.57 (17.75)		31	119	

NOTES: - molar conductivities at 25°C :

	1:1	2:1
Nitromethane	(70-90),	(150-170)
Methanol	(100-130),	(210-250)
Nitrobenzene	(20-30),	(45-55)
Acetone	(100-130)	
Ethanol	(60-80)	

- d = dark; Ac. = acetone

CHAPTER 6

COPPER COMPLEXES OF 2-(3,3-DIMETHYL-2-THIABUTYL)QUINOLINE(tbmq) AND 3-(2-METHYLTHIOPHENYLIMINO)CAMPHOR(I)

2-(3,3-dimethyl-2-thiabutyl)quinoline: $Cu(tbmq)Cl_2$ and $Cu(tbmq)Br_2$ were the only Cu(II) complexes that were isolated pure, even where the reactions involved a two-fold excess of the ligand. The electronic, far-infrared and electron spin resonance spectra are consistent with both complexes having flattened tetrahedral structures. In the reactions with $Cu(ClO_4)_2.6H_2O$, only very small quantities of an impure Cu(II) complex were isolated, as the solutions decompose to give a Cu(I) complex.

The Cu(I) complexes, Cu(tbmq)Br, $Cu(tbmqH)Br_2$ and $Cu(tbmq)_2ClO_4$ are also briefly discussed in this Chapter.

3-(2-methylthiophenylimino)camphor: This ligand is very susceptible to Cu(II) catalysed hydrolysis in protic solvents (e.g. EtOH) where a coordinating anion such as Cl^- is present. Consequently the only complexes that could be isolated, from a reaction in acetone, were $CuI(ClO_4)_2$.acetone.xH_2O (x = 0 or 2). The electronic spectra of these complexes suggest that they probably have flattened tetrahedral structures.

6.1 ELECTRONIC SPECTRA

The tentative assignments for the Cu(II) complexes of these ligands are presented in Table 32.

2-(3,3-DIMETHYL-2-THIABUTYL)QUINOLINE COMPLEXES.

Cu(II) COMPLEXES

i) Ligand Field Transitions

The two low energy, ligand field maxima in the reflectance spectra of Cu(tbmq)Cl_2 (850, 1200 nm) and Cu(tbmq)Br_2 (850, 1462 nm) (Figure 31), are typical of distorted tetrahedral Cu(II) complexes[43] such as the well characterized bis(N-alkylsalicylaldiminato)copper(II) (R = isopropyl, t-butyl),[156] Cu(dmaep)X_2 (dmaep = 2-(N,N-dimethylamino)ethylpyridine)[39] and Cu(β-isosparteine)X_2[96] systems.

On dissolution in dichloromethane, the ligand field maxima move to higher energies and this is an indication that the complexes are not as distorted in solution.[43] The assignment of flattened, tetrahedral structures to Cu(tbmq)Cl_2 and Cu(tbmq)Br_2 is consistent with both the electronic and electron spin resonance spectral data.

ii) Charge Transfer Transitions

There is some uncertainty as to the assignment of the $\sigma(S) \longrightarrow Cu(II)$ charge transfer transitions in these complexes because of the nearby $X^- \longrightarrow Cu(II)$ absorptions. However, the assignment of the low energy $Br^- \longrightarrow Cu(II)$ absorptions is consistent with the observations that have been reported for distorted tetrahedral Cu(II) complexes containing coordinated bromide ions.[59,157] The low intensity $Br^- \longrightarrow Cu(II)$ charge transfer absorption at 592 nm (ϵ = 564 $l.mol^{-1}\ cm^{-1}$)

FIGURE 31

Electronic Spectra - Cu(tbmq)X_2 Complexes (Reflectance)

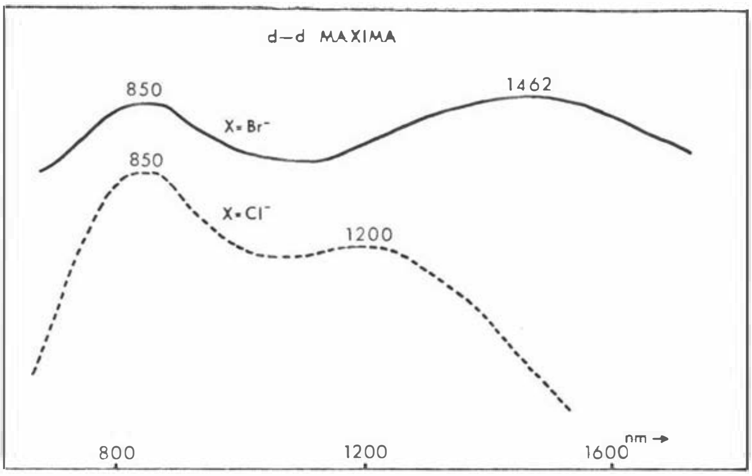


TABLE 32

ELECTRONIC SPECTRA, tbmq AND I COMPLEXES

COMPLEX	REFLECTANCE	ASSIGNMENT	$CH_2Cl_2(\epsilon)$	ASSIGNMENT	ACETONE(ϵ)	ASSIGNMENT
Cu(tbmq)Cl_2	ca395(sh)	$\sigma(S) \rightarrow Cu(II)$	395(2190)	$\sigma(S) \rightarrow Cu(II)$		
	ca410(sh)	$Cl^- \rightarrow Cu(II)$	ca435(sh)	$Cl^- \rightarrow Cu(II)$		
	540	$\pi(S) \rightarrow Cu(II)$				
	850	LF	ca800(sh)	LF		
	1200	LF	1075(201)	LF		
Cu(tbmq)Br_2			ca362(sh)	$\sigma(S) \rightarrow Cu(II)$		
	495	$Br^- \rightarrow Cu(II)$	ca450(sh)	$Br^- \rightarrow Cu(II)$		
	615	$Br^- \rightarrow Cu(II)$	592(564)	$Br^- \rightarrow Cu(II)$		
	850	LF	770(269)	LF		
	1462	LF	1150(298)	LF		
ϕ CuI$(ClO_4)_2$.ac.			ca395(1075)	$\sigma(S) \rightarrow Cu(II)$	ca390(1666)	$\sigma(S) \rightarrow Cu(II)$
	755	LF	760(150)	LF	ca620(sh)	LF
	1300	LF	†		1200(102)	LF

NOTES: - sh = shoulder; LF = Ligand Field; all maxima are in nm.
- extinction coefficients are $l.mol.^{-1}cm^{-1}$
ϕ solutions contained triethylorthoformate
† poorly resolved, weak shoulder on low energy side of 760 nm. maximum.
- ac. = acetone.

in dichloromethane may be a "forbidden" transition[157] and similar absorptions have been recognised as $Br^- \longrightarrow Cu(II)$ charge transfer maxima by other workers.[47,82] The blue-shift that is exhibited by the $Br^- \longrightarrow Cu(II)$ absorptions in dichloromethane is also good evidence for Cu(tbmq)Br_2 being less distorted in solution. Blue-shifts are expected as the $Cu(II) \longrightarrow Br$ bonds become more "in-plane". [43,59,157]

The assignment of the absorption at 540 nm for Cu(tbmq)Cl_2 (reflectance), is in agreement with the assignments made by Schugar et al, for $\pi(S) \longrightarrow Cu(II)$ charge transfer transitions.[47] This absorption (540 nm) is too high in energy to be a ligand field component of a distorted tetrahedral complex[157] and it appears to be too low in energy to be a $Cl^- \longrightarrow Cu(II)$ absorption. Even in tetrahedral $CuCl_4{}^{2-}$, the charge transfer absorptions are observed only as low as about 455 nm.[158]

Cu(I) COMPLEXES

Although an interpretable reflectance spectrum could not be obtained for Cu(tbmqH)Br_2, the spectrum of $Cu(tbmq)_2$-ClO_4 shows a distinct absorption at 378 nm and a lower intensity shoulder at about 475 nm. In methanol the former absorption shifts to 360 nm and the latter absorption disappears. The Cu(I) complexes of tbmp and $tbmpH^+$ (see Chapter 3) also showed maxima at about 365 ± 10 nm and these were tentatively assigned as being $Cu(I) \longrightarrow S$ charge transfer transitions.

By analogy with the Cu(I) complexes of 1,10-phenanthroline (λ_{max} = 435 nm)[159] and 2,9-dimethyl-1,10-phenanthroline (λ_{max} = 454 nm),[160] the shoulder at about 475 nm is probably a charge transfer transition from the Cu(I) d-orbitals to the ligand's empty π^*-orbitals.[161]

3-(2-METHYLTHIOPHENYLIMINO)CAMPHOR

In both the solid state and in solution, the CuI^{2+} chromophore appears to have a flattened tetrahedral structure similar to that of the bis(N-alkylsalicylaldiminato)-copper(II) complexes, where that substituent is isopropyl or t-butyl,[156] and the complexes of related substituted camphorquinone ligands.[162,163] The blue-shift of the ligand field maxima in acetone (Table 32) suggests that the complex is less distorted towards a tetrahedral geometry than it is in the solid state, as observed for the Cu(tbmq)X_2 (X = Cl^-, Br^-) complexes that were discussed above.

In acetone and dichloromethane, thioether binding is apparent, but this region (ca 390 nm) is poorly resolved in the reflectance spectrum.

6.2 ELECTRON SPIN RESONANCE SPECTRA

The g and A parameters for these complexes are presented in Table 33a. All of the spectra were recorded at 77K.

i) 2-(3,3-DIMETHYL-2-THIABUTYL)QUINOLINE COMPLEXES

Acetone: The spectra of Cu(tbmq)Cl_2 ($g_{\parallel}$ = 2.412, $g_{\perp}$ = 2.108; $|A_{\parallel}|$ = 143 x 10^{-4}cm^{-1}) and Cu(tbmq)Br_2 ($g_{\parallel} \sim$ 2.412, $g_{\perp}$ = 2.116; $|A_{\parallel}| \sim$ 135 x 10^{-4}cm^{-1}) are consistent with the complexes having flattened tetrahedral structures. The relatively high $g_{\parallel}$ values suggest that the Cu(II)-ligand bonding in these complexes is less covalent[60] than in other distorted tetrahedral systems (Table 33b and this may be a result of steric effects imposed by the ligand.

TABLE 33a

ESR SPECTRA, tbmq AND L COMPLEXES

COMPLEX	SOLVENT	$g_{\parallel}$	$10^4\lvert A_{\parallel}\rvert$	$g_{\parallel}/\lvert A_{\parallel}\rvert$	$g_{\perp}$	$10^4\lvert A_{\perp}\rvert$
$Cu(tbmq)Cl_2$	Acetone	2.412	143	169	2.108	
	$CHCl_3$	2.264	164	138		
	† CH_2Cl_2				2.140	
$Cu(tbmq)Br_2$	Acetone	*ca*2.41	*ca*135	179	2.116	
	$CHCl_3$	*ca*2.40	*ca*144	169	2.115	
$CuL(ClO_4)_2.ac.$	Acetone a)	2.412	141	171		
	b)	2.352	157	150		
	+ TEOF a)	2.414	135	179		
	b)	*ca*2.35	*ca*159	*ca*148		
	Φ CH_3NO_2 a)	2.381	133	179		
	b)	2.342	142	165		
	Φ CH_2Cl_2 a)	2.426	120	202		
	b)	*ca*2.01	*ca*94		2.194	82
	Φ MeCN	2.427	124		2.095	

NOTES: † isotropic spectrum; (g_{iso} = 2.140),

Φ these solutions contained triethylorthoformate (TEOF),

- all spectra recorded at 77K.
- units of $A_{\parallel}$ and $A_{\perp}$ are cm^{-1},
- units of $g_{\parallel}/\lvert A_{\parallel}\rvert$ are cm.

TABLE 33b

ESR SPECTRA, DISTORTED T_d Cu(II) COMPLEXES

COMPLEX	$g_{\parallel}$	$10^4\lvert A_{\parallel}\rvert$	$g_{\parallel}/\lvert A_{\parallel}\rvert$	$g_{\perp}$	REFERENCE
$Cu(N\text{-}t\text{-}butyl\text{-}sal)_2$	2.270	145	157	2.068	61
$Cu(N\text{-}s\text{-}butyl\text{-}sal)_2$	2.253	156	144	2.055	61
CuL^1Cl_2	2.303	127	181	2.085	162
$CuL^1(BF_4)_2$	2.299	139	165	2.073	162
$Cu(dmaep)Cl_2$	2.305	98	235	2.118 2.057	39
$Cu(dmaep)Br_2$	2.371	59	402	2.116	39
$Cu(sparteine)Cl_2$	2.299	85	270	2.075	157
$Cu(thioacetamide)_4^{2+}$	2.152	87	247		164
Cu:tmtd	2.125	93	228	2.021 2.051	165
$Cu(SPR_2NPR_2S)_2$	2.107	119	177	2.030	166

NOTES: - Cu:tmtd = Cu(II) doped tetramethylthiouramdisulphide

- units of $\lvert A_{\parallel}\rvert$ and $g_{\parallel}/\lvert A_{\parallel}\rvert$ are cm^{-1} and cm. resp.

The ratio $g_{\parallel}/|A_{\parallel}|$ has been suggested by Addison and Sakaguchi,[60] to be a possible guide in estimating the degree of distortion towards a tetrahedral geometry in four-coordinate Cu(II) complexes. For example, the distorted tetrahedral complexes $Cu(dmaep)Cl_2$[39] and $Cu(sparteine)Cl_2$,[95] have $g_{\parallel}/|A_{\parallel}|$ ratios of 236 cm and 270 cm respectively, while for square planar complexes, the ratio lies in the range from about 105 to 135 cm.[60] The ratios for $Cu(tbmq)Cl_2$ (169 cm) and $Cu(tbmq)Br_2$ (179 cm) lie at values that are consistent with the complexes being flattened tetrahedra.

Chloroform: The spectra (Table 33a) indicate that the complexes are less distorted towards tetrahedral geometries in this solvent, the $g_{\parallel}/|A_{\parallel}|$ ratios being 138 cm ($X=Cl^-$) and 169 cm ($X=Br^-$).

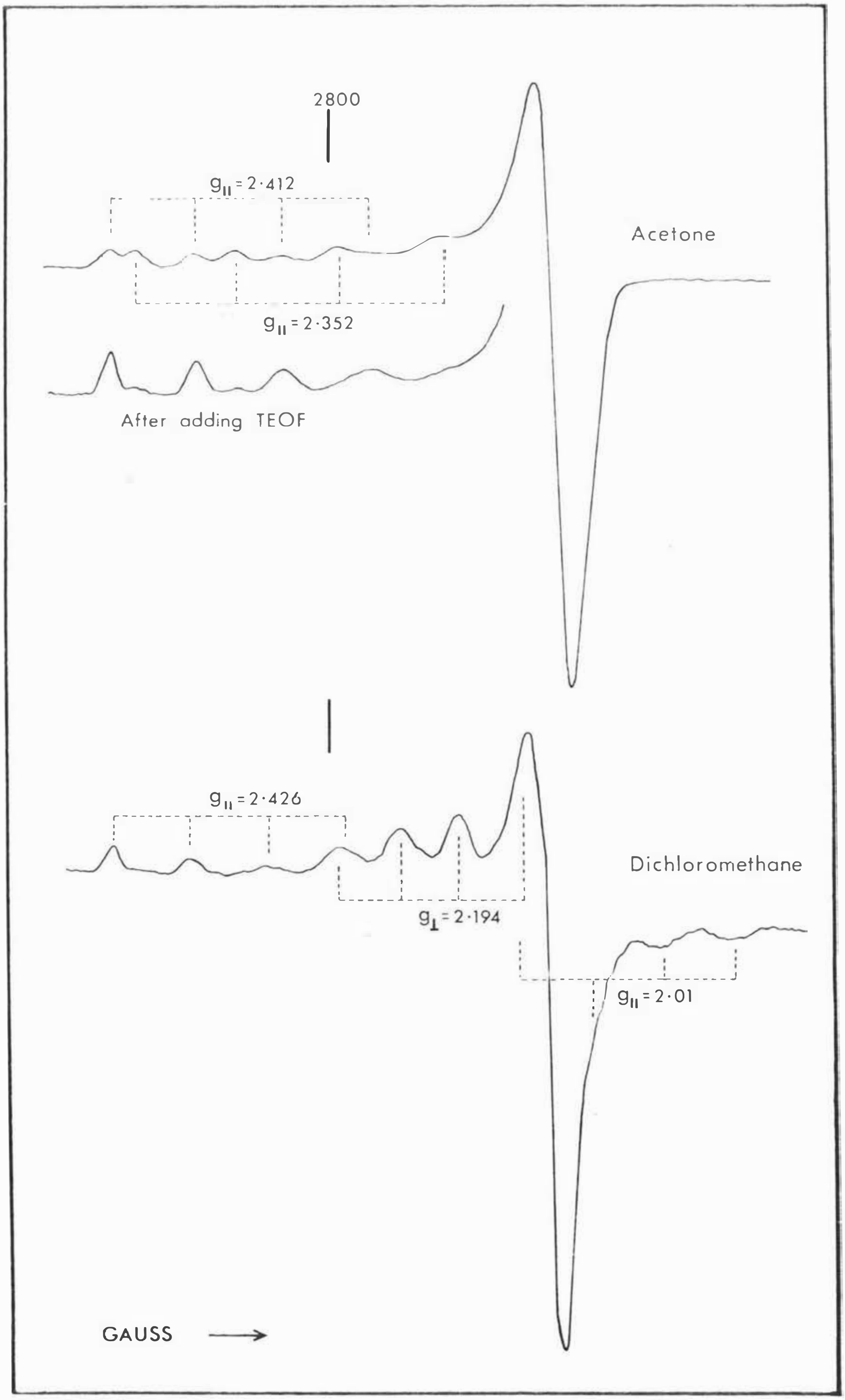
ii) 3-(2-METHYLTHIOPHENYLIMINO)CAMPHOR COMPLEXES

Acetone: Two species are present in the glasses of the $CuI(ClO_4)_2$ complexes. At least one of these species contains coordinated water and this is demonstrated by its almost complete disappearance (Figure 32) in the presence of the drying reagent, triethylorthoformate (TEOF). The $g_{\parallel}$ and $|A_{\parallel}|$ values of both species are consistent with them having flattened tetrahedral geometries, similar to those that have been proposed for other Cu(II) complexes (Table 33b) of this type.[162]

Nitromethane: Two distorted tetrahedral species are observed as in acetone, except that the presence of TECF has no effect on their relative concentrations. This suggests that one of the complexes contains coordinated CH_3NO_2, perhaps being a $[CuI(CH_3NO_2)]^{2+}$ species.

FIGURE 32

ESR Spectra - CuI(ClO$_4$)$_2$ at 77K



Dichloromethane: Even in the presence of TEOF, two species are evident in the spectra (Figure 32). The "reversal" of the spectrum at high-field ($g \approx 2.007$, $|A| \approx 94 \times 10^{-4}\,cm^{-1}$) implies that one of the species has a trigonal bipyramidal structure. Complexes such as $[CuL(ClO_4).H_2O]^+$ or $[CuL(ClO_4)_2]$ may have this type of structure. The second complex in these spectra probably has a distorted tetrahedral structure.

Methanol-TEOF: Direct evidence for the instability of this Cu(II)-ligand system in polar solvents is provided the esr spectrum, which is identical to that of Cu(II) in methanol.

Discussion: It is not very clear from these results as to what the fourth ligand is, in the distorted tetrahedral species. In order to achieve a four-coordinate geometry, the complexes of this tridentate ligand have a choice of perchlorate ions, water or solvent molecules (if a ligating solvent is used), as potential ligands.

6.3 INFRARED SPECTRA

2-(3,3-DIMETHYL-2-THIABUTYL)QUINOLINE COMPLEXES

i) Far-Infrared: Although at least two $\nu(Cu—X)$ absorptions are expected for tetrahedral Cu(II) complexes,[167] only one could be assigned in each spectrum. For $Cu(tbmq)Cl_2$, a $\nu(Cu—Cl)$ absorption is assigned at 268 cm^{-1} and for $Cu(tbmq)Br_2$, a $\nu(Cu—Br)$ absorption is assigned at 230 cm^{-1}. Both assignments are consistent with the spectra that have been reported for other distorted tetrahedral Cu(II) complexes such as the $Cu(sparteine)X_2$[157] and $Cu(isosparteine)Cl_2$[96] systems.

A satisfactory spectrum was not obtained for the Cu(I) complex, Cu(tbmq)Br.

ii) General Infrared: Four ring stretching modes are normally observed for 2-substituted quinoline ligands in the region from 1700 to 1500 cm^{-1} [98] but very little is known about the effects of metal ion coordination on these absorptions.[98]

Cu(II) and Cu(I) Complexes: The spectra (Table 34a) show that there is generally little change in the ring stretching frequencies (1700-1500 cm^{-1}) of tbmq upon complexation. Only three absorptions are observed.

TABLE 34a

INFRARED SPECTRA - tbmq COMPLEXES (1700-1500 cm^{-1})

COMPLEX	SPECTRUM (cm^{-1}, Nujol Mull)
tbmq	1613(w), 1601(s), 1560(m)
Cu(tbmq)Cl_2	1619(w), 1604(m), 1565(w)
Cu(tbmq)Br_2	1610(w), 1602(m), 1563(w)
$Cu(tbmq)_2ClO_4$	1615(m), 1594(s), 1560(m)
Cu(tbmq)Br	1620(m), 1601(s), 1562(m)
Cu(tbmqH)Br_2	1617(w), 1597(s), 1560(w) [also 1640(w)]

iii) Cu(I) Complexes, General Infrared: The ν_3 mode of the perchlorate anion in the spectrum of $Cu(tbmq)_2ClO_4$, is quite sharp (1084 cm^{-1}) and this shows that the anion is not coordinated (see Chapter 2).

In contrast to $[Cu(tbmpH)Cl_2]_2$ and $[Cu(tbmpH)Br_2]_2$ (see Chapter 2), the spectra of Cu(tbmqH)Br_2 in Nujol Mulls do not show any broad absorptions that can be readily assigned as $\nu(N^+—H)$ modes.

3-(2-METHYLTHIOPHENYLIMINO)CAMPHOR COMPLEXES

The hygroscopic Cu(II) complexes have almost identical infrared spectra (Nujol Mulls), both showing broad ν(CH) absorptions.

TABLE 34b

INFRARED SPECTRA OF $CuL(ClO_4)_2$.acetone.xH_2O

Complex	$\nu(C=O)^{\phi}/cm^{-1}$	$\nu(C=N)^{\phi}$	$\nu_3(ClO_4^-)$	$\nu_1(ClO_4^-)$
Ligand	1743(s)	1672(ms)		
$CuL(ClO_4)_2$.acetone.$2H_2O$	1702(m)	1633(m)	1100(vs),1052(vs)	928(w)
$CuL(ClO_4)_2$.acetone	1701(m)	1627(m)	1106(vs),1071(vs)	936(w)

ϕ Assignments are in agreement with Reference 168 .

The ν(C=O) absorption, which also has a higher frequency shoulder, will also have an acetone ν(C=O) absorption component as this is expected to be in the same region,[151] depending on hydrogen bonding and other interference effects. The relative sharpness of the absorption in these spectra suggests that the ketone oxygen of the ligand may be bound to Cu(II).

Unambiguous shifts in the ν(C=N) absorption are apparent and this is good evidence for the involvement of the imine nitrogen in the Cu(II) coordination sphere.

The perchlorate ν_3 modes are broad and weakly split and the appearance of the ν_1 mode implies that at least one of the perchlorate anions in each complex may be weakly bound.

6.4 PARAMAGNETIC ^{1}H nmr LINE BROADENING EXPERIMENT

Cu(II) interactions with 3-(2-methylthiophenylimino)-camphor

When Cu(II) is added to a $CDCl_3$ solution of the ligand, the —SMe resonance absorption is significantly broadened (Figure 33) and this is good evidence for the existence of Cu(II)—thioether interactions under these hydrophobic conditions.

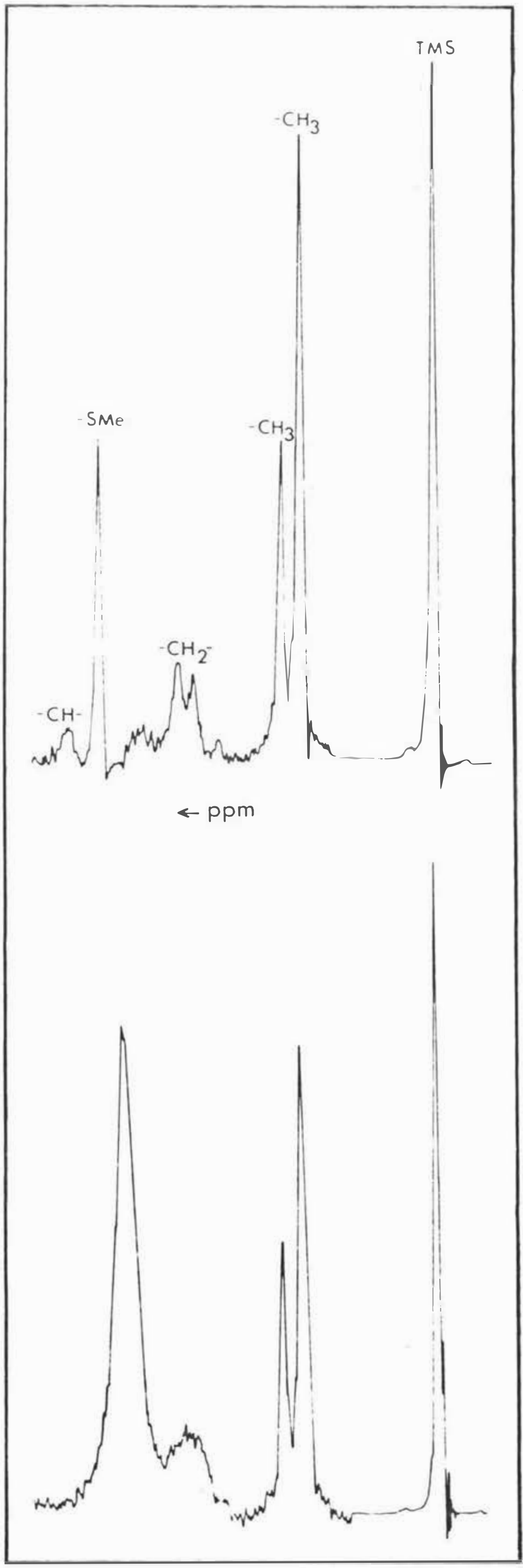


FIGURE 33

^1H nmr - Addition of Cu(II) to I

(in $CDCl_3$)

- in absence of Cu(II)

- in presence of Cu(II)

[8.9 x 10^{-4} mol.l.$^{-1}$]

SYNTHESES

For the synthesis of the tbmq complexes, the general method is described elsewhere in this thesis (see Appendices).

Dichloro[2-(3,3-dimethyl-2-thiabutyl)quinoline]copper(II)

In an attempt to synthesize Cu(tbmq)$_2$Cl$_2$, 1 mmole of CuCl$_2$.2H$_2$O (0.170 g.) was added to 2 mmole of ligand to give a brown-green solution. The light brown complex that precipitated from this solution gave analyses corresponding to Cu(tbmq)Cl$_2$.

YIELD: 0.175 g. (48%)

Dibromo[2-(3,3-dimethyl-2-thiabutyl)quinoline]copper(II)

There was no change in the solution of 1 mmole of CuBr$_2$(0.223 g.) as the ligand (1 mmole, 0.231 g.) was added. When all of the ligand had been added a black precipitate appeared. The mixture was left to stand for about 30 minutes and then it was filtered.

YIELD: 0.176 g. (39%)

Bromo[2-(3,3-dimethyl-2-thiabutyl)quinoline]copper(I)

1 mmole of ligand (0.231 g.) was slowly added to 1 mmole of anhydrous CuBr (0.143 g.), that had been dissolved in the presence of excess LiBr. This resulted in the deposition of yellow crystals.

YIELD: 0.194 g. (52%)

Bis[2-(3,3-dimethyl-2-thiabutyl)quinoline]copper(I)perchlorate

The addition of 1 mmole of Cu(ClO$_4$)$_2$.6H$_2$O (0.370 g.) to 2 mmole of ligand (0.462 g.) gave a green solution which gradually turned brown while it was being filtered. The solution was concentrated in vacuo and cooled to give a brown-black oil. This was solidified (brown solid) by prolonged "scratching" with a spatula. Clumps of brownish crystals were grown from an Abs. EtOH solution of the brown solid.

NOTE: The rate of reduction of the green solution depends on the age of the ligand. If freshly precipitated ligand is used, the green solution will persist for several hours. Attempts were made to isolate the pure Cu(II) complex, but the green solids that were obtained, were impure.

Bromo[2-(3,3-dimethyl-2-thiabutyl)quinoline hydrobromide] copper(I)

Hypophosphorous acid (ca 5 drops) was added to 1 mmole of Cu(thmq)Br_2 suspended in warm methanol. When the dissolution of the Cu(II) complex was complete, a yellow-gold complex precipitated out. This was filtered and washed with MeOH.

YIELD: 0.094 g. (25%)

Complexes of 3-(2-methylthiophenylimino)camphor

Two Cu(II) complexes were isolated from acetone using $Cu(ClO_4)_2.6H_2O$ as the Cu(II) source. However, if $CuCl_2.2H_2O$ is used (in Abs. EtOH) hydrolysis of the ligand occurs.

Syntheses: An acetone solution (plus TEOF) of $Cu(ClO_4)_2.6H_2O$ (1.5 mmole, 0.556 g.) was added while filtering, to a filtered acetone solution of the ligand. The solvent was removed (in vacuo) from the black solution to leave a black oil. The solidification of the oil was induced by thoroughly drying it in vacuo and then adding dry ether and working the residue with a spatula. A dark green hygroscopic solid [$CuL(ClO_4)_2$.acetone.$2H_2O$] was isolated in this way. If TEOF is added to the ether, a darker, almost brown hygroscopic solid [$CuL(ClO_4)_2$.acetone] is isolated. Both complexes revert to the oil if they are washed with acetone.

YIELDS: $CuL(ClO_4)_2$.acetone.$2H_2O$: 0.219 g.

$CuL(ClO_4)_2$.acetone : 0.060 g.

TABLE 35

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/%				CONDUCTIVITY/$ohm^{-1}mol^{-1}cm^2$	
			C	H	N	Other	CH_3NO_2	MeCN
$Cu(tbmq)Cl_2$	l.brown	110-112	45.97 (46.02)	4.68 (4.61)	3.83 (4.02)	Cl, 19.38 (19.10)	8	64
$Cu(tbmq)Br_2$	black	99-101	36.98 (37.12)	3.77 (3.70)	3.08 (3.35)	Br, 35.15 (35.44)	11	75
ϕ Cu(tbmq)Br	yellow	198-200	44.86 (44.58)	4.57 (4.44)	3.74 (3.88)			
$Cu(tbmqH)Br_2$	gold	98-99	36.89 (36.90)	3.67 (3.98)	3.21 (3.07)			
$Cu(tbmq)_2ClO_4$	or./brown	-	53.75 (53.38)	5.48 (5.67)	4.48 (4.54)		81	85 ϕNO_2: 27
$CuL(ClO_4)_2.Ac.2H_2O$	d.green	-	37.30 (37.80)	4.85 (4.56)	2.18 (2.29)			
$CuL(ClO_4)_2.Ac.$	br./green	-	39.51 (39.22)	4.48 (4.57)	2.30 (2.44)			

NOTES: - molar conductivities at 25°C : Nitromethane 1:1 (70-90)
Methanol (100-130)
Nitrobenzene (20-30)

- l = light; or. = orange: d = dark; br. = brown; Ac. = acetone.

ϕ in chloroform, apparent M.W. = 660 g. Calc. for monomer and dimer, 375 g. and 750 g. resp.

CHAPTER 7

PLATINUM(II) AND PALLADIUM(II) COMPLEXES
OF
1,2-BIS(PENTAFLUOROPHENYLTHIO)ETHANE
AND A PLATINUM(II) COMPLEX
OF
ETHYLTHIOPENTAFLUOROBENZENE

Although ethylthiopentafluorobenzene (C_6F_5SEt) forms the very unstable complexes $M(CO)_5C_6F_5SEt$ (M=Cr,W) (see Section (II), 1,2-bis(pentafluorophenylthio)ethane (fpte) is quite unreactive towards the Group VIB metal carbonyls, Cu(II) and Ni(II). The reactions of these ligands with Pt(II) and Pd(II) were thus investigated and as a consequence, the complexes cis-MCl_2fpte (M=Pt(II), Pd(II)) and trans-$PtCl_2(C_6F_5SEt)_2$ have been characterized by far-infrared and electronic spectroscopy.

There have been at least three recent investigations on related ligands where highly electronegative perfluoroalkyl or perfluoroaryl substituents are adjacent to the sulphur donor(s). As a result, crystallographic and/or nmr data is available for Pt(II) complexes of the pentafluorothiophenolate anion[169,170] and the ligands $CF_3SCH_2CH_2SCF_3$, $MeSCF_2CH_2SMe$ and $CF_3SCHMeCH_2SCF_3$.[171] The electronic and far-infrared spectral properties (where appropriate) of these compounds, have not been investigated.

7.1 FAR-INFRARED SPECTRA

i) cis-MCl_2fpte (M=Pt(II),Pd(II)

The spectra of $PtCl_2$fpte and $PdCl_2$fpte are quite similar (Figure 34) except for the strong, tentatively assigned, ν(M--Cl) absorption in each spectrum (Table 36). In the absence of the spectra for the analogous MBr_2fpte complexes, the second ν(M--Cl) band that is expected for each spectrum,[172] has not been identified.

ii) trans-$PtCl_2(C_6F_5SEt)_2$

The assignment of a cis structure to $PtCl_2(C_6F_5SEt)_2$ can be ruled out on the basis of the dissimilarity between the Pt--Cl stretching frequencies of this complex and $PtCl_2$fpte. Ligands of similar donor abilities are expected, on the basis of the trans-effect,[172] to give rise to similar ν(M--X) frequencies for their cis-MX_2L_2 complexes.

In Table 36 , the ν(M--Cl) data for the cis and trans complexes are compared with the data for other thioether—M(II) (M=Pt, Pd) complexes.

TABLE 36

FAR INFRARED SPECTRA; Pt(II),Pd(II) THIOETHER COMPLEXES

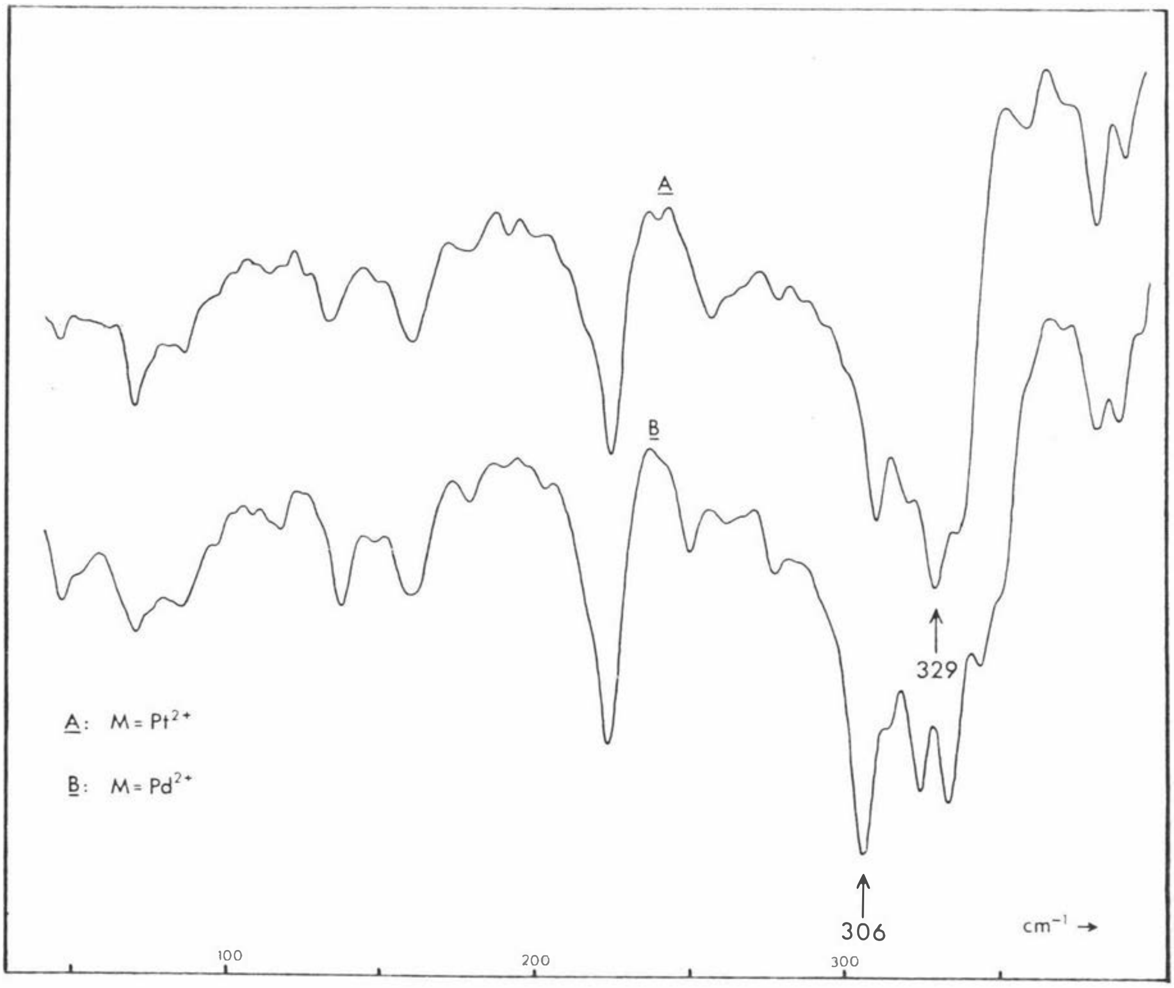
cis-COMPLEXES	ν(M-Cl)	REF.	trans-COMPLEXES	ν(Pt-Cl)	REF.
$PtCl_2(Me_2S)_2$	342,330	173	$PtCl_2(Me_2S)_2$	344	173
$PtCl_2(Et_2S)_2$	330,318	172	$PtCl_2(Et_2S)_2$	343	175
$PtCl_2(PhSC_3H_6SPh)$	317,312	174	$PtCl_2$(dpd)	346	176
$PtCl_2$fpte	329	This Work	$PtCl_2(C_6F_5SEt)_2$	342	This Work
$PdCl_2(PhSC_2H_4SPh)$	277	174	$PtCl_2(pms)_2$	341	177
$PdCl_2(PhSC_3H_6SPh)$	278,262	174			
$PdCl_2$fpte	306	This Work			

NOTES: - dpd = 1,12-bis(phenylthio)dodecane

- pms = phenylmethylsulphide
- ν(M-Cl) frequencies are in cm^{-1}

FIGURE 34

Far-IR Spectra - cis-MCl$_2$fpte Complexes



- the ν(M-Cl) absorptions are shown.

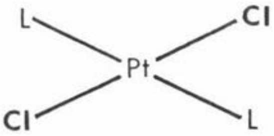
DISCUSSION

cis-Complexes: The apparent increase in the M-Cl stretching frequencies for $PtCl_2$fpte and $PdCl_2$fpte, when they are compared with the analogous complexes of the $PhS(CH_2)_nSPh$ ligands (n=2,3), is consistent with the general observation that as ligand electronegativities increase, the M-Cl stretching frequencies also increase.[172]

The cause of this effect is discussed in 7.4.

trans-Complexes: In their study of a wide variety of trans-PtX_2L_2 complexes, Adams et al[172] noted that ν(Pt-X) remains relatively constant compared to the variations that are observed for the corresponding cis complexes. For $PtCl_2(C_6F_5SEt)_2$ then, ν(Pt-Cl) is not inconsistent with this complex having a trans structure.

Figure 35



Proposed trans-structure.

L = C_6F_5SEt

7.2 ELECTRONIC SPECTRA

The outstanding features in the electronic spectra (340-740 nm) of both the cis $C_6F_5SCH_2CH_2SC_6F_5$ and trans C_6F_5SEt complexes, are the red-shifts of the ligand field maxima (Table 37). These shifts imply that the net ligand field strengths at Pt(II) and Pd(II) are lower than in the complexes of the other thioether ligands.[178-181]

The most probable explanation for the lower ligand field strengths of fpte and C_6F_5SEt, is the inductive electronegativity effect of the pentafluorophenyl substituents on the sulphur donor atoms (see 7.4). Molecular model studies tend to rule out the possibility that steric

TABLE 37

ELECTRONIC SPECTRA, Pt(II) AND Pd(II) COMPLEXES

cis-COMPLEXES	$d_{xy} \rightarrow d_{x^2-y^2}$[182]	SOLVENT	REFERENCE	*trans*-COMPLEXES	ABSORPTION	SOLVENT	REFERENCE
$PtCl_2$(dmedt)	365	DMSO	183	$PtCl_2$(dpd)	325,351 294,357	CH_2Cl_2 Refl.	176
$PtCl_2$(dnxdt)	372	DMSO	183	$PtCl_2(pms)_2$	394,427	Null	177
$PtCl_2$(dbedt)	375	DMSO	183	$PtCl_2(C_6F_5SEt)_2$	*ca*405,*ca*490 *ca*417,*ca*500	Acetone Refl.	This work
$PtCl_2$(fpte)	397(223) 398	Acetone Refl.	This work				
$PdCl_2$(dmedt)	388	Acetone	183				
$PdCl_2$(dmmnt)	389	Acetone	183				
$PdCl_2$(dnxdt)	392	Acetone	183				
$PdCl_2$(SN)	392	Acetone	184				
$PdCl_2$(fpte)	422(1077) 417	Acetone Refl.	This work				

NOTES: - all complexes are MS_2Cl_2 chromophores,

- maxima are nm.; extinction coefficients are in parentheses,
- shoulders are indicated by prefix *ca*,
- for $PtCl_2(pms)_2$, maxima assigned as Singlet $d_{xy} \rightarrow d_{x^2-y^2}$ (394 nm.) and Triplet $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (427 nm.)[177] Assignments probably analogous for other *trans*-complexes.

effects are responsible for the differences in the spectra.

7.3 PHOTOELECTRON SPECTRA OF fpte, bmtt, bett and m-bmtb

The U.V. photoelectron spectra* were measured for bmtt, bett, m-bmtb (see Section (II)) and fpte in an attempt to rationalize the apparent basicity differences between dithioethers such as bmtt, bett and m-bmtb, and the ligands that are the subject of this Chapter. However, the photoelectron spectrum of C_6F_5SEt could not be measured as it appeared to damage the instrument's detector.

RESULTS

For thioether ligands such as R_2S (R=Me,Et etc), the highest occupied molecular orbital is largely localised on the sulphur atom and is perpendicular to the molecular plane[186]. However, where a ligand contains two RS-groups (as in bmtt, bett, m-bmtb, fpte), the highest occupied molecular orbitals on both sulphurs are coupled to form a symmetric (n_s) and an antisymmetric combination.

bmtt, bett and m-bmtb: The antisymmetric combination interacts with the aryl π-orbital to give rise to IP1 and IP4 (Table 38). IP2 is largely due to the n_s combination and the orbital is localised on the sulphur atoms, while IP3 is derived mainly from the aryl π-orbital. IP5, which has more bonding character than IP2, arises from the "other" lone pair orbital on each sulphur (n_σ).

fpte: Only three bands were observed for this ligand. The first band is probably analogous to either IP1 or IP2 that were observed for the other thioether ligands.

---

* The spectra were measured and analysed by Dr. Michael Weiner.[185]

TABLE 38

IONISATION POTENTIALS (eV) FOR DITHIOETHER LIGANDS

LIGAND	IP1	IP2	IP3	IP4	IP5
bmtt	7.85	8.43	9.11	9.93	10.70
bett	7.78	8.28	9.01	9.79	10.45
m-bmtb	8.09	8.34	9.66	10.23	10.99
p-bmtb*	7.93	8.80		9.28	10.10
fpte	9.07		9.70(br)		11.65

NOTES:
- * See Reference 187 .
- br = broad
- IP2 and IP5 are essentially lone pair orbitals, localised on sulphur.

DISCUSSION:

In considering bmtt and bett, the inductive effects of the R=Me and R=Et substituents parallel the observations for Me_2S and Et_2S [188] . That is, the ionisation potentials of the sulphur lone pair electrons (IP2 and IP5) decrease in going from R=Me to R=Et. When $C_6F_5SCH_2CH_2SC_6F_5$ is compared with the other dithioether ligands in Table 38, the ionisation potentials indicate that there are significant electronegativity effects on the energy of the sulphur lone pair orbitals. This is shown by the IP5 data, which suggests that the lone pair electrons are more tightly held than in the other dithioether ligands containing aryl substituents. Similar electronegativity effects have been reported for thioether ligands such as $(CH_3)(CH_2Cl)S$ [186] and for phosphine ligands such as PF_3, [189] the latter ligand having a significantly reduced σ-donor capacity compared to other substituted phosphine ligands.[189]

7.4 ANALYSIS OF THE ELECTRONEGATIVITY EFFECTS

In addition to the relatively high ionisation potentials of the sulphur lone pair electrons of fpte (see above), the effects of the electronegative pentafluorophenyl substituents are also reflected in the low pK_a of pentafluorothiophenol (pK_a=2.68) compared to thiophenol (pK_a=6.43).[170] The net result of these effects is that S--M σ-interactions are weakened. This is apparent in the red shifts of the ligand field maxima in the electronic spectra of the Pt(II) and Pd(II) complexes (see 7.2) and these effects may also help to explain why stable complexes are not formed in the reactions of these ligands with Cu(II), Ni(II) and the zero-valent Group VIB metals (M(O)=Cr, Mo, W).

The weakening of S—M(II) interactions (M=Pt,Pd) also explains why the M(II)—Cl stretching frequencies of the cis-MCl_2fpte complexes are higher than in the complexes of the related $PhS(CH_2)_nSPh$ (n=2,3) ligands (Table 36). As fewer electrons are placed in the M(II) molecular orbitals trans to the coordinated chloride ligands, the M(II)--Cl bonds are strengthened by an inductive mechanism.[172]

Conclusions: The spectral investigations into the properties of these Pt(II) and Pd(II) complexes and the chemical studies into the "reactions" of fpte and C_6F_5SEt with other transition metals (see above and Appendices to Sections I and II) tend to suggest that M--S π-backbonding is a relatively minor contributor to the net strength of

M-thioether interactions. Support for this conclusion comes from the results of crystallographic investigations into the Pt(II) complexes of $CF_3SCHMeCH_2SCF_3$[171] and $(CF_3)_2PCH_2CH_2PPh_2$.[190] In the latter complex, there is a substantial shortening of the Pt--$P(CF_3)_2$ bond, but in the former complex, Pt--thioether π-interactions do not appear to be very significant.

SYNTHESES

cis-Dichloro[1,2-bis(pentafluorophenylthio)ethane]-platinum(II)

1 mmole of $Pt(PhCN)_2Cl_2$ (0.472 g.) (see Reference 292) was added to a filtered toluene solution of 1 mmole of fpte (0.426 g.) and the mixture was refluxed for 20 minutes. A yellow precipitate appeared during the dissolution of the $Pt(PhCN)_2Cl_2$ and this was filtered off while the mixture was hot, washed with ether and dried *in vacuo*. The toluene filtrate was refluxed for a further 20 minutes to give a second crop of the yellow complex.

YIELD: 0.445 g. (64%)

cis-Dichloro[1,2-bis(pentafluorophenylthio)ethane]-palladium(II)

A methanol solution of 1 mmole of Na_2PdCl_4 (0.294 g.) was added to a suspension of 1 mmole of the ligand (0.426 g.) in methanol and the mixture was heated to dissolve the ligand. During the heating, an orange precipitate appeared. This was filtered off and then washed thoroughly with $MeOH/H_2O$, MeOH and ether respectively. A further quantity was isolated from the first MeOH filtrate, after it had been cooled.

YIELD: 0.283 g. (47%)

trans-Dichlorobis(ethylthiopentafluorobenzene)platinum(II)

Excess ligand ($>$ 0.228 g.) was added to a hot filtered solution of $Pt(PhCN)_2Cl_2$ (0.5 mmole, 0.236 g.) in toluene. After 45 minutes of refluxing, the yellow solution was filtered, concentrated (*in vacuo*) to about 1-2 cm^3 and then cooled to yield an orange crystalline product. The orange, diethylether-soluble complex was washed with petroleum ether after filtering and then recrystallized from toluene.

YIELD: 0.174 g. (48%) - before
recrystallization.

TABLE 39

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/%			
			C	H	Halogen	S
ϕ $PtCl_2(fpte)$	Yellow	>230	24.29 (25.11)	0.58 (1.23)	10.24 (10.30)	
$PdCl_2(fpte)$	Orange	>230	27.85 (27.77)	0.67 (1.11)	11.75 (11.63)	10.62 (13.04)
$PtCl_2(C_6F_5SEt)_2$	Orange	135-140	26.60 (27.64)	1.39 (1.87)	9.81 (9.80)	

ϕ although the complex was recrystallized from acetone and washed with hot toluene, the C and H analyses did not improve.

APPENDIX I

i) LIGAND SYNTHESES

2-(3,3-dimethyl-2-thiabutyl)pyridine (tbmp)

Sodium (0.4 mole, 9.196 g.) was dissolved in about 300 cm^3 of Abs.EtOH and the resulting solution was cooled. 2-picolyl chloride hydrochloride (0.2 mole, 32.808 g.) and then t-butyl thiol (0.2 mole, 18.038 g.) were added to this solution. Refluxing the solution (under N_2) caused the rapid precipitation of a large quantity of NaCl after about 30 minutes. This caused the solution to start bumping violently. After the mixture had been left to stand overnight, it was filtered and distilled water was added to precipitate a brown oil. This was extracted into ether. The ether extracts were dried with anhydrous $MgSO_4$ and filtered. After the removal of the solvent (*in vacuo*), the dark brown oil was distilled to yield the colourless ligand.

YIELD: 27.535 g. (76%)

2-(3,3-dimethyl-2-thiabutyl)quinoline (tbmq)

After sodium (0.140 mole, 3.220 g.) had been dissolved in cold Abs.EtOH, 2-(chloromethyl)quinoline hydrochloride (0.070 mole, 14.987 g.) was added to the solution. The slow addition of t-butyl thiol (0.070 mole, 6.313 g.), while agitating the flask, helped the 2-(chloromethyl)quinoline to dissolve and NaCl was deposited. The resulting suspension was refluxed for 15 minutes, cooled and filtered. The filtrate was concentrated and distilled water was added to precipitate a brown oil. This was extracted into ether. The ether solutions were dried with anhydrous Na_2SO_4, filtered and the solvent removed in vacuo.

With some difficulty, small quantities of the pure, off-white, solid ligand can be isolated by cooling a concentrated Abs.EtOH solution of the impure oil* to dry ice/acetone temperatures. When solidification has been induced, the mixture must be filtered rapidly. The semi-dry solid must then be put under vacuum to dry.

The unstable ligand turns grey over a period of about a month.

---

* Extensive decomposition occurred during an attempt to distil this oil.

3-(2-methylthiophenylimino)camphor (I)

A slight excess of 2-methylthioaniline (> 1.392 g.), (–)camphorquinone (10 mmole, 1.662 g., prepared as in Ref. 293) and a trace of dry $ZnCl_2$ (ca 5 mg.) were sealed in a teflon bomb and heated for 2 hours at 185 °C in an oven. The reaction products were then dissolved in dry ether. The solution was filtered through Kieselguhr before the ether was removed and the residue dried in vacuo. Pentane was added to the residue to precipitate yellow crystals. These were recrystallized from ligroin, washed with pentane and air dried.

YIELD: 0.981 g. (34%)

NOTE: A 2 mole ratio of 2-methylthioaniline also results in the 1:1 condensation product being isolated. Prolonged heating reduces the yield and the presence of $ZnCl_2$ is essential.

1,2-bis(pentafluorophenylthio)ethane (fpte)

Pentafluorothiophenol (0.050 mole, 10.006 g.) was added to a slight excess of sodium (>1.150 g.) dissolved in cold Abs.EtOH. 1,2-dibromoethane (0.025 mole, 4.697 g.) was then added to the yellow solution before it was refluxed (under N_2) for about 30 minutes. During this time, it lost its yellow colour and NaBr precipitated. As the mixture was cooled, the ligand also precipitated. Distilled water (ca 400 cm^3) was added and the insoluble white ligand was filtered off. It was washed with distilled water and then Abs.EtOH before being dried *in vacuo*.

YIELD: 9.439 g. (89%)

Ethylthiopentafluorobenzene (C_6F_5SEt)

A solution of sodium (0.025 mole, 0.575 g.) and pentafluorothiophenol (0.025 mole, 5 g.) in Abs.EtOH was prepared, to which ethyl iodide (0.025 mole, 3.899 g.) was added. This solution was refluxed (under N_2) for an hour and left to stand overnight. Distilled water was added to precipitate a light red oil. The oil was extracted into ether. The ether extracts were then dried with anhydrous Na_2CO_3 and filtered before the ether was removed *in vacuo*.

The oil was used without any further purification.

ii) LIGAND PREPARATIONS

2-ethylthioethylamine (etea)

In a typical preparation, 2-ethylthioethylamine hydrochloride (0.069 mole, 9.821 g.) was neutralised with a slight excess of 2.0M. NaOH. An orange oil which was isolated after several ether extractions, was distilled to give the colourless ligand.

YIELD: 6.330 g. (87%)

TABLE 40

LIGAND PROPERTIES AND ANALYTICAL RESULTS

LIGAND	APPEARANCE	M.P/B.P/Other	ANALYSES: Calc.(Found)/%
tbmp	colourless oil	128-130 °C [12 mm.Hg]	C 66.25, H 8.34, N 7.73, S 17.68 (66.31) (8.43) (7.18) (17.10)
tbmq	off-white solid	51-57°	C 72.68, H 7.41, N 6.06, S 13.86 (72.48) (7.20) (6.05) (13.29)
fpte	white solid	127-130°	Mass Spect. - small $C_6F_5\overset{+}{S}=S$ peak (disulphide impurity)
C_6F_5SEt	pale-red oil	-	^1H nmr - weak impurity peaks at 3.5, 4.4 ppm downfield TMS
L	yellow solid	100-104° $[\alpha]_D=+218.79°$ in Abs.EtOH	C 71.04, H 7.37, N 4.87, S 11.15 (71.04) (7.44) (4.54) (11.29)
etca	colourless oil	92° [14 mm.Hg]	^1H nmr - no impurities
mti	white solid	70-72°	^1H nmr - no impurities

2-methylthio-2-imidazoline (mti)

In a typical preparation, 2-methylthio-2-imidazoline hydroiodide (0.062 mole, 15 g.) was neutralised with a slight excess of NaOH. The white, flaky ligand was isolated after several ether extractions had been carried out, and dried in vacuo.

YIELDS: 62-79%

iii) DISTILLATION OF LIGANDS

All ligand distillations were carried out under reduced pressure using quickfit microdistillation equipment. To prevent oxidation of the ligands, oxygen-free, dry dinitrogen was slowly bled through the system during each distillation.

iv) LIGAND REACTIVITY STUDIES

a) Preparation of (tbmpH)PF_6

The ligand (tbmp) was added to about 1-2 cm^3 of 65% HPF_6 until the fuming ceased. After warming the solution for about 1 minute, Abs.EtOH (ca 10 cm^3) was added to it. A white precipitate was isolated by adding ether to this solution.

b) Preparation of (tbmpH)Br

Excess HBr was bubbled through an Abs.EtOH solution of tbmp before removing the solvent. The addition of dry ether to the residue precipitated an oil. After being thoroughly dried in vacuo, the oil was crystallized (by "scratching") to give an off-white solid.

Infrared Spectra of (tbmpH)X salts

The frequencies of the $\nu(N^+—H)$ absorptions (above 2000 cm^{-1}) are dependent on the counterion, X^-. In general, $\nu(N^+—H)$ decreases with increased $^+NH\text{----}X^-$ hydrogen bonding.[98]

Protonation of the pyridyl nitrogen also increases the frequency of the pyridine ring vibration that is found at 1593 cm^{-1} in tbmp.

COMPLEX	$\nu(N^+-H)/cm^{-1}$	ν(pyr.ring)/cm^{-1}
tbmp		1593
tbmpH)PF_6	3252(w); 3172(w-sh); 3110(s); ca 3042(s)	1622
tbmpH)Br	ca 2707(m); ca 2557(m); ca 2381(m) (all broad)	1612

NOTE: - Nujol mull spectra.

c) Preparation of 3-(2-methylthiophenylamino)camphor

The $>$C=N- bond of yellow 3-(2-methylthiophenylimino)camphor can be reduced by the method of Forster and Thornley.[191] Distilled water was added to the colourless reduced solution to precipitate a white complex. This was extracted into pentane and the pentane solution dried with anhydrous $MgSO_4$. After filtering the mixture the pentane was removed *in vacuo*. Creamy flakes (M.P.=84-88°) crystallized from the residue on "scratching".

YIELD: 0.230 g. (46%)

Infrared Spectrum (Nujol mull)

The medium intensity ν(C=N) band at 1671 cm^{-1} in the imine[168] disappears on forming the white complex and a sharp, weak ν(N-H) band appears at 3356 cm^{-1}.

^{1}H nmr Spectrum (in $CDCl_3$)

A sharp double (J=4 Hz) appears at 4.00 ppm in the spectrum of the reduced complex. This resonance is not present in the spectrum of the imine and it is assigned to the -NH- proton.

APPENDIX II

i) CHEMICAL SYNTHESIS OF COMPLEXES

Unless it is specifically stated otherwise, all ligands and metal salts were dissolved separately in a minimum of Abs.EtOH before mixing and each solution was filtered.

Upon isolation, each complex was carefully washed with Abs.EtOH and thoroughly dried *in vacuo*.

In all cases where solvents were removed *in vacuo*, a rotary evaporator was used. Where complexes or residues were dried *in vacuo*, an evacuated (*ca* 2-5 mm.Hg) drying line was used.

The melting points of perchlorate salts were not determined.

ii) REACTIVITY STUDIES: EXPERIMENTAL DETAILS

a) Addition of pyridine to $Cu(tbmp)_2X_2$ ($X=BF_4^-$ and Cl^-)

Both complexes were prepared (*in situ*) in their respective solvents ($X=BF_4^-$, acetone; $X=Cl^-$, Abs.EtOH) to give concentrations of 5×10^{-3} mol.l.$^{-1}$. Successive aliquots of pyridine were added to these solutions as required.

b) Addition of pyridine to $Cu(etea)_2(ClO_4)_2$

1 mmole of the complex was prepared (*in situ*) in about 100 cm^3 of Abs.EtOH. For a 1:1 ratio of pyridine:Cu(II), 0.08 cm^3 of the base were used.

c) Addition of pyridine to $Cu(mti)_4(BF_4)_2$

0.5 mmole of $Cu(mti)_4(BF_4)_2$ was prepared (*in situ*) in Abs.EtOH. Successive aliquots of pyridine were added to this solution as required.

d) Reaction of Ph_4AsCl with $[Cu(tbmpH)Cl_2]_2$

Ph_4AsCl (0.247 g., 0.565 mmole) was added to a solution of freshly prepared $[Cu(tbmpH)Cl_2]_2$ (0.179 g. 0.565 mmole) in warm MeOH. A couple of drops of H_3PO_2 were added to prevent oxidation. The separation of small amounts of yellow and white crystals was effected by carefully removing the solvent *in vacuo*.

The white crystals had melting points and analyses corresponding to those required for $[Ph_4As]CuCl_2$.[128]

The yellow crystals appeared to be impure $[Cu(tbmpH)Cl_2]_2$ as their M.P. (124-126°) was roughly similar to that required for a pure sample (123-125°).

	M.P/°C	ANALYSES/%		
White crystals	179-180	C 55.74,	H 3.85,	Cl 14.22
$[Ph_4As]CuCl_2$	176-178	(55.67)	(3.89)	(13.69)

APPENDIX III

i) INSTRUMENTS AND RECORDING OF SPECTRA

Electronic Spectra were recorded on a Shimadzu MPS-5000 spectrophotometer.

Reflectance spectra were recorded for either finely ground samples that had been diluted with magnesium oxide or the pure samples were crushed onto filter paper. The choice depended on the quality of the spectra that could be obtained.

The solution spectra (10 mm. quartz cells) were recorded, where possible, in solvents of varying ligating ability.

The recording of spectra at liquid air temperatures (90K) in 20% Glycerol/MeOH (20 parts Glycerol/80 parts MeOH) depended on the Cu(II) compounds' stabilities in this solvent. Although several other solvent systems were tried, this system was consistently found to give uncracked, transparent glasses of good optical quality. However, care must be taken to ensure that the cuvettes are cooled slowly and that frost does not form on the cuvette windows. Standard 2 mm. acrylic cuvettes (Shimadzu) were used.

Electron spin resonance spectra were recorded on a Varian E104A spectrometer. The solutions were cooled to 77K using liquid nitrogen and all data is for this temperature.

Regular calibrations of the instrument (with DPPH) have shown that the single absorption peak of DPPH consistently falls at 3220 ± 5 Gauss. This value has been used in calculating the g and A parameters from the spectra. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ lines were measured using the normal first-order perturbation procedures[192] and the parameters were calculated using formulae a) and b).

a) $g = g_{DPPH} \times (\nu_{DPPH} / \nu_{sample})$

where ν_{DPPH} = 3220 Gauss

and g_{DPPH} = 2.0036

b) $|A(\text{energy})| = g \times |A(\text{Gauss})| \times \beta$

where β = 1.39969 MHz/G.

$= 0.46686 \times 10^{-4}$ cm^{-1}/G.

Hence $|A| = g \times |A(\text{Gauss})| \times 0.46686 \times 10^{-4}$ cm^{-1}

NOTE: DPPH = diphenyl picryl hydrazyl

Where isotropic spectra could not be improved the isotropic g has been reported.

Infrared spectra (4000-600 cm^{-1}) were recorded on a Beckman IR-20 spectrophotometer and calibrated with polystyrene film.

Far-infrared spectra (400-40 cm^{-1}) were obtained (using a Grubb-Parsons Cube MkII Interferometer) at room temperature for petroleum jelly mulls on polythene discs. The ν(M-X) absorptions were tentatively assigned by comparing the spectra where the halogen has been changed, and by intensity considerations.

Conductivities were measured (for ca 1 x 10^{-3} $mol.l^{-1}$ solutions at room temperature) using a Philips PR9500 conductivity meter, fitted with a Philips PW9510 cell.

^{1}H nmr spectra (paramagnetic studies) were recorded using a JEOL C-60HL High Resolution NMR spectrometer. Tetramethylsilane (TMS) was used as an internal standard for all spectra.

For each experiment, a concentrated solution of the ligand in $CDCl_3$ (CH_2Cl_2 for the Co(II)/tbmp experiment) was prepared. The spectrum was measured for a 1.0 cm^3 sample with the required M(II) concentration.

Standard methanol solutions of $CuCl_2.2H_2O$ and $CoCl_2.6H_2O$ were used as the sources of Cu(II) and Co(II).

Microanalyses were performed by Professor A.D. Campbell and his staff at Otago University.

Molecular weights were determined using a Hitachi Perkin-Elmer 115 Molecular Weight apparatus.

ii) SOLVENTS

a) Spectroscopic Investigations: All solvents were redistilled before use. Nitromethane and nitrobenzene were stored over molecular sieves.

b) Preparative Work: Ethanol and methanol were redistilled: acetone was A.R. grade. Diethyl ether was redistilled over Na wire.

APPENDIX IV

i) MISCELLANEOUS REACTIONS

a) Synthesis of dichloro 2-(3,3-dimethyl-2-thiabutyl)-pyridine zinc(II)

2 mmole of ligand (0.363 g.) were added to an excess of dry $ZnCl_2$ (> 0.272 g.). The solution, after being concentrated and cooled, yielded the white crystalline complex.

YIELD: 0.254 g. (39%)

M.P. = 188-189 °C

Analyses: Calc.(Found)/%: C 37.82, H 4.76, N 4.41
(38.08) (4.85) (4.20)

Conductivity: CH_3NO_2 ($\Lambda = 4$); MeCN ($\Lambda = 27$)

Far-IR: ν(Zn-Cl) at 316, 330 cm^{-1}.

^1H nmr in $(CD_3)_2SO$

	$-CH_3$	$-CH_2S-$	α-H
tbmp	1.28	3.93	8.53d(4)
Zn(tbmp)Cl_2	1.30	3.87	8.45d(4)

- chemical shifts are ppm downfield from TMS
- d = doublet; coupling constants are in parentheses (Hz)

The two ν(Zn-Cl) absorptions are consistent with this complex having a distorted tetrahedral structure in the solid state.[273] However, in $(CD_3)_2SO$, the ^1H nmr spectrum is virtually unchanged from the free-ligand spectrum. This is in contrast to the significant downfield shifts that are observed for the α-H and $-CH_2S-$ resonances in the $M(CO)_4$tbmp (M=Cr,Mo,W) complexes (see Chapter 3, Section II).

The ^1H nmr spectrum thus suggests that the complex decomposes on dissolution (to yield the free ligand). Stability constant measurements for the related ligand, 2-(methylthiomethyl)pyridine[3] [logK = 3.27(Cu^{2+}), 2.06

(Ni^{2+}), $\leqslant 1(Zn^{2+})]$ suggest that $Zn(tbmp)Cl_2$ may not be very stable compared to the Cu(II) and Ni(II) complexes of tbmp.

b) <u>Cu(I) complex of cysteamine hydrochloride</u>

The formation of an unstable, yellow-white complex from the reaction of $CuCl_2.2H_2O$ with cysteamine hydrochloride ($HSCH_2CH_2NH_2.HCl$) was first reported by Tanaka *et al* in 1970.[193] However, the complex was not analysed.

A ratio of 2 cysteamine hydrochloride to 1 Cu(II) was used in the following reaction.

The ligand was dissolved in a minimum of water and the pH of the solution was adjusted (with dilute aqueous ammonia) to *ca* pH 8. The $CuCl_2.2H_2O$ was then added dropwise (aqueous solution) while stirring the solution. The white precipitate which appeared was filtered and washed with water and then Abs.EtOH. Care must be taken to ensure that the compound is not exposed to air.

The damp complex was dried *in vacuo* and sealed *in vacuo*. Prolonged exposure to light causes the complex to turn a darker yellow.

Two independent preparations both gave good analyses for $Cu_2(SCH_2CH_2NH_2.HCl)Cl$.

	C	H	Cl	S
Calculated:	C 8.73,	H 2.56,	Cl 25.77,	S 11.65 %
Found:	(8.74)	(2.57)	(26.12)	(11.68)
	(9.00)	(2.99)	(26.12)	

c) <u>Reaction of $Cu(BF_4)_2.6H_2O$ with mti (1:2)</u>

In Abs.EtOH, a very fine, light blue complex precipitates on mixing the starting materials.

The complex gave analyses approximating those required for $Cu_2(mti)(BF_4)_4.4H_2O$

Calculated: C 7.25, H 2.43, N 4.23 %

Found : (7.21) (2.88) (3.69)

d) Reaction of $CuCl_2.2H_2O$ with mti (1:2)

In acetone, an insoluble gold complex results. The complex gives reproducible analyses for $Cu_8(mti)_9Cl_{12}$.

Calculated: C 21.84, H 3.67, N 12.74, Cl 21.49

Found : (21.71) (3.94) (12.74) (21.12)

A similar gold complex precipitated from Abs. EtOH, but its analyses were ambiguous.

ii) UNSUCCESSFUL REACTION ATTEMPTS

During the course of this work, the following unsuccessful reactions were investigated:

- synthesis of CuLCl (L = tbmp, tbmc),
- reduction of $Cu(tbmp)_2(BF_4)_2$ with H_3PO_2 and $Cu(tbmp)_2Cl_2$ with non-protic reducing agents,
- synthesis of $Cu(tbmc)_2X_2$ ($X = ClO_4^-, BF_4^-$),
- reaction of $Co(tbmp)_2(ClO_4)_2.H_2O$ with LiCl (1:1),
- syntheses of $Zn(tbmp)_2Cl_2$ and $Zn(mti)_4(ClO_4)_2$,
- reduction of $Cu(etea)_2(ClO_4)_2$ and $Cu(mti)_4Cl_2$
- reactions of etea with $Cu(NO_3)_2.3H_2O$ and $Cu(CH_3CN)_4ClO_4$,
- isolation of $Co(mti)_4(ClO_4)_2$ and pure $Co(mti)_4(BF_4)_2$,
- reactions of fpte with Cu(II) and Ni(II),
- reactions of C_6F_5SEt with Na_2PdCl_4 in MeOH and EtOH,
- formation of imines from camphorquinone and methionine, methionine ethyl ester and etea,
- reactions of $CuCl_2$ with 3-(2-methylthiophenylimino) camphor and 3-(2-methylthiophenylamino)camphor,

- formation of imines from mta and 2,6-diacetylpyridine.

iii) STUDIES ON $Cu(tbmr)_2X_2$ ($X = Cl^-$, Br^-) MELTS

Both complexes give orange melts that do not crystallize on cooling. An insignificant loss of weight on melting shows that there is no loss of volatile hydrocarbon derivatives such as $(CH_3)_3CX$.

In Abs.EtOH, the electronic spectra of both melts are consistent with their being Cu(I) complexes. In the visible region, the spectra are dominated by an intense absorption at 465 nm.

The esr spectra (77K) are also consistent with the melts being Cu(I) complexes.

APPENDIX V

STRUCTURE FACTOR TABLES

$[Cr(tbmp)Br_2]_2$

**** L = 0 ****

H	K	OBS	CALC
-11	7	25	24
-10	6	46	44
-10	9	19	22
-9	-1	17	18
-9	7	27	31
-8	4	36	34
-8	6	17	17
-7	10	47	45
-6	-5	19	17
-6	0	46	58
-6	2	18	23
-6	3	31	32
-6	4	72	75
-6	7	18	21
-6	8	36	42
-5	-6	27	24
-5	-2	30	34
-5	-1	42	54
-5	5	18	18
-5	6	34	43
-5	7	42	45
-4	-5	16	12
-4	-1	33	44
-4	2	55	51
-4	5	21	23
-3	-6	42	41
-3	-3	72	85
-3	-2	38	46
-3	-1	81	96
-3	0	68	82
-3	1	35	37
-3	2	19	17
-3	3	55	61
-3	6	77	91
-3	7	71	82
-2	-9	20	18
-2	-6	76	76
-2	-5	70	78
-2	-4	21	26
-2	-3	100	115
-2	-2	30	36
-2	-1	87	108
-2	0	41	48
-2	1	76	69
-2	3	85	100
-2	8	51	56
-2	13	24	16
-1	-6	37	42
-1	-5	37	47
-1	0	143	200
-1	3	62	62
-1	6	16	20
-1	9	25	23
-1	10	21	18
-1	12	27	21
0	-11	16	12
0	-8	25	21
0	-7	13	16
0	-4	115	111
0	1	131	174
0	2	120	148
0	3	198	223
0	5	42	42
0	6	42	43
1	-8	37	36
1	-7	39	43
1	-5	18	19
1	-4	30	37
1	-2	60	67
1	-1	102	124
1	1	41	42
1	7	26	26
2	-7	22	28
2	-6	42	54
2	-4	57	65
2	-2	12	11
2	7	34	31
3	-11	20	12
3	-10	27	26
3	-9	29	30
3	-8	38	43
3	-4	50	58
3	5	50	55
3	7	24	24
4	-13	21	16
4	-11	38	35
4	-10	45	45
4	-9	41	46
4	-7	113	134
4	-6	82	98
4	0	11	10
4	4	35	37
5	-10	20	21
5	-4	35	42
5	-2	43	50
5	0	15	17
5	3	32	35
5	5	21	20
6	-11	26	27
6	-10	63	66
6	-6	16	22
6	-1	13	14
6	1	47	54
6	2	20	21
7	-11	24	24
7	-6	47	50
7	-5	52	50
7	-4	31	29
7	-3	36	40
7	-2	14	17
7	-1	23	29
7	0	55	66
7	1	26	29
7	2	15	19
8	-12	17	20
8	-9	23	27
8	-8	19	24
8	-7	47	53
8	-5	53	53
8	-3	20	19
8	-2	16	0
9	-8	43	49
9	-6	49	48
9	-5	67	60
11	-5	16	18

**** L = 1 ****

H	K	OBS	CALC
-10	1	24	28
-10	5	32	38
-9	1	27	34
-9	2	22	26
-9	4	17	17
-9	8	32	36
-8	-2	18	14
-8	3	32	36
-8	4	16	17
-8	7	52	64
-8	8	46	52
-7	-3	16	11
-7	-2	20	1
-7	-1	20	6
-7	0	38	22
-7	1	20	22
-7	3	42	37
-7	4	25	24
-7	6	32	37
-7	7	80	91
-7	8	41	42
-7	9	32	34
-7	10	21	22
-6	-6	23	18
-6	-5	25	26
-6	-3	17	16
-6	1	39	46
-6	2	14	11
-6	3	17	14
-6	4	21	28
-6	5	20	27
-6	7	17	20
-6	9	20	17
-6	10	24	20
-6	12	24	18
-5	-4	33	34
-5	-3	37	41
-5	-2	14	14
-5	0	20	25
-5	1	48	53
-5	2	13	14
-5	3	30	32
-5	4	88	109
-5	5	31	38
-5	6	54	59
-5	7	51	58
-5	8	32	34
-5	10	60	56
-5	12	31	26
-5	13	20	17
-4	-8	16	11
-4	-6	29	27
-4	-5	17	20
-4	-4	60	47
-4	-3	63	75
-4	-2	35	42
-4	-1	16	19
-4	0	45	53
-4	1	122	117
-4	2	34	38
-4	3	44	55
-4	4	67	82
-4	5	14	22
-4	6	76	90
-4	7	22	23
-4	8	22	19
-4	10	20	20
-4	12	20	15
-3	-9	24	20
-3	-8	17	15
-3	-6	35	39
-3	-5	14	15
-3	-4	34	35
-3	-3	62	72
-3	0	80	31
-3	1	174	144
-3	2	29	31
-3	4	16	17
-3	5	56	63
-3	6	14	12
-3	7	41	42
-3	8	26	23
-3	9	43	44
-3	10	35	32
-3	11	21	13
-3	13	28	19
-2	-6	31	32
-2	-3	105	117
-2	-2	124	135
-2	-1	74	68
-2	0	68	58
-2	1	46	40
-2	2	12	9
-2	3	44	51
-2	4	31	33
-2	5	55	59
-2	7	12	9
-2	8	38	38
-2	9	42	38
-2	10	23	15
-1	-7	42	44
-1	-6	40	45
-1	-4	77	36
-1	-2	117	126
-1	0	175	152
-1	1	28	30
-1	2	27	28
-1	3	96	112
-1	4	41	45
-1	5	63	69
-1	6	43	50
-1	7	32	38
-1	8	32	30
-1	10	16	15
0	-10	23	17
0	-8	16	15
0	-7	52	60
0	-6	15	13
0	-5	60	72
0	-4	106	112
0	-3	142	152
0	-2	17	18
0	-1	69	60
0	1	19	22
0	2	133	158
0	3	59	66
0	4	20	27
0	7	30	28
0	8	16	17
0	9	21	18
0	10	21	20
1	-8	20	15
1	-7	12	9
1	-6	84	95
1	-5	58	41
1	-4	100	63
1	-3	31	31
1	-2	52	42
1	-1	148	122
1	0	136	156
1	1	19	21
1	2	183	222
1	3	99	115
1	4	47	47
1	6	32	33
1	7	25	26
1	8	16	16
2	-13	23	17
2	-10	28	31
2	-9	43	44
2	-6	53	56
2	-5	17	20
2	-4	52	55
2	-3	14	8
2	-2	35	25
2	-1	24	23
2	0	71	79
2	1	67	71
2	2	113	134
2	3	44	48
2	4	36	37
2	5	24	21
2	6	34	35
2	7	39	34
2	8	20	24
3	-13	25	21
3	-10	44	46
3	-9	56	59
3	-8	18	18
3	-5	54	58
3	-4	49	50
3	-3	135	121
3	-1	55	70
3	0	74	79
3	1	61	71
3	3	52	60
3	4	14	15
3	5	34	29
3	8	21	19
4	-11	16	11
4	-9	40	43
4	-8	51	59
4	-7	34	38
4	-6	19	19
4	-5	116	127
4	-4	39	36
4	-3	95	79
4	-2	44	41
4	-1	91	102
4	0	71	63
4	1	18	20
4	2	55	60
4	3	65	72
4	5	18	15
4	6	18	13
5	-13	27	22
5	-11	28	28
5	-10	25	30
5	-9	22	20
5	-8	20	25
5	-7	61	73
5	-6	69	70
5	-5	74	69
5	-4	64	59
5	-3	59	60
5	-2	100	113
5	-1	28	34
5	0	42	50
5	1	30	46
5	2	31	33
5	6	16	14
6	-11	30	31
6	-9	19	20
6	-8	17	16
6	-7	30	32
6	-6	39	39
6	-5	23	20
6	-4	32	33
6	-3	59	67
6	-2	89	100
6	0	58	64
6	1	35	41
6	2	15	7
6	3	16	13
6	5	22	21
6	6	19	16
7	-10	40	44
7	-8	66	67
7	-7	36	40
7	-4	35	37
7	-2	16	24
7	3	19	19
7	4	20	14
8	-10	27	27
8	-9	22	22
8	-8	69	72
8	-7	34	32
8	-6	16	13
8	-4	36	40
9	-10	19	20
9	-9	40	42
9	-8	26	24
9	-7	14	16
9	-5	17	14
9	-3	22	21
9	-2	17	17
10	-11	19	15
10	-5	20	14
11	-7	16	10

**** L = 2 ****

H	K	OBS	CALC
-11	4	17	17
-10	5	19	24
-10	7	17	16
-9	1	36	40
-9	3	43	40
-9	4	80	71
-9	5	44	48

```
  H    K   OBS  CALC
 -9    6    24    26
 -9    7    34    59
 -8    0    21    24
 -8    1    26    33
 -8    3    54    53
 -8    4    57    62
 -8    5    36    35
 -8    6    14    16
 -8    7    19    23
 -8    9    22    26
 -8   10    25    25
 -7    0    36    37
 -7    2    94    65
 -7    3    81    68
 -7    5    24    24
 -7    6    26    32
 -7    7    22    51
 -7    8    35    42
 -7    9    32    57
 -7   10    41    44
 -6   -5    26    22
 -6   -4    33     1
 -6   -3    21    26
 -6   -2    40    56
 -5    1    56    45
 -6    2    57    62
 -6    3    40    34
 -6    4    67    78
 -6    6    22    21
 -6    7    60    69
 -6    8    17    18
 -6    9    69    66
 -6   10    46    43
 -5   -7    17    16
 -5   -6    45    46
 -5   -5    36    42
 -5   -3    61    69
 -5   -2    75    62
 -5   -1    43    46
 -5    1    19    17
 -5    2    22    23
 -5    3    51    69
 -5    4    26    28
 -5    5    30    33
 -5    7    14    17
 -5    8    23    25
 -5    9    46    44
 -4   -6    33    36
 -4   -5    24    31
 -4   -4    18    24
 -4   -3    50    50
 -4   -2   105   112
 -4   -1    79    61
 -4    0    24    16
 -4    2    39    40
 -4    3    83    91
 -4    4    32    37
 -4    5    16    18
 -4    6    59    64
 -4    7    32    34
 -4    8    26    29
 -4    9    14    11
 -4   10    38    31
 -4   11    17    15
 -3   -6    20    18
 -3   -5    53    57
 -3   -4    22    24
 -3   -3    51    53
 -3   -2    24    27
 -3   -1    26    27
 -3    0    61    52
 -3    1   103    98
 -3    2    17    20
 -3    3   102   110
 -3    4    11    14
 -3    5    56    64
 -3    6    62    68
 -3    7    14    20
 -3    9    31    27
 -3   10    35    30
 -3   11    16    14
 -2   -8    16    16
 -2   -7    42    46
 -2   -6    42    45
 -2   -5    57    76
 -2   -4    22    25
 -2   -3    32    64
 -2   -2    33    19
 -2   -1    51    45
 -2    1   163   109
 -2    2    15    22
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  H    K   OBS  CALC
 -2    3   130   143
 -2    4    91   104
 -2    5    56    58
 -2    7    43    39
 -2    8    21    17
 -1  -11    20    21
 -1   -9    32    36
 -1   -8    66    73
 -1   -7    22    24
 -1   -6    25    27
 -1   -5    15    16
 -1   -3    47    48
 -1   -2    77    62
 -1    0    66    67
 -1    1    14     4
 -1    2    23    21
 -1    3    52    53
 -1    4    21    21
 -1    5    40    45
 -1    6    13    12
 -1    7    43    39
 -1    8    19    15
  0  -12    18    13
  0  -11    22    20
  0   -9    47    49
  0   -8    65    66
  0   -6    23    25
  0   -5    77    78
  0   -3    35    31
  0   -2   128   110
  0   -1   174   160
  0    1    12    13
  0    2    42    49
  0    3    48    50
  0    4    86    93
  0    5    34    40
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-1	-1	27	24
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-4	-5	50	54
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H	K	OBS	CALC
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2	-5	49	51
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2	-3	23	25
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H	K	OBS	CALC
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1	-10	26	35
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1	-3	27	25
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3	-14	19	23
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4	-8	20	17
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0	-5	30	33
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1	-12	40	49
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3	-10	31	37
4	-12	44	54
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4	-8	20	21

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  6    1    32    30

  H    L   OBS  CALC
  6    2    22    18
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  6    8    35    38
  6   10    27    28
  7    1    14    14
  7    2    26    32
  7    3    28    32
  7    5    28    30
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  7    8    32    34
  7   10    31    33
  7   13    35    36
  7   15    33    28
  8    1    27    31
  8    2    31    32
  8    3    40    35
  8    4    40    41
  8    5    23    24
  8    6    29    31
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  9    2    23    25
  9    3    27    30
  9    4    24    26
  9    5    45    44
  9    7    54    54
  9    9    19    20
 10    1    25    21
 10    2    16    16
 10    3    30    30
 10    4    35    34
 10    6    16    14
 11    1    64    64
 11    2    46    44
 11    3    17    21
 11    4    36    38
 11    6    19    22
 12    1    20    21
 12    2    24    20
 12    3    20    21
 12    4    26    25
 12    6    35    31
 12    8    21    18
 13    1    39    36
 13    2    22    19
 13    3    30    26
 13    4    26    25
 14    1    24    24
 14    2    19    16
 14    4    27    28
 14    5    23    23
 14    6    26    25
 14    8    26    24
 15    4    18     9

   ****  K  =  5  ****

-14    0    25    26
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-13    7    22    21
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-12    0    54    54
-12    2    48    51
-12    4    31    32
-12    6    26    24
-11    1    21    22
-11    5    35    35
-11    6    24    24
-11    7    38    37
-11    9    25    28
-11   13    17     2
-11   16    20     4
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-10    2    67    68
-10    4    55    56
-10    6    72    74
-10    8    68    72
-10   10    32    41
 -9    0    17    19
 -9    1    25    23
 -9    4    17    12
 -9    5    47    47
 -9    7    81    65
 -9    9    59    60
 -9   13    29    24
 -8    1    23    19
 -8    2    32    32
 -8    3    27    32
 -8    4    47    45
 -8    5    23    23
 -8    6    75    76
 -8    8    67    67

 -8   10    44    57
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 -7    1    32    29
 -7    2    15    11
 -7    7    35    34
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 -7   13    34    37
 -7   15    47    44
 -7   17    42    37
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 -6    5    15     6
 -6    6    63    61
 -6    8    57    63
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 -6   16    24    19
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 -5    4    15    14
 -5    6    14    10
 -5    7    26    24
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 -5   15    37    33
 -5   17    30    34
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 -4    1    34    40
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 -4    4    37    44
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 -4    6    61    62
 -4    7    19    18
 -4    8    58    63
 -4    9    19    24
 -4   10    20    30
 -3    1   104   103
 -3    2    14    19
 -3    3    78    80
 -3    4    18    13
 -3    5    36    37
 -3    6    37    39
 -3    8    18    18
 -3   15    34    28
 -3   17    22    21
 -2    2    81    79
 -2    3    25    28
 -2    4    34    38
 -2    6    33    32
 -2   16    21    15
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 -1    1   149   148
 -1    2    18    16
 -1    3    87    89
 -1    5    50    53
 -1    8    17    19
 -1   13    17    19
 -1   15    26    24
 -1   16    18    14
 -1   17    27    26
  0    1    13     1
  0    2    38    38
  0    3    42    40
  0    4    46    52
  0    5    20    19
  0    6    60    63
  0    8    87    90
  0   10    74    89
  0   12    48    46
  1    1   113   116
  1    2    14    18
  1    3    87    97
  1    4    22    22
  1    5    44    45
  1    6    24    21
  1    7    19    19
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  2    1    41    38
  2    2    69    64
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  2    6    49    47
  2    8    77    84
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  3    2    31    27
  3    3   111   110
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  3    5    77    80
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  3    7    52    56
  3    8    16    16
  3    9    20    19
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  4    1    31    32
  4    3    29    24
  4    4    15    17
```

```
  H     L   OBS  CALC

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  4     8    59    62
  4    10    49    50
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  4    15    17     4
  5     3    33    36
  5     5    52    51
  5     7    63    67
  5     8    36    37
  5     9    31    32
  5    13    20    25
  6     2    20    19
  6     3    20    24
  6     5    17    23
  6     6    49    47
  6     8    63    64
  6    10    37    38
  6    12    37    36
  7     1    60    56
  7     3    53    49
  7     4    23    26
  8     1    19    12
  8     2    16    15
  8     6    20    21
  8     7    24    23
  9     1    32    34
  9     3    45    45
  9     5    33    31
 10     2    47    45
 10     4    19    17
 11     1    29    31
 11     3    25    25
 11     5    25    18
 11     7    25    21
 12     2    69    63
 12     4    57    54
 12     6    36    36
 13     1    27    26
 13     3    33    30
 13     5    27    29
 14     1    21    16
 14     2    35    32
 14     4    32    33
 16     2    21    15

  ****  K  =  6  ****

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-14     6    19    14
-13     1    23    24
-13     3    21    19
-13     5    18    14
-13     7    18    17
-13     9    23    28
-12     1    24    26
-12     3    25    26
-12     4    18    16
-12     5    25    24
-12     6    24    25
-11     0    23    25
-11     1    54    55
-11     2    20    20
-11     3    56    52
-11     4    30    23
-11     5    41    41
-11     6    30    28
-11     8    31    32
-11    12    30    33
-10     4    20    19
-10     6    19    25
-10     8    21    19
-10    12    22    20
 -9     0    22    20
 -9     1    45    44
 -9     3    61    63
 -9     4    25    24
 -9     5    36    29
 -9     6    18    18
 -9     7    23    23
 -9    12    32    27
 -9    14    21    17
 -8     0    23    21
 -8     1    28    27
 -8     2    32    29
 -8     3    35    39
 -8     4    17    16
 -8     5    53    53
 -8     7    20    24
 -8     8    24    32
 -8    12    43    40
```

```
 -8    14    42    37
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 -7     2    21    21
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 -6     0    45    47
 -6     1    16    16
 -6     2    52    55
 -6     3    32    31
 -6     4    49    50
 -6     5    43    44
 -6     6    45    46
 -6     7    34    36
 -6     9    19    19
 -6    12    41    42
 -6    14    30    29
 -6    15    21    18
 -5     0    55    52
 -5     2    62    61
 -5     4    50    47
 -5     6    27    30
 -5     7    16    20
 -5     8    22    17
 -5     9    23    27
 -5    13 [illegible] 14
 -5    14    23    45
 -5    16    21    16
 -4     0    24    24
 -4     1    79    74
 -4     3    91    93
 -4     4    25    26
 -4     5    79    79
 -4     6    48    50
 -4     7    39    36
 -4     9    23    18
 -3     0    42    40
 -3     1    36    38
 -3     2    42    42
 -3     3    63    64
 -3     4    38    39
 -3     5    37    37
 -3     6    36    34
 -3     7    17    23
 -3     8    18    22
 -3    12    24    20
 -3    13    25    27
 -3    15    23    16
 -2     0    36    36
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 -2     5    70    71
 -2     7    56    62
 -2     9    53    57
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 -1     3    99   102
 -1     5    82    83
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  0     4    15     6
  0     6    18    22
  0     7    28    31
  0     9    43    45
  0    13    32    34
  0    14    24    20
  0    15    30    31
  1     0    14    10
  1     1    14    13
  1     2    17    15
  1     3    44    44
  1     5    40    40
  1     7    41    46
  1    12    24    25
  1    14    35    30
  1    15    19    10
  2     1    77    77
  2     2    77    74
  2     3    24    22
  2     4    62    63
  2     6    49    50
  2    12    27    29
  2    14    29    30
  2    16    27    22
  3     1    20    19
  3     2    39    34
  3    13    18    13
  4     1    29    30
  4     2    37    38
  4     3    28    31
  4     4    59    60
  4     6    59    61
```

```
  H     L   OBS  CALC

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  5     3    17    20
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  5     6    47    46
  5     7    16    13
  5     8    29    30
  6     2    20    20
  6     4    21    19
  6     6    37    36
  6     8    33    36
  7     2    46    43
  7     3    27    28
  7     4    58    53
  7     5    26    29
  7     6    43    45
  7     7    24    24
  7     8    53    50
  7    12    19    16
  8     1    21    19
  8     2    16    19
  9     2    24    27
  9     4    26    24
  9     5    32    31
  9     6    35    30
  9     7    25    30
  9     8    21    19
 10     3    22    21
 10     4    18    15
 11     1    28    28
 11     2    29    28
 11     4    22    26
 11     6    23    20
 13     1    21    22
 13     4    22    17

  ****  K  =  7  ****

-15     1    20    19
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-13     1    26    23
-13     3    27    24
-13     5    20    21
-13     6    24    20
-12     8    20    16
-11     6    31    27
-11     8    23    22
-10     3    23    18
-10    12    20    25
 -9     0    31    31
 -9     1    26    25
 -9     2    26    24
 -9     3    19    17
 -9     4    27    20
 -9     7    24    22
 -8     0    41    42
 -8     5    29    27
 -8     6    22    26
 -8     7    23    15
 -8     8    20    13
 -8    12    22    16
 -8    14    21    13
 -7     1    41    39
 -7     2    16    20
 -7     3    39    38
 -7     5    35    35
 -7     7    21    17
 -7     8    27    21
 -6     0    64    64
 -6     1    32    33
 -6     2    44    39
 -6     3    20    22
 -6     6    28    22
 -6     7    25    25
 -6     8    21    23
 -6     9    37    38
 -5     1    31    32
 -5     2    20    20
 -5     3    58    60
 -5     5    53    52
 -5     7    42    40
 -5     9    24    23
 -4     0    64    62
 -4     1    66    66
 -4     2    54    50
 -4     3    16    15
 -3     0    27    26
 -3     1    39    37
 -3     3    50    49
 -3     4    32    34
 -3     5    42    40
 -3     6    66    66
 -3     7    53    52
 -3     8    45    48
```

```
 -3     9    44    49
 -3    13    23    16
 -2     0    45    45
 -2     2    52    55
 -2     4    23    20
 -2     6    25    23
 -2    12    22    20
 -2    16    23    20
 -1     0    17    15
 -1     5    23    23
 -1     6    37    38
 -1     7    62    65
 -1     8    41    47
 -1     9    52    55
 -1    12    21    22
 -1    13    24    25
  0     5    17    13
  0     7    18    15
  0    15    25    22
  1     2    27    28
  1     4    22    23
  1     9    30    28
  2     2    59    59
  2     8    18    19
  3     3    17 [illegible]
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  4     2    56    58
  4     3    22    24
  4     4    33    32
  5     1    26    24
  5     2    19    22
  5     4    25    29
  6     1    41    41
  6     2    71    71
  6     3    47    47
  6     4    49    46
  6     5    41    40
  6     6    36    35
  7     1    29    24
  8     2    30    32
  8     4    24    27
  8     6    27    29
  8     8    28    24
  9     1    20    19
  9     2    34    34
  9     3    27    28
  9     4    25    22
  9     5    21    20
  9     8    22    19
 10     6    18    17
 11     2    24    21
 11     3    20    19
 11     4    21    15
 11     5    18    11

  ****  K  =  8  ****

-12     5    18     7
-12     6    26    22
-11     2    25    24
-11     4    25    24
-11     7    21    21
-10     0    29    27
-10     1    21    16
 -9     0    29    28
 -9     2    36    34
 -9     4    25    26
 -8     0    26    26
 -8     2    30    28
 -8     4    23    20
 -7     0    22    22
 -7     2    34    29
 -7     4    28    28
 -7     6    30    25
 -7     7    21    10
 -7     9    22    19
 -7    12    19    17
 -6     0    34    33
 -6     2    36    35
 -6     4    26    27
 -6     6    33    31
 -5     1    56    53
 -5     3    35    36
 -5     4    20    15
 -5     5    23    20
 -5     7    20    17
 -5     9    25    23
 -4     0    20    19
 -4     2    39    37
 -4     3    22    20
 -4     4    38    38
 -4     5    18    13
 -4     6    50    51
 -4     8    40    37
 -4    13    19    13
 -3     1    33    35
```

```
  H     L   OBS  CALC

 -3     3    42   42
 -3     4    30   25
 -3     5    30   31
 -3     6    30   30
 -2     1    21   19
 -2     2    22   17
 -2     4    51   48
 -2     6    62   60
 -2     8    52   56
 -2    12    27   27
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 -1     3    26   26
 -1     5    17   21
  0     1    38   36
  0     3    29   33
  0     5    33   33
  0     6    17   20
  0     7    21   21
  0     8    21   19
  0    12    21   22
  1     2    41   38
  1     4    26   27
  1     6    27   25
  1    13    22   15
  2     3    34   32
  2     5    48   45
  2     7    32   33
  2     9    24   19
  3     1    36   34
  3     2    18   18
  3     4    28   32
  3     6    23   22
  4     2    26   24
  4     4    17   15
  4     5    23   23
  5     1    44   43
  5     3    59   57
  5     5    48   47
  5     7    29   26
  6     2    25   25
  6     3    21   17
  6     5    22   23
  7     1    22   23
  7     3    44   44
  7     5    38   39
  7     7    29   27
  8     2    26   26
  9     5    20   16
  9     7    22   17
 10     2    31   29
```

```
 **** K = 9 ****

-10     4    20   21
-10     5    23   20
 -9     1    20   19
 -9     8    24   21
 -8     2    30   27
 -8     4    31   33
 -8     5    32   29
 -8     6    34   33
 -8     7    35   31
 -6     4    20   15
 -6     5    19   20
 -6     6    25   24
 -6     7    31   29
 -6     8    24   26
 -6     9    25   20
 -5     0    24   22
 -5     3    20   19
 -5     4    17    6
 -5     6    19   11
 -4     4    19   16
 -3     0    30   28
 -3     2    31   32
 -3     3    20   21
 -3     4    19   16
 -2     4    18   15
 -2     6    21   22
 -1     1    29   26
 -1     2    50   43
 -1     4    30   27
  0     7    22   22
  1     0    50   48
  1     1    33   35
  1     2    41   39
  1     3    44   43
  1     4    36   37
  1     5    41   41
  1     6    22   21
  1     7    31   28
  2     4    24   24
  2     6    33   31
  2     7    25   26
  2     8    25   26
  2     9    25   26
  3     2    34   31
  3     3    28   25
  3     4    24   28
  3     5    26   25
  4     5    18   17
  4     7    22   20
  4     8    22   11
  5     2    18   12
  5     3    23   18
  6     2    23   20
  6     6    26   22
  6     7    23   19
  7     5    24   16
 10     2    19   14
```

```
 **** K =10 ****

 -7     5    26   27
 -6     1    21   20
 -6     3    25   21
 -5     7    20   20
 -4     0    19   16
 -3     0    20   18
 -2     2    26   25
 -1     4    37   23
  0     0    49   49
  0     2    45   43
  1     7    20   22
  2     0    33   33
  2     2    33   30
  2     4    26   28
  2     6    22   19
  3     7    30   28
  8     2    19   10

 **** K =11 ****

 -2     1    19   20
 -2     3    23   23
  0     4    21   16
  1     3    22   16
  0     0     0    0
```

SECTION II

THIOETHER LIGAND COMPLEXES OF THE GROUP VIB METALS, Cr(0), Mo(0), W(0).

SECTION II

INTRODUCTION

There have only been two studies on the Group VIB metal carbonyl complexes of bidentate dithioether ligands where the sulphur donor atoms are attached directly to substituted aryl rings. These involved a series of ligands of the type $RSCH_2CH_2SR$ where $R=p\text{-}XC_6H_4$[194] and the aryl dithioether ligands, 1,2-bis(methylthio)benzene and 1,8-bis(methylthio)naphthalene.[195]

The bulk of the research into complexes of both monodentate and bidentate thioether ligands has concentrated on ligands where the sulphur donor is attached to an aliphatic carbon chain (Table 1) and little has been done to study the effects of the substituents on the donor properties of the ligands.

The studies on the Group VIB metal carbonyl complexes of 3,4-bis(methylthio)toluene (bmtt) and 3,4-bis(ethylthio)toluene (bett) that are reported in this section, were therefore instigated for the following reasons:

(i) to study the chemical and physical properties of the complexes of these ligands so that direct comparisons can be made with other ligands;

(ii) to determine whether or not the aromatic ring that is attached to the thioether donor atoms, has any influence on the donor properties of the ligand; and

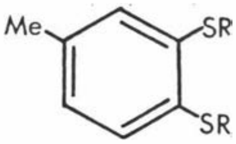
(iii) to carry out studies on the reactions of these ligands with the specific intention of synthesizing bridged-ligand complexes. These were not reported in the study of the complexes of 1,2-bis(methylthio)benzene and 1,8-bis(methylthio) naphthalene.[195]

TABLE 1

GROUP VIB METAL CARBONYL COMPLEXES OF THIOETHER LIGANDS

LIGAND TYPE	LIGAND SUBSTITUENTS	REFERENCES
	n = 2	
$RS(CH_2)_nSR$	R = Me	196-198
	R = Et	198, 199
	R = t-Bu	194,198,200,201, 260
	R = $p-XC_6H_4$	194
	n = 3	
	R = t-Bu	200, 202
	n = 4	
	R = Et	198
	n = 6	
	R = Me	198
R_1SR_2	R_1= Me, R_2= $PhCH_2$	198
	R_1= Et, R_2= $PhCH_2$	203
	R_1= Ph, R_2= $PhCH_2$	204
	R_1= Ph, R_2= Ph	204, 205
	R_1= $PhCH_2$, R_2= $PhCH_2$	204
	R_1= Et, R_2= Et	203, 204, 186
	R_1= Me, R_2= Me	186, 205
	R_1= $(CH_2=CH-)$= R_2	186
	R_1= CH_3, R_2= (CH_2Cl)	186
	R_1=$(Ph)(CH_3)CH-$, R_2=CH_3	206
$o-C_6H_4(SR)_2$	R = Me	195
$1,8-(C_{10}H_6)(SR)_2$	R = Me	195
Tetrakis(thioalkyl)- olefins		207

FIGURE 1



R = Me; 3,4-bis[methylthio]toluene [bmtt]
R = Et; 3,4-bis[ethylthio]toluene [bett]

Most of the studies on the Group VIB metal carbonyl complexes of thioether ligands (Table 1), have been reported since this work was started.

There have been very few investigations into the Group VIB metal carbonyl complexes of mixed sulphur-nitrogen donor ligands (Table 2) and only two of these studies have involved ligands with both thioether sulphur and nitrogen donor atoms. With all of these ligands, it is not possible to form chelated-ligand complexes and bridged-ligand complexes have not been reported. Consequently, nothing is known about the chemical and spectroscopic properties of the chelated and bridged-ligand carbonyl complexes of mixed sulphur-nitrogen donor ligands.

Complexes of the following ligands, which contain both nitrogen and thioether sulphur donor atoms, are studied in this section.

LIGAND NAME	ABBREVIATION
2-ETHYLTHIOETHYLAMINE	etea
2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE	tbmp
2-METHYLTHIO-2-IMIDAZOLINE	mti
2-METHYLMERCAPTOBENZIMIDAZOLE	mmbi
2-METHYLTHIOANILINE	mta

The reactions of these ligands have also been investigated in order to complement the studies on the Cu(II) complexes of sulphur-nitrogen ligands (Section I). Information on the metal coordinating sites in these ligands can be more conveniently obtained from metal carbonyl complexes using infrared spectroscopy and nuclear magnetic resonance spectroscopy, as probes.

TABLE 2

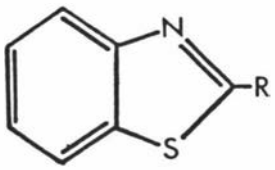
COMPLEXES OF SULPHUR-NITROGEN DONORS

LIGAND TYPE	BONDING MODE	REFERENCES
Alkylthiocyanates	Cr-N (X-rayed)	208
RSCN	M-N	209
Thiazolidine-2-thione $S=\overline{CNHCH_2CH_2S}$	M-thione(S)	210
Thiomorpholin-3-one $\overline{S-CH_2CH_2NHCOCH_2}$	M-S	211
Benzothiazole (R=H) a	M-N	212
2-methylbenzothiazole ($R=CH_3$) a	Cr-S, Cr-N† W-S, W-N	213
Isothiazole b	Cr-N, W-N Mo-N, Mo-S	213
Sulphurdiimines R-N=S=N-R	Mo-N⌖	214
5,6-dimethyl-2,1,3-benzothiadiazal c	M-N⌖	214

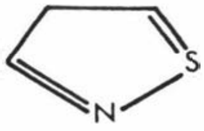
NOTES: -bonding modes deduced from spectroscopic studies except where indicated,

† linkage isomers

⌖ in solution, the metal "glides" along N=S=N system.



a



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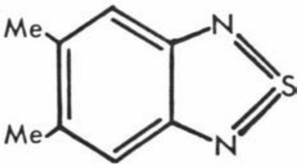


c

CHAPTER 1

BRIDGED-LIGAND COMPLEXES OF 3,4-BIS(METHYLTHIO)TOLUENE (bmtt) AND 3,4-BIS(ETHYLTHIO)TOLUENE (bett)

Bridged-ligand complexes of the Group VIB metal carbonyls (M=Cr,Mo,W), consist of two $M(CO)_5$ groups that are "bridged" by a bidentate ligand. This type of complex is generally synthesized in the reaction

$$2M(CO)_5THF + L \longrightarrow [(CO)_5M \leftarrow L \rightarrow M(CO)_5]$$

the $M(CO)_5THF$ being synthesized by the ultraviolet irradiation of $M(CO)_6$ in tetrahydrofuran (THF) (Appendices). The bridged-ligand complexes are designated as $[M(CO)_5]_2L$ and it is implied that L is a bidentate ligand. Complexes of the type $M(CO)_5L$ (see Chapter 3) are also referred to in this work.

The bridged-ligand complexes $[M(CO)_5]_2$bmtt (M=Cr,W) and $[M(CO)_5]_2$bett (M=Cr,W) that are discussed in this Chapter, were generally isolated from specific attempts to synthesize the chelated-ligand complexes $M(CO)_4$bmtt and $M(CO)_4$bett respectively (Chapter 2). The formation of both types of complex under the reaction conditions meant that careful and time-consuming separations, using column chromatography, were required. Subtle solubility differences and subtle differences in the behaviour of the complexes on these columns added to the difficulties in their purification.

Bridged-ligand complexes were not formed in the reactions involving molybdenum carbonyls.

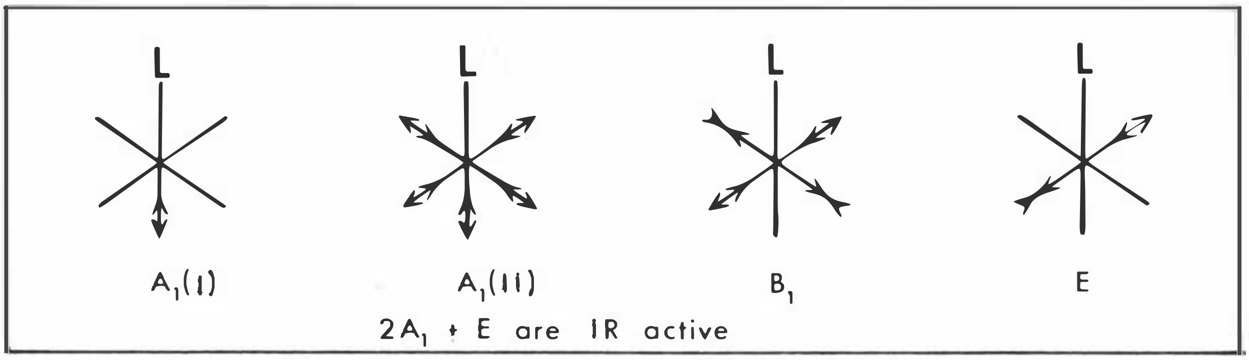
1.1 INFRARED SPECTRA (CARBONYL STRETCHING ABSORPTIONS)

Although the infrared and Raman-active carbonyl stretching modes can be theoretically derived from group theory, the assignment of these modes is not straightforward. Hence the spectral assignments are usually based on the arguments of Orgel[215], Cotton and Kraihanzel[216] and other workers.[217]

The CO stretching modes that are expected for C_{4v} $M(CO)_5L$ complexes are shown in Figure 2. The bridged-ligand complexes that are discussed in this Chapter can be regarded as being $M(CO)_5L$ complexes when the CO frequencies are being considered, although because of the asymmetry of the ligands bmtt and bett, the complexes will actually have symmetries lower than C_{4v}.

FIGURE 2

$M(CO)_5L$ CARBONYL STRETCHING MODES



Three infrared-active absorptions are expected for complexes of C_{4v} symmetry, but because the asymmetry of the ligands lifts the selection rules, the B_1 mode becomes weakly infrared-active and four absorptions are normally observed.[218] This asymmetry can also lead to a splitting of the E mode and this is observed in the spectrum of $[W(CO)_5]_2$bmtt in nitromethane (Figure 3a). The B_1 mode in this spectrum has not been resolved, but in some cases it is possible, (e.g. for the series of $M(CO)_5SPR_3$ complexes), to observe five absorptions.[219]

TABLE 3

ν(CO) ABSORPTIONS FOR $[M(CO)_5]_nL$ COMPLEXES

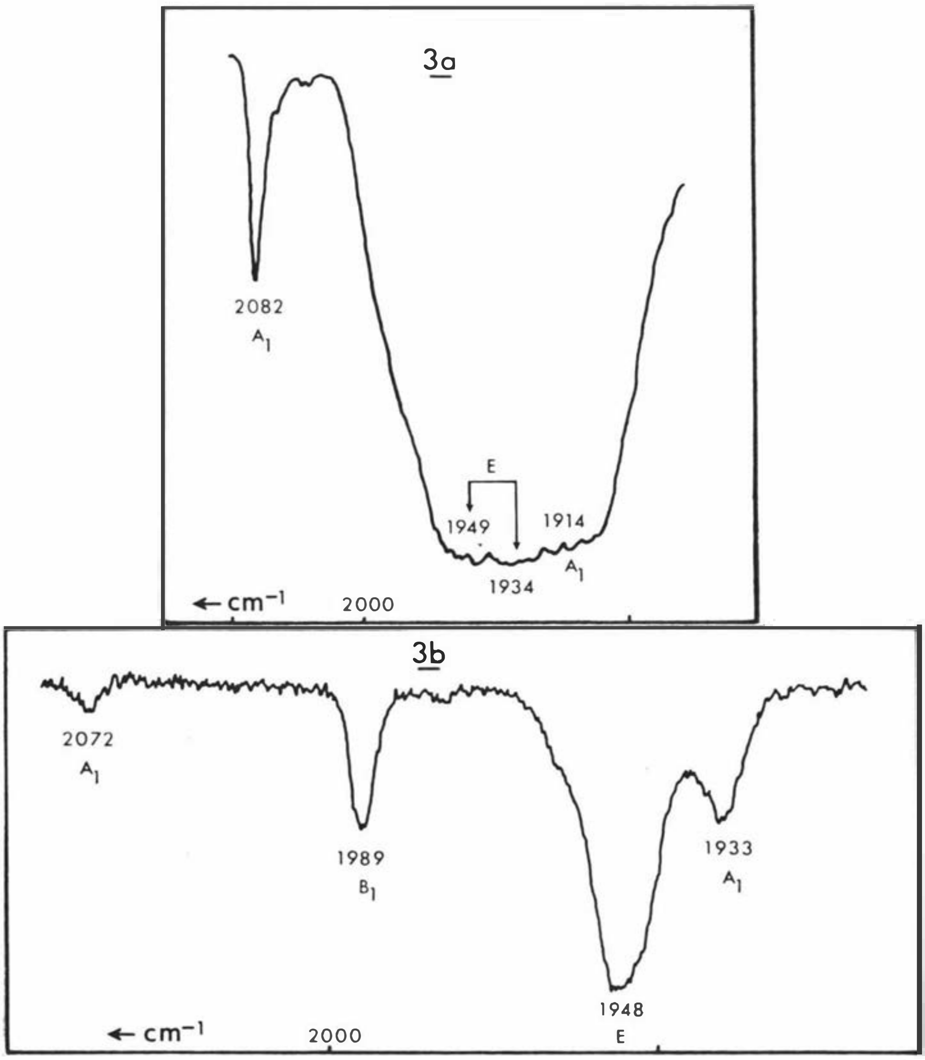
COMPLEX	A_1(II)/cm^{-1}	B_2	E	A_1(I)	SOLVENT
$[Cr(CO)_5]_2$bmtt	2072(w)	1989(w)	1948(s)	1933(m)	a
$[Cr(CO)_5]_2$bett	2076(w)	1990(ms)	1948(s)	1938(sh)	a
$[W(CO)_5]_2$bmtt	2065(w)	1987(w)	1942(s)	1947(sh)	a
$[W(CO)_5]_2$bmtt	2082(m)	n.o.	1949(vs) 1934(vs)	1914(vs)	b
$[W(CO)_5]_2$bett	2074(w)	1986(w)	1947(s)	1936(sh)	a
$Cr(CO)_5C_6F_5SEt$	2073(m)	†	1950(vs)	1954(s-sh)	a
$W(CO)_5C_6F_5SEt$	2079(m)	†	1948(vs)	1942(sh)	a

NOTES:
- a = cyclohexane; b = nitromethane,
- w = weak; m = medium; s = strong; v = very; sh = shoulder,
- n.o. = not observed,

† intense $M(CO)_6$ peak in this region.

FIGURE 3

IR Spectra - $[M(CO)_5]_2$bmtt Complexes



3a - M = W, in nitromethane

3b - M = Cr, in cyclohexane

The carbonyl stretching absorptions for the bridged-ligand complexes $[M(CO)_5]_2L$ (M=Cr,W; L=bmtt,bett) are given in Table 3 and a typical spectrum (recorded in cyclohexane solution) is shown in Figure 3b. The spectra are normal for this type of complex.[194, 198]

For the complex $[W(CO)_5]_2$bmtt, and B_1 mode is observed in cyclohexane solution but not in nitromethane and this appears to be due to poorer resolution in the latter, more polar solvent. It is also observed for this complex that the A_1(I) mode undergoes a significant (33 cm $^{-1}$) shift to lower frequencies in nitromethane and this is consistent with previous observations for bridged-ligand complexes[194] . Less significant shifts are observed for the A_1(II) and E modes. The effects of solvent polarities on the infrared spectra of carbonyl complexes have been discussed by Braterman[220] and these can be related to interactions between solvent local multipoles and permanent dipoles in the carbonyl complex.

1.2 FORCE CONSTANT CALCULATIONS

The force constant of a bond is a measure of the attractive forces between the atoms participating in the bond and by definition is related to the bond order. Thus as the bond order increases, the force constant for that bond also increases.[129]

The calculation of approximate CO force constants from the carbonyl stretching frequencies of octahedral metal carbonyl complexes, has been the centre of controversy ever since Cotton and Kraihanzel published their approximate force constant method in 1962[216] . Much of the controversy has been related to the assumptions that are made in developing the approximate secular equations upon which the calculations are based. The assumptions are:

i) interactions between CO stretching and other deformations of the molecules are neglected;

ii) no attempts are made to correct for anharmonicity; and

iii) approximations relating the stretch-stretch interaction constants must be made.

"Exact" calculations can be made where these three factors are taken into account, but either detailed isotopic enrichment data is needed or calculations employing iterative procedures must be carried out.[221] Although there may be differences between the absolute values of the force constants calculated by the "approximate" method and those calculated using the "exact" methods, the relative trends indicated are similar and the qualitative use of data calculated by the "approximate" method appears to be justified.[220]

Other factors such as solvent and environmental effects, differences in metal electronegativities and orbital following effects must also be taken into account.[220] The first two factors can be eliminated by ensuring that the force constants are not calculated from spectra that have been measured in solvents of widely differing properties and that force constants are compared within a series of complexes of the same metal. Although the quantitative effects of orbital following in the CO bond are largely unknown, it is apparent that the "real" force constants will be lower than the calculated values and that comparisons should not be made between complexes of widely differing stereochemistries.[220]

The approximate CO force constants that are presented in Table 4 for the $[M(CO)_5]_2L$ (M=Cr,W; L=bmtt,bett) complexes were calculated from the approximate secular equations presented by Cotton and Kraihanzel[216]. The data for other complexes is also presented.

INTERPRETATION OF FORCE CONSTANT DATA

a) Metal-Ligand and Metal-CO Bonding Schemes

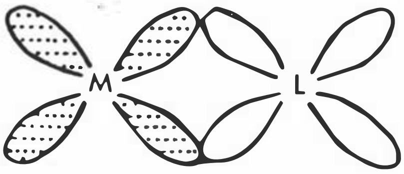
Using a simple, qualitative, molecular orbital approach,[222] the M-L and M-CO bonding in carbonyl complexes can be depicted as shown in Figure 4a and Figure 4b.

FIGURE 4a

σ-Bond

Empty M_{Eg} orbital,
Full L orbital.

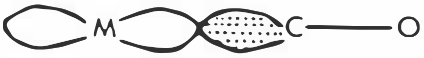
π-Bond



Full $M_{T_{2g}}$ orbital,
Empty L d-orbital.

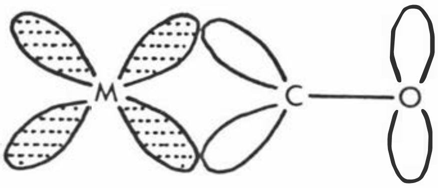
FIGURE 4b

σ-Bond



Empty M_{Eg} orbital,
Lone-pair CO orbital.

π-Bond



Full $M_{T_{2g}}$ orbital,
Empty CO π*-orbital.

b) General Effects of Metal-Ligand Bonding

With reference to these bonding schemes, it can be deduced that the bonding in the carbonyl groups of these complexes will be influenced in several ways by changes in the Metal-Ligand bonding:

i) A π-accepting ligand will strengthen the C-C bond(s) trans to it. Hence the trans CO force constant, K_1, will increase with increasing π-acceptance. This effect will be extended to the cis carbonyls, but to a lesser extent.[216]

ii) A good σ-donor ligand will increase metal back-donation to the carbonyl groups by an inductive mechanism. As this applies equally to all of the carbonyl groups, K_1 and K_2 will decrease with increasing σ-donation.

iii) Ligand σ-donation also has two directional effects. A σ-trans effect lowers K_1 by decreasing carbonyl ⟶ metal σ-donation[223] and the Fenske direct-donation effect which decreases K_2[224]. Various attempts have been made to quantify the σ and π bonding components of the metal-ligand bond using carbonyl force constant data[225,226]. These attempts can not be really justified however, because so little is known about the relative effects of these bond components on the CO force constants.

As the trans CO force constant (K_1) is affected the most by changes in metal-ligand bonding,[216] the following discussion concentrates on comparisons between K_1 for the complexes that are being considered.

c) Discussion

i) Chromium Complexes

There are no obvious trends in both the cis and trans force constants for $[Cr(CO)_5]_2L$ and $Cr(CO)_5L$ complexes where L is a thioether donor ligand, except for the complex $Cr(CO)_5C_6F_5SEt$. Although this complex was quite unstable and could not be isolated (Appendix II), its infrared spectrum, from which these force constants were calculated, was successfully recorded. While there do not appear to be any significant differences between the complexes where L is an aryl thioether (bmtt, bett, o-bmtb, pte and $S(Ph)_2$) and where L is an alkyl thioether (dto, bms, $S(Et)CH_2Ph$ and $S(Et)_2$), the effect of the strongly electronegative pentafluorophenyl group of C_6F_5SEt is readily apparent. The trans force constant (K_1) is significantly higher than previously observed for $Cr(CO)_5$thioether complexes and it is comparable to the values that are normally

TABLE 4

COTTON-KRAIHANZEL FORCE CONSTANTS

$[Cr(CO)_5]_nL$ COMPLEXES

COMPLEX	DONOR	$K_1 (N.m^{-1})$	$K_2 (N.m^{-1})$	REFERENCE
$Cr(CO)_5C_6F_5SEt$	S	1563	1601	This Work
$Cr(CO)_5dmpe$	P	1556	1578	† 234
$Cr(CO)_5P(Ph)_3$	P	1551	1585	235
$[Cr(CO)_5]_2bett$	S	1538	1600	This Work
$[Cr(CO)_5]_2pte$	S	1533	1600	† 194
$Cr(CO)_5S(Ph)_2$	S	1532	1597	† 204
$[Cr(CO)_5]_2o\text{-}bmtb$	S	1532	1597	236
$[Cr(CO)_5]_2dto$	S	1530	1592	† 198
$Cr(CO)_5bms$	S	1530	1592	† 198
$Cr(CO)_5S(Et)CH_2Ph$	S	1529	1584	203
$[Cr(CO)_5]_2bmtt$	S	1529	1598	This Work
$Cr(CO)_5S(Et)_2$	S	1528	1581	203
$Cr(CO)_5mta$	S	1528	1590	This Work
$Cr(CO)_5NH_2(C_6H_{11})$	N	1508	1577	235
$Cr(CO)_5NH_2(C_6H_5)$	N	1503	1582	237
$Cr(CO)_5SP(Me)_3$	S	1494	1590	† 198

NOTES: - all spectra recorded in saturated hydrocarbon solvents

† Force constants calculated from published data

- errors are ± 3 $N.m^{-1}$ in K_1 and K_2 except for $Cr(CO)_5C_6F_5SEt$ (± 5 $N.m^{-1}$)

TABLE 4 (continued)

COTTON-KRAIHANZEL FORCE CONSTANTS

$[W(CO)_5]_nL$ COMPLEXES

COMPLEX	DONOR	$K_1 (N.m^{-1})$	$K_2 (N.m^{-1})$	REFERENCE
$W(CO)_5[PPh_2(OBu)]$	P	1571	1587	226
$W(CO)_5P(Ph)_3$	P	1557	1589	235
$W(CO)_5C_6F_5SEt$	S	1556	1590	This Work
$[W(CO)_5]_2bmtt$	S	1556	1595	This Work
$[W(CO)_5]_2o\text{-}bmtb$	S	1556	1587	236
$W(CO)_5PhSH$	S	1537	1596	226
$[W(CO)_5]_2m\text{-}bmtb$	S	1533	1576	236
$[W(CO)_5]_2bett$	S	1533	1594	This Work
$[W(CO)_5]_2dto$	S	1531	1590	† 198
$W(CO)_5mta$	S	1526	1589	This Work
$W(CO)_5(PhNH_2)$	N	1513	1580	226
$W(CO)_5NH_2(C_6H_{11})$	N	1513	1572	226

NOTES: - as for $[Cr(CO)_5]_nL$ complexes

- errors for $W(CO)_5C_6F_5SEt$ are ±5 $N.m^{-1}$ in K_1 and K_2

observed for phosphine donors (Table 4). In this type of complex, an increase in K_1 will be observed because the electronegativity effect will increase, by an inductive mechanism, Cr $\longrightarrow$ S π- donation and decrease S $\longrightarrow$ Cr σ- donation. The opposite of this effect is shown in the complex $Cr(CO)_5SP(Me)_3$[219] for which K_1 (1494 ± 3 $N.m^{-1}$) is similar to that of amine donors where no M $\longrightarrow$ N π- interactions are possible.[226] A crystallographic study on this complex[227] has shown that there is little or no Cr $\longrightarrow$ S π- donation and this is thought to be due to the sulphur atom of $SPMe_3$ having a slight excess of negative charge.[199] None of these effects are apparent then, in the complexes $[Cr(CO)_5]_2L$ where L is bmtt and bett and so from these results, the net basicities of these ligands <u>appear</u> to be similar to those of other thioether ligands when they are bound to chromium (O).

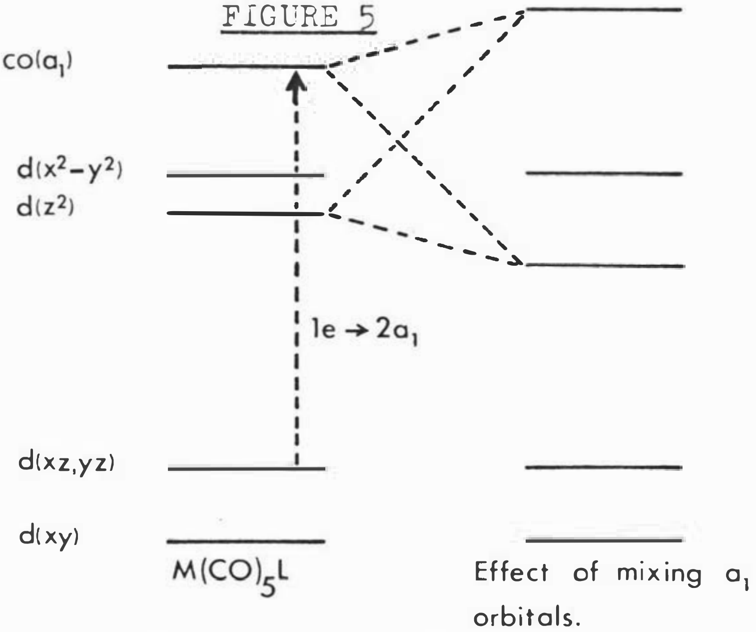
ii) <u>Tungsten Complexes</u>

It appears from the results presented in Table 4, that there is a greater π- component and/or a smaller σ- component in the W —— S bond for the ligands bmtt, o-bmtb and C_6F_5SEt (as observed for the Cr complex) compared to the ligands m-bmtb, bett, PhSH and dto. For the former group of ligands, the <u>trans</u> CO force constants are comparable to K_1 for triphenylphosphine which suggests that the net basicities of these ligands are similar to the phosphine donor in these complexes.

1.3 <u>ELECTRONIC SPECTRA</u>

The basis for identifying the d-d and charge transfer transitions in $M(CO)_5L$ and <u>trans</u> - $M(CO)_4L_2$ complexes was recently proposed by Braterman, Milne and Walker[228] in a detailed study of a series of these complexes. Assuming that the ligand L is a poorer π-acceptor and a better σ-donor than CO, the molecular orbital diagram for $M(CO)_5L$ complexes can be derived (Figure 5). The possible mixing of $d(\sigma^*)$ and vacant ligand orbitals can be ignored where the field of I is small.

FIGURE 5



The nature of the metal and the ligand's net donor ability will determine the energy of the $M(d) \longrightarrow CO(\pi^*)$ charge transfer transitions. Braterman _et al_ observed that the frequencies of the lowest energy charge transfer band ($1e \rightarrow 2a_1$) follow the general sequences:

i) phosphite > phosphorous triamide > phosphine

and ii) Cr > Mo > W

These observations were used as the basis for assigning the lowest energy charge transfer absorption as being a transition from metal orbitals. Transitions of pure d-d character were identified by their loss of intensity on cooling.

It is now recognised from this and earlier studies that[229,230] it is the lowest energy charge transfer transition ($1e \rightarrow 2a_1$) which is sensitive to the nature of the ligands. Stronger metal-ligand interactions can naively be expected to stabilize the d-orbitals with a resulting increase in the energy of the $1e \rightarrow 2a_1$

transition. In general then, the energy of this transition will decrease in the order M-CO > M-P$_{\text{ligand}}$ > M-S$_{\text{ligand}}$ > M-N$_{\text{ligand}}$

SPECTRA AND ASSIGNMENTS FOR $[M(CO)_5]_2L$

Typical spectra for the $[Cr(CO)_5]_2L$ and $[W(CO)_5]_2L$ (L=bmtt, bett) complexes are shown in Figures 6a and 6b and the results for these complexes are given in Tables 5a and 5b. Where possible, tentative assignments for the d-d, 1e → $2a_1$ and Singlet ⟶ Triplet d-d transitions (tungsten complexes only) have been made. For the chromium complexes, the d-d and 1e ⟶ $2a_1$ transitions appear to be under the same low-energy envelope while for the tungsten complexes they occur as distinct absorptions in ethanol solution. The d-d and 1e ⟶ $2a_1$ absorptions in the latter complexes have been assigned on the basis of energy considerations. From Figure 5 it is apparent that the d-d absorptions will occur at lower energies than the 1e ⟶ $2a_1$ C.T. transition, although both absorptions will lie close to each other.[228]

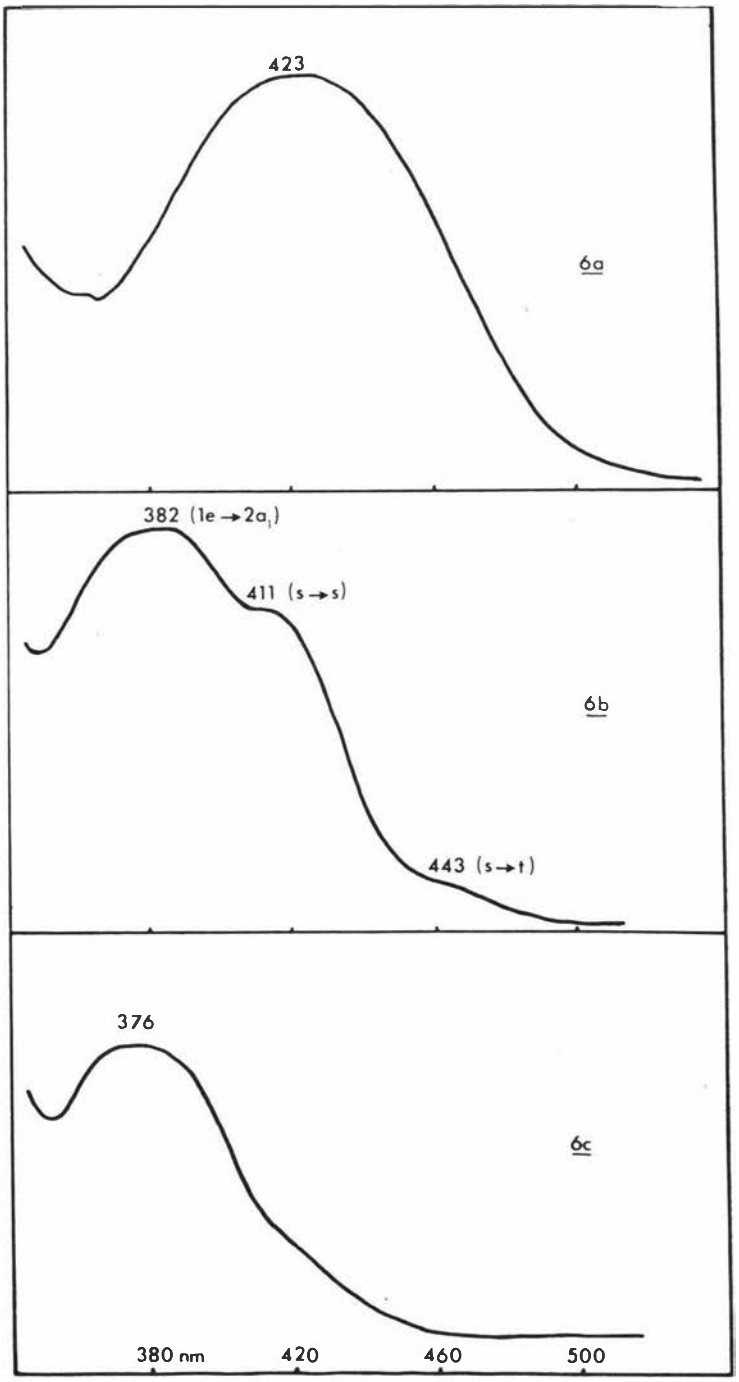
DISCUSSION

i) Chromium Complexes

The 1e ⟶ $2a_1$ C.T. transitions for $[Cr(CO)_5]_2$bmtt and $[Cr(CO)_5]_2$bett are compared with those of other $Cr(CO)_5L$ complexes of phosphorus, sulphur and nitrogen donors, in Table 6a. The results for these complexes suggest that Cr-Ligand interactions are weaker for bmtt, bett and 2-methylthioaniline (which appears to bind via the thioether only - see Chapter 3) than for the complexes of the alkyl thioethers (e.g. 3,8-dtd, dto and $S(Et)_2$) where the thioether donor is attached to an aliphatic carbon chain. For the former complexes the Cr—S interaction appears to be comparable in its strength to the Cr—Ligand interactions of amine ligands and where L is

FIGURE 6

Electronic Spectra - $[M(CO)_5]_2$bett Complexes



6a - M = Cr, in Abs. EtOH

6b - M = W, in Abs. EtOH

6c - M = W, in n-hexane

TABLE 5a

ELECTRONIC SPECTRA FOR Cr COMPLEXES

COMPLEX	ABSORPTION (nm)	ϵ (l.mol.$^{-1}$cm^{-1})	Assignment
$[Cr(CO)_5]_2$bmtt	252	16455	
	300	3269	
	445	1664	$1e \rightarrow 2a_1$/d-d
$[Cr(CO)_5]_2$bett	268	16503	
	288	7552	
	423	3161	$1e \rightarrow 2a_1$/d-d

TABLE 5b

ELECTRONIC SPECTRA FOR W COMPLEXES

COMPLEX	ABSORPTION (nm)	ϵ (l.mol.$^{-1}$cm^{-1})	ASSIGNMENT
$[W(CO)_5]_2$bmtt	265	18372	
	277(sh)	7984	
	298(sh)	6279	
	395 [274]	4186 [3921]	$1e \rightarrow 2a_1$
	417 [ca382]	4380 [3905]	d-d (s-s)
	442(sh)	953	d-d (s-t)
$[W(CO)_5]_2$bett	265	18846	
	281(sh)	7923	
	293(sh)	6385	
	306(sh)	4846	
	382 [ca376]	3269 [4141]	$1e \rightarrow 2a_1$
	411 [ca376]	2677 [4141]	d-d (s-s)
	443(sh)	430	d-d (s-t)

NOTES:

- all spectra recorded for Abs. EtOH solutions except where given in parentheses ([ ], spectra recorded in n-hexane),
- sh = shoulder; extinction coefficients are approximate,
- (s—s) denotes a singlet → singlet transition,
- (s—t) denotes a singlet → triplet transition

TABLE 6a

$1e \rightarrow 2a_1$ C.T. TRANSITIONS: $[Cr(CO)_5]_nL$ COMPLEXES

COMPLEX	$1e \rightarrow 2a_1$ (nm)	SOLVENT	REFERENCE
L = P donor			
$Cr(CO)_5P(OPh)_3$	329	Hexane	230
$Cr(CO)_5P(NMe_2)_3$	340	Hexane	230
$Cr(CO)_5P(Ph)_3$	359	Hexane	230
L = S donor			
$Cr(CO)_5S(Et)_2$	393	Hexane	203
$[Cr(CO)_5]_2(3,8\text{-dtd})$	395	Chloroform	198
$Cr(CO)_5S(Et)CH_2Ph$	395	Hexane	203
$[Cr(CO)_5]_2$tmdto	396	Ethanol	194
$[Cr(CO)_5]_2$dto	398	Ethanol	198
$[Cr(CO)_5]_2$bett	423	Ethanol	This Work
† $Cr(CO)_5SPMe_3$	424	Ethanol	198
	424	Hexane	This Work
† $Cr(CO)_5SP(Me_2Ph)$	425	Hexane	This Work
$[Cr(CO)_5]_2$pte	430	Ethanol	194
$Cr(CO)_5$mta	437	Ethanol	This Work
$[Cr(CO)_5]_2$bmtt	445	Ethanol	This Work
$[Cr(CO)_5]_2$nte	450	Ethanol	194
L = N donor			
$Cr(CO)_5$bi	405	Ethanol	This Work
$Cr(CO)_5$mmbi	406	Ethanol	This Work
$Cr(CO)_5$mti	407	Ethanol	This Work
$[Cr(CO)_5]_2$en	410	Ethanol	198
$[Cr(CO)_5]_2$dad	419	Chloroform	198
$Cr(CO)_5HNC_5H_{10}$	426	Cyclohexane	230
L = S-N donor			
$[Cr(CO)_5]_2$etea	412	Ethanol	This Work

NOTES: † Samples were gifts from Drs. E.W. Ainscough & A.M. Brodie

TABLE 6b

$1e \rightarrow 2a_1$ C.T. TRANSITIONS; $[W(CO)_5]_nL$ COMPLEXES

COMPLEX	$1e \rightarrow 2a_1$ (nm)	SOLVENT	REFERENCE
L = P donor			
$W(CO)_5P(OMe)_3$	343	Mch:ip	228
$W(CO)_5P(NMe_2)_3$	348	Mch:ip	228
$W(CO)_5PBu^n_3$	351	Mch:ip	228
L = S donor			
$[W(CO)_5]_2$tmdto	368	Chloroform	198
$[W(CO)_5]_2$dto	371	Chloroform	198
$[W(CO)_5]_2$(2,9-dtd)	372	Chloroform	198
$W(CO)_5SPMe_3$	378	Ethanol	198
$[W(CO)_5]_2$bett	382	Ethanol	This Work
$W(CO)_5$mta	ca392	Ethanol	This Work
$[W(CO)_5]_2$bmtt	395	Ethanol	This Work
$[W(CO)_5]_2$m-bmtb	ca405	Ethanol	This Work†
L = N donor			
$W(CO)_5$mmbi	392	Ethanol	This Work
$W(CO)_5$bi	395	Ethanol	This Work
$[W(CO)_5]_2$en	397	Ethanol	198
$W(CO)_5$mti	398	Ethanol	This Work
$[W(CO)_5]_2$dad	406	Benzene	198
L = S-N donor			
$[W(CO)_5]_2$etea	390	Ethanol	This Work

NOTES: - Mch:ip = methylcyclohexane:isopentane,

† sample prepared by method of Ainscough, Brodie and Mathews,[236]

- complexes of mta, bi, mmbi, mti and etea are discussed in Chapter 3.

a substituted phosphine sulphide ligand, SPR_3. These results appear to disagree with the observations based on the calculation of force constants. It is apparent though, that direct perturbations of the metal d-orbitals will be more sensitive to changes in metal-ligand bonding than the effects of such changes on the more distant C —— O bonding. Hence for these chromium complexes more significant differences between the ligand types are observed in the electronic spectra. The sensitivity of the visible absorption maximum to changes in metal-ligand bonding has also been demonstrated for a series of bridged ligand complexes of $RSCH_2CH_2SR$, where R is p-XC_6H_4.[194] In this study it was shown that where X is an electron withdrawing substituent such as $-NO_2$, the $1e \rightarrow 2a_1$ transition was red-shifted by up to 40 nm compared to the spectra where X is an electron donating group such as $-NMe_2$.

ii) Tungsten Complexes

The $1e \rightarrow 2a_1$ C.T. transitions for $[W(CO)_5]_2$bmtt and $[W(CO)_5]_2$bett are compared with those of other $W(CO)_5L$ chromophores in Table 6b.

The results are in agreement with the observations that were made for the analogous chromium complexes in that the $1e \rightarrow 2a_1$ C.T. transition energies are lower for bmtt and bett than in complexes of alkyl thioether ligands. The ligands 2-methylthioaniline (mta) and 1,3-bis(methylthio)benzene (m-bmtb) which also have aromatic rings attached to the thioether donor, exhibit a similar trend. The consistent results for both the chromium and tungsten complexes enable the ligands to be placed in the following order of decreasing net M —— L bond strengths;

$$\text{tmdt}_0 \sim \text{dto} > \text{bett} > \text{mta} \sim \text{bmtt}$$

When the spectra of the tungsten complexes of bmtt, bett and m-bmtb are recorded in non-polar hydrocarbon solvents, significant shifts in the visible maxima occur and as a consequence, the resolution is poorer (Figure 6c). Although the d-d absorptions should be largely insensitive to changes in solvent polarity,[231,232] the observed shifts combined with the relatively high intensities of the absorptions in both the chromium and tungsten complexes, suggest that they have acquired some charge transfer character. This could occur by a ligand-metal orbital mixing mechanism.[229]

1.4 NUCLEAR MAGNETIC RESONANCE STUDIES

^1H nmr Spectra

It is generally observed that the chemical shifts of protons in close proximity to electron donating groups such as sulphur and nitrogen, move downfield (i.e. to higher ppm) on complexation of the ligand. This effect is due to the withdrawal of electronic charge from the hydrogen nuclei. The ^1H nmr spectral results for the bridged-ligand complexes $[M(CO)_5]_2L$ (M=Cr, W and L=bmtt, bett) together with the data and assignments for the free ligands, are given in Table 7.

TABLE 7

^1H nmr DATA, $[M(CO)_5]_2L$ COMPLEXES OF bmtt, bett

COMPLEX	$-SCH_3$	$-SCH_2\overline{CH}_3$	$-SCH_2-$	$Ar-CH_3$	Ar-H
bmtt	2.05			2.02	6.9
† $[Cr(CO)_5]_2$bmtt	1.57			1.46	ca6.7
$[W(CO)_5]_2$bmtt	2.24			1.90	6.5
bett		1.18t(8)	2.81q(7)	2.22	6.8
$[Cr(CO)_5]_2$bett		0.96t(8)	2.57t(6)	1.83	6.5
$[W(CO)_5]_2$bett		0.92t(8)	2.81q(7)	2.00	6.7

NOTES:
- spectra recorded in C_6D_6,
- t = triplet; q = quartet; coupling constants are in parentheses (Hz),
- chemical shifts are ppm downfield from TMS,
- chemical shifts for aryl protons (Ar-H) are the centres of the observed multiplets

† complex decomposed

The results show that, except for $[W(CO)_5]_2$bmtt, the hydrogen nuclei adjacent to the thioether donors are effectively shielded on complexation to the bulky $W(CO)_5$ groups as upfield shifts in the resonance frequencies are observed.

^{13}C nmr Spectra

The ^{13}C nmr spectrum was recorded for $[W(CO)_5]_2$bmtt and this is discussed in Chapter 2 along with the spectra of the chelated-ligand complexes, $M(CO)_4L$ (M=Cr,W and L=bmtt, bett).

1.5 REACTIVITY STUDIES

The reactivity studies were designed to determine the ease with which the bridged-ligand complexes convert to the chelated ligand complexes and to determine the stability of the thioether metal bonding towards replacement by triphenylphosphine and triphenylphosphite. For the experiments, $[W(CO)_5]_2$bett was used and the experimental details are given in the Appendices.

i) Reflux $[W(CO)_5]_2$bett in n-hexane

The IR spectrum of the solution after about one hour of refluxing shows that the conversion

$$[W(CO)_5]_2\text{bett} \longrightarrow W(CO)_6 + W(CO)_4\text{bett}$$

has occurred. The six carbonyl-stretching frequencies that are assigned to $W(CO)_4$bett (Figure 7a) almost correspond to those observed for $Cr(CO)_4$bett (Chapter 2) for which the multiplicity (only four ν(CO) modes are expected) is postulated to be due to conformational isomerism. Only four peaks were observed in the spectrum (cyclohexane solution) of the photochemically synthesized $W(CO)_4$bett (Chapter 2).

The conversion of the bridged-ligand complex to a chelated-ligand complex was similarly observed for $[W(CO)_5]_2$dto, where dto is 3,6-dithiaoctane.[198]

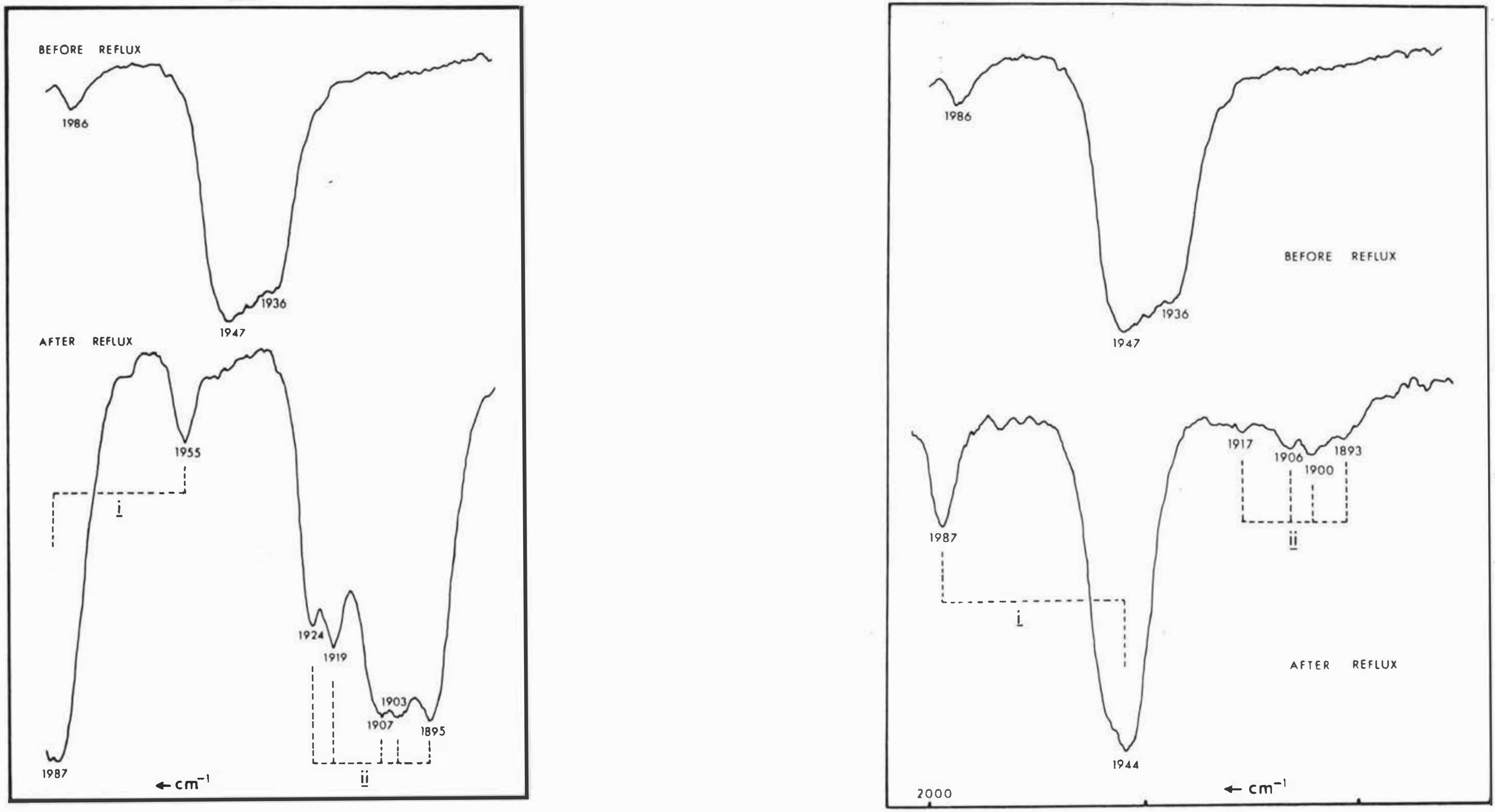
ii) Reflux $[W(CO)_5]_2$bett with excess Triphenylphosphine

After 2.5 hours of refluxing in cyclohexane, an IR spectrum

FIGURE 7

IR Spectra - $[W(CO)_5]_2$bett Reactivity Studies

7a 7b



Reflux in n-hexane

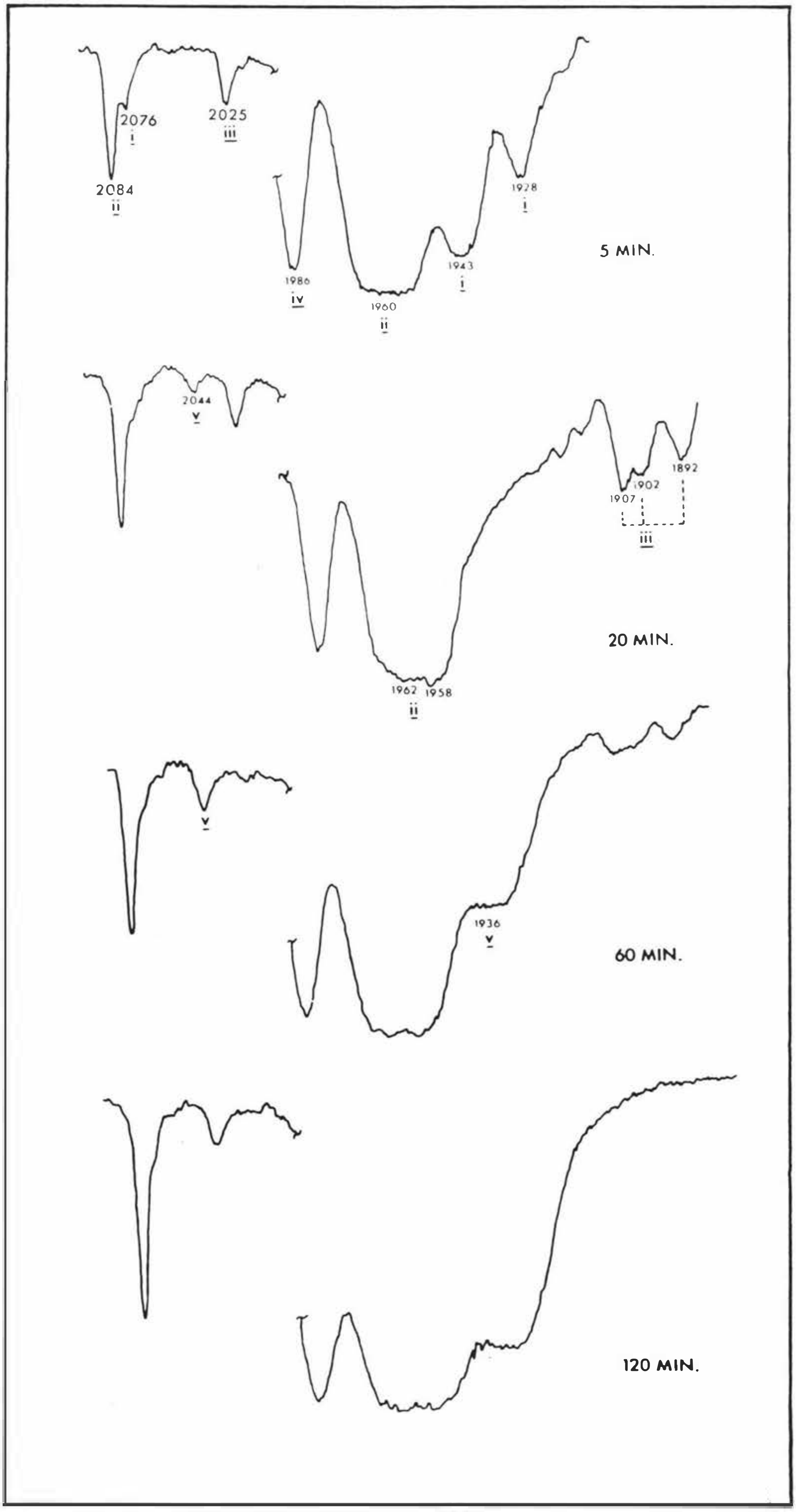
- species i is $W(CO)_6$
- species ii is $W(CO)_4$bett

Reflux with excess $P(Ph)_3$

- species i is $W(CO)_5P(Ph)_3$ [$W(CO)_6$ has increased 1987 cm^{-1} absorption intensity]
- species ii is $W(CO)_4$bett

Reflux with excess P(OPh)$_3$

7c



KEY TO FIGURE 7c

Species	Identity
i	$[W(CO)_5]_2$bett
ii	$W(CO)_5P(OPh)_3$
iii	$W(CO)_4$bett
iv	$W(CO)_6$
v	*cis*-$W(CO)_4[P(OPh)_3]_2$

On refluxing $[W(CO)_5]_2$bett with $P(OPh)_3$, two distinct processes are occurring:

a) Within the first 20 minutes, the complete breakdown of $[W(CO)_5]_2$bett occurs, via two competing pathways (below).

b) Over a period of 2 hours, the complete conversion of $W(CO)_4$bett to *cis*-$W(CO)_4[P(OPh)_3]_2$ occurs.

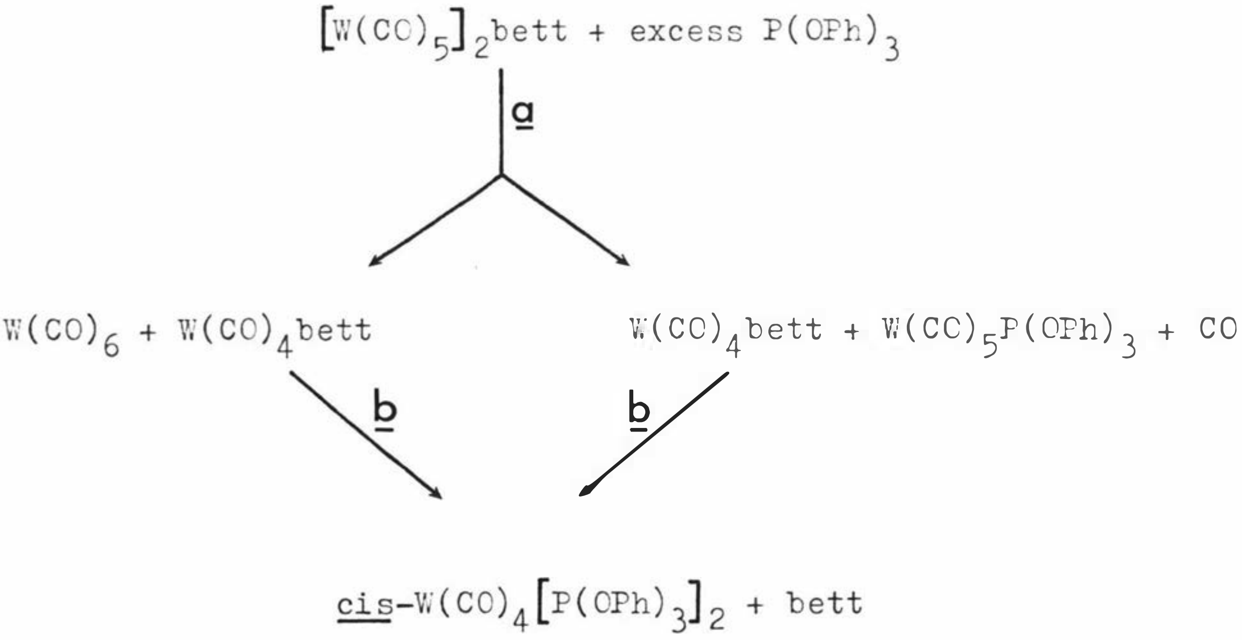


TABLE 8

^{1}H nmr SPECTRUM, REFLUX $[W(CO)_5]_2$bett WITH PPh_3

PROTONS	bett AFTER REFLUX	$W(CO)_4$bett	bett
$Ar-CH_3$	2.46	2.42	2.35
$-SCH_2C\underline{H}_3$	1.32, 1.45, 1.57 1.28, 1.40, 1.53	1.24, 1.35, 1.49	1.16, 1.20, 1.30, 1.35, 1.43, 1.47
$-SC\underline{H}_2-$	3.03, 3.14†	2.99, 3.07, 3.24 3.33	2.71, 2.75, 2.83, 2.86, 2.95, 2.98, 3.06, 3.09

NOTES: - spectrum recorded in $CDCl_3$; chemical shifts are ppm downfield from TMS,

† only two peaks can be distinguished above the noise.

The chemical shifts for bett after refluxing suggest that the ligand remains coordinated and that the tetracarbonyl complex that is apparent in the IR spectrum, is $W(CO)_4$bett.

and the ^1H nmr spectrum of the products indicated that the colourless solution contained $W(CO)_5PPh_3$, $W(CO)_4$bett and $W(CO)_6$. Figure 7b shows the IR spectra and the assignments while in Table 8, the ^1H nmr spectrum of the products is compared with the known spectra for the free ligand and $W(CO)_4$bett. The significance of these results is discussed below.

iii) Reflux $[W(CO)_5]_2$bett with excess Triphenylphosphite

The carbonyl complexes of $P(OPh)_3$ exhibit $\nu(CO)$ absorptions that are sufficiently removed from those of the analogous thioether complexes to enable unambiguous assignments to be made.

The products from this reaction were monitored by infrared spectroscopy at regular intervals and the spectra and their assignments are shown in Figure 7c. The results can be interpreted as outlined in the flow diagram accompanying Figure 7c and this is referred to in the following discussion.

DISCUSSION

The observed conversion of $W(CO)_4$bett to cis-$W(CO)_4[P(OPh)_3]_2$ in the presence of excess $P(OPh)_3$ is consistent with $P(OPh)_3$ being a stronger ligand than $P(Ph)_3$[228] as the analogous conversion was not observed in the presence of an excess of the latter ligand. This supports the observation by Ainscough *et al*[198] that chelated dithioether ligands are reasonably stable towards replacement by $P(Ph)_3$. Detailed kinetic and substitution studies on the replacement of chelated dithioether ligands (such as $MeSCH_2CH_2SMe$ and $tBuSCH_2CH_2StBu$) by phosphite ligands, indicate that substitution proceeds largely through a ring-opening mechanism.[197,201,202]

1.6 MASS SPECTRAL STUDY

Although the mass spectra of metal carbonyl complexes appear, in principle, to be a convenient means of determining the composition of a sample, an inherent danger is the assumption that the highest mass peak observed in the spectrum is a direct result of ionisation of the molecular species in the sample.[233] This is particularly evident in the mass spectrum of $[W(CO)_5]_2$-bmtt which indicated that the apparent parent molecular ion has the composition $[W(CO)_4bmtt]^+$. This ion undergoes successive CO loss in the normal manner[233] to yield the ions $[W(CO)_3bmtt]^+$, $[W(CO)_2bmtt]^+$, $[W(CO)bmtt]^+$ and $[W\ bmtt]^+$. The instability of Group VIB carbonyl complexes under the conditions of volatilisation and electron bombardment that are employed in mass spectral studies, has also been observed for complexes of $RSCH_2CH_2SR$ ($R=p-XC_6H_4$)[194] and some monodentate bis-phosphine complexes, $M(CO)_5I$.[234]

The most unusual feature of the spectrum is the appearance of peaks due to the ions $[W(CO)_8]^+$ and $[W(CO)_7]^+$, although they are relatively lower in abundance than the highly abundant $[W(CO)_6]^+$ ion. A very weak feature at about m/e = 508 appears to be $W(CO)_5$bmtt, but the origin of this species is unknown. It may be present as an impurity in the sample of $[W(CO)_5]_2$bmtt but it is also possible that it could be formed from the decomposition of $[W(CO)_5]_2$bmtt in the mass spectrometer.

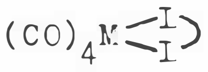
SYNTHESIS OF THE BRIDGED-LIGAND COMPLEXES

As these complexes were usually isolated in conjunction with the chelated-ligand complexes $M(CO)_4$bmtt and $M(CO)_4$bett, their syntheses are described in Chapter 2.

CHAPTER 2

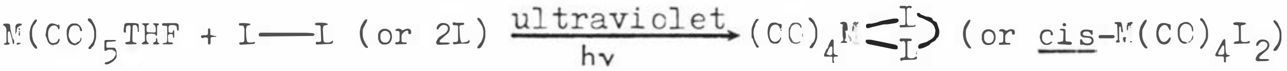
CHELATED-LIGAND COMPLEXES
OF
3,4-BIS(ALKYLTHIO)TOLUENE
(ALKYL=METHYL,ETHYL)

The Group VIB metal carbonyl, chelated-ligand complexes have the basic structure



$$(\mathrm{CO})_4\mathrm{M}\begin{smallmatrix}\mathrm{I}\\ \mathrm{I}\end{smallmatrix}$$

and these are analogous to <u>cis</u>-$M(CO)_4L_2$ complexes where L is a monodentate ligand. Both types are generally synthesized in the reaction,



$$\mathrm{M(CO)_5THF} + \mathrm{L{-\!\!-}L}\ (\text{or } 2\mathrm{L}) \xrightarrow[h\nu]{\text{ultraviolet}} (\mathrm{CO})_4\mathrm{M}\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\ (\text{or } \underline{\text{cis}}\text{-}\mathrm{M(CO)_4L_2})$$

but the accompanying formation of bridged-ligand complexes ($[M(CO)_5]_2L$) or <u>trans</u>-$M(CO)_4L_2$ if L is monodentate, requires the careful separation and purification of the products on silica-gel columns (see Introduction to Chapter 1). As the ligands that were used in this study are bidentate, the formation of the <u>trans</u> complexes was eliminated.

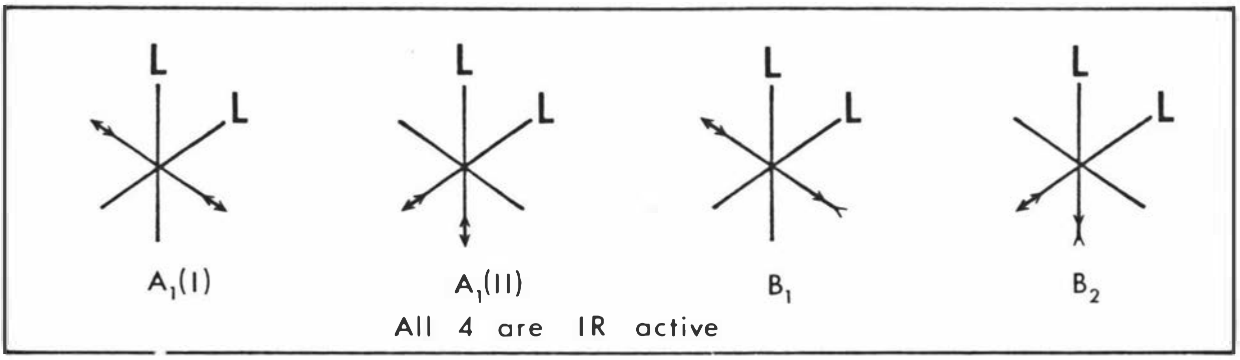
The chelated-ligand complexes that are discussed in Chapter 2, are given the general designation $M(CO)_4L_2$ and it is implied that L_2 is a bidentate ligand, such as bmtt or bett.

2.1 INFRARED SPECTRA (CARBONYL-STRETCHING ABSORPTIONS)

The stretching modes that are expected for C_{2v} cis-$M(CO)_4L_2$ complexes are shown in Figure 8 and the assignment of these modes follows from literature-presented arguments (see Chapter 1).

FIGURE 8

cis-$M(CO)_4L_2$ CARBONYL-STRETCHING MODES



The four IR-active absorptions that are predicted from group theory are generally observed in the spectra of chelated-ligand complexes of dithioether ligands[194,196,198] and in this respect the spectra of $Cr(CO)_4$bmtt, $W(CO)_4$bmtt and $W(CO)_4$bett are normal in cyclohexane solution. A typical spectrum is shown in Figure 9a. The spectra of $Cr(CO)_4$bett, $Mo(CO)_4$bett, $Mo(CO)_4$bmtt and $W(CO)_4$bett (synthesized by refluxing $[W(CO)_5]_2$bett in n-hexane:- see Chapter 1) though, are quite unusual in that an apparent splitting of at least one of the $\nu(CO)$ absorptions below 2000 cm^{-1} is observed. The spectrum of $Cr(CO)_4$bett is shown in Figure 9b and an example of the $Mo(CO)_4L_2$ complexes in Figure 9c. The spectral assignments are given in Table 9a for all of the chelated-ligand complexes.

The splitting of the carbonyl-stretching modes in the spectra of cis-$M(CO)_4L_2$ complexes has not been reported before and the spectra of the analogous $M(CO)_4$FDS complexes,[195] (M=Cr, Mo, W; FDS = o-bis(methylthio)benzene) were normal.

FIGURE 9

IR Spectra - M(CO)$_4$L$_2$ Complexes in Cyclohexane

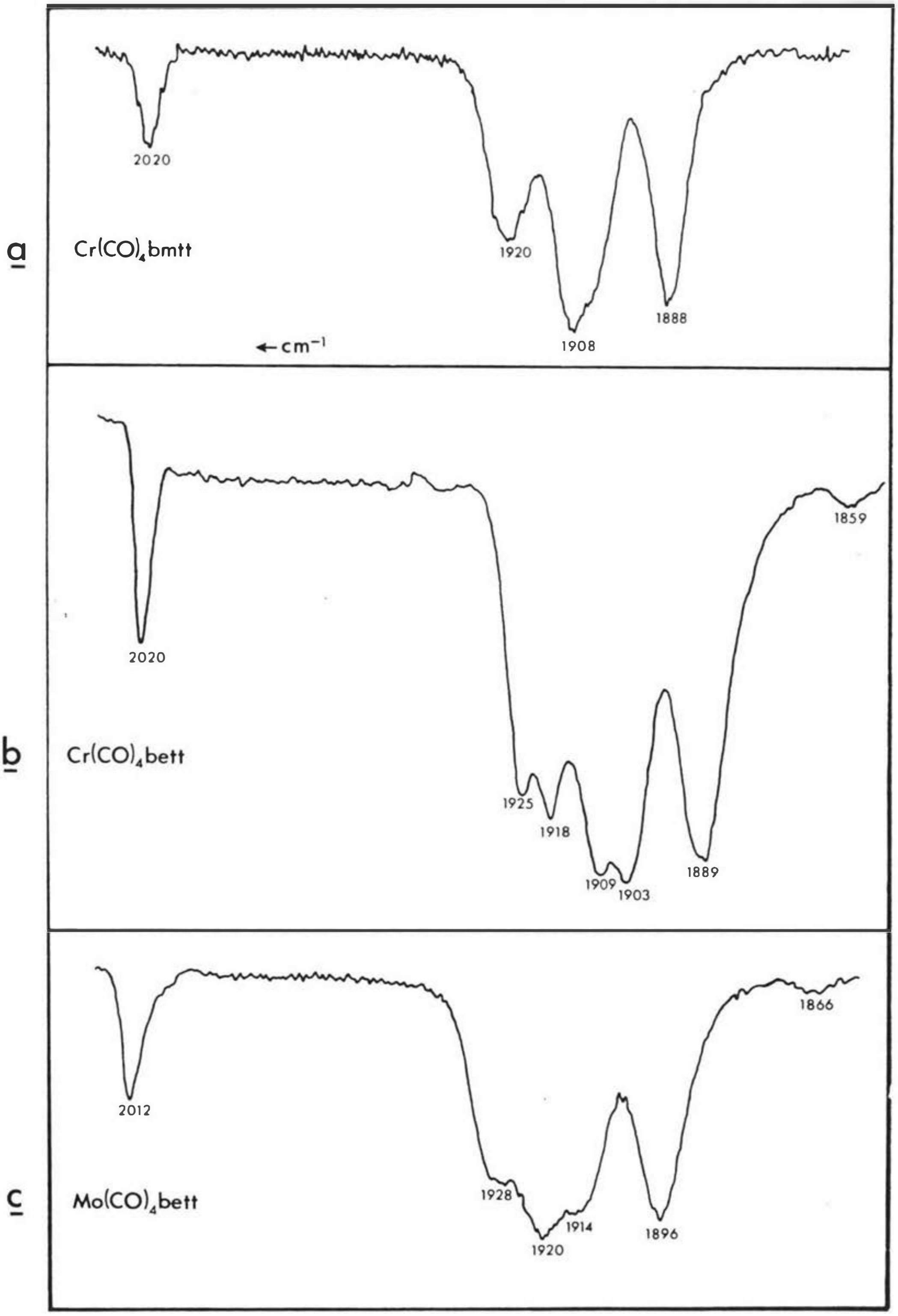


TABLE 9a

ν(CO) ABSORPTIONS FOR $M(CO)_4I_2$ COMPLEXES

	COMPLEX	$A_1(I)/cm^{-1}$	$A_1(II)$	B_1	B_2
	$Cr(CO)_4$bmtt	2020(w)	1920(m)	1908(s)	1888(s)
†	$Cr(CO)_4$bett	2020(m)	1925(s) 1918(s)	1909(s) 1903(s)	1889(s)
†	$Mo(CO)_4$bmtt	2027(m)	1925(sh)	1916(s) 1909(sh)	1894(s)
†	$Mo(CO)_4$bett	2012(m)	1928(s)	1920(s) 1914(s)	1896(s)
	$W(CO)_4$bmtt	2025(w)	1918(m)	1907(s)	1893(s)
	$W(CO)_4$bett	2025(m)	1918(m)	1905(s)	1891(s)
		[2027(m)]	[1924(m-s)] [1919(m-s)]	[1907(s)] [1903(s)]	[1895(s)]

NOTES:
- all spectra recorded in cyclohexane solution,

† these spectra also have very weak absorptions at 1859, 1862, and 1866 cm^{-1} respectively,

- absorptions in parentheses ([ ]) are for a sample of $W(CO)_4$bett that was prepared by refluxing $[W(CO)_5]_2$bett.

TABLE 9b

COTTON-KRAIHANZEL FORCE CONSTANTS

$M(CO)_4I_2$ COMPLEXES

COMPLEX	$K_1(N.m^{-1})$	$K_2(N.m^{-1})$	REFERENCE
M=Cr			
$Cr(CO)_4$diphos	1492	1566	234
$Cr(CO)_4$bmtt	1404	1542	This Work
$Cr(CO)_4[I_2^{SMe}]$	1398	1562	207
$Cr(CO)_4$o-bmtb	1396	1559	195
$Cr(CO)_4$dto	1386	1557	198
$Cr(CO)_4Me_4$ed	1338	1506	238
M=W			
$W(CO)_4$diphos	1404	1579	234
$W(CO)_4$bmtt	1397	1571	This Work
$W(CO)_4$bett	1393	1571	This Work
$W(CO)_4$o-bmtb	1388	1581	195
$W(CO)_4[I_2^{SEt}]$	1383	1594	207
$W(CO)_4$dto	1367	1585	198

NOTES:
- all spectra recorded in saturated hydrocarbon solvents,
- except for complexes of bmtt and bett, all force constants were calculated from published IR data,
- estimated errors are ± 4 $N.m^{-1}$.

Neither the A_1(II) nor the B_1 and B_2 modes are degenerate in cis-$M(CO)_4L_2$ complexes and so for each complex the presence of at least two conformational isomers appears to be the most plausible explanation for the observed spectra. There is no support for this suggestion though, in the ^1H nmr and ^{13}C nmr spectra where they have been recorded and this may be due to the rate of interchange between the conformational isomers being too rapid for the nmr time scales.

Conformational isomerism was observed in the complexes $(h^5-C_5H_5)Fe(CO)_2(h^1-C_5H_5)$ and $(h^5C_5H_5)Mo(CO)_2C_3H_5$ as a splitting of the carbonyl-stretching absorptions[129].

Another unusual feature of the spectra of $M(CO)_4$bett (M=Cr,Mo) and $Mo(CO)_4$bmtt, is the appearance of a weak carbonyl-stretching absorption at about 1860 cm^{-1}, coincident with the observation of the split absorption modes.

2.2 FORCE CONSTANT CALCULATIONS

The calculation of Cotton-Kraihanzel approximate CO force constants for cis-$M(CO)_4L_2$ complexes, and the interpretation of the resulting parameters, is analogous to that of the bridged-ligand complexes that were discussed in Chapter 1.

DISCUSSION

There is a paucity of infrared data for cis-$M(CO)_4L_2$ complexes in saturated hydrocarbon solvents, but as Table 9b shows, some trends are apparent.

i) Chromium Complexes

There appears to be little difference between an alkyl dithioether ligand such as 3,6-dithiaoctane and the dithioether ligands 3,4-bis(methylthio)toluene, ortho-bis(methylthio)benzene and 1,2-tetrakis(methylthio)ethylene where π-bonding systems are adjacent to the thioether donors. These results are in agreement with the results for the bridged-ligand $[Cr(CO)_5]_2L$ complexes that were discussed in Chapter 1.

ii) Molybdenum Complexes

The multiplicity of the carbonyl-stretching absorptions for the cis-$Mo(CO)_4L_2$ complexes (L=bmtt, bett) precludes the calculation of force constant data for these complexes, but K_1 for $Mo(CO)_4$(ortho-bis(methylthio)benzene) is 1408 ± 4 $N.m^{-1}$ and this is similar to K_1 (1404 ± 4 $N.m^{-1}$) for $Mo(CO)_4$(3,6-dithiaoctane). The force constants were calculated from IR data published in References 195 and 198 respectively.

iii) Tungsten Complexes

The complex $W(CO)_4$dto (dto=3,6-dithiaoctane) has a lower trans-carbonyl force constant (K_1) than the analogous complexes of bmtt, bett, ortho-bis(methylthio)benzene and 1,2-tetrakis (methylthio)ethylene. This suggests then, that the latter ligands are better π-acceptors and / or poorer σ-donors than dto in cis-$W(CO)_4L_2$ complexes.

2.3 ELECTRONIC SPECTRA

The weakness of the selection rules for complexes of C_{2v} symmetry does not make it possible for a simple molecular-orbital model to be set up as in the case of the C_{4v} bridged-ligand complexes (Chapter 1).[228] Braterman et al suggest however, that the lowest frequency absorption found in cis-$M(CO)_4L_2$ complexes may have both charge transfer and d-d character. While this is consistent with the observation that where L is a substituted phosphine donor the absorptions occur at higher energies[228] than where L is a substituted amine donor,[239] it does not explain why the complexes of the dithioethers, bmtt, bett and dto, have absorption energies similar to that of a phosphine donor (Table 10b).

TABLE 10a

ELECTRONIC SPECTRA FOR $M(CO)_4L_2$ COMPLEXES

	L_2 = bmtt		L_2 = bett	
METAL	ABSORPTION (nm)	ϵ(l.mol.$^{-1}$cm^{-1})	ABSORPTION	ϵ
Cr	248	13663	240	18974
	295(sh)	3514	331(sh)	2744
	333(sh)	1766	374(sh)	1385
	374(sh)	1103		
Mo	252	18947	256	15714
	289(sh)	5842	296(sh)	6857
	307(sh)	3609	358	1736
	407	1188		
W	243	20513	244	22281
	293(sh)	7872	250(sh)	21140
	368	1906	287(sh)	8860
			365	1991
			ca 397(sh)	-

NOTES: - all spectra recorded for Abs. EtOH solutions,

- sh = shoulder; extinction coefficients are approximate.

TABLE 10b

ELECTRONIC SPECTRA

LOWEST ENERGY MAXIMA, $M(CO)_4L_2$ COMPLEXES

COMPLEX	DONOR	λ_{max}(nm)	SOLVENT	REFERENCE
M=Cr				
$Cr(CO)_4(PPh_2)_2NMe$	P	373	Methanol	228
$Cr(CO)_4$dto	S	372	Ethanol	246
$Cr(CO)_4$bmtt	S	374(sh	Ethanol	This Work
$Cr(CO)_4$bett	S	374(sh)	Ethanol	This Work
$Cr(CO)_4$dte	S	400	Ethanol	194
$Cr(CO)_4$mte	S	404	Ethanol	194
$Cr(CO)_4$en	N	424	Methanol	239
M=W				
$W(CO)_4(PPh_2)_2NMe$	P	363	Methanol	228
$W(CO)_4$dto	S	364	Ethanol	246
$W(CO)_4$bett	S	365, *ca*397(sh)	Ethanol	This Work
$W(CO)_4$bmtt	S	368	Ethanol	This Work
$W(CO)_4$en	N	397, 450(sh)	Methanol	239
$W(CO)_4$tmeda	N	402, 450(sh)	Benzene	240
$W(CO)_4$tn	N	405, 450(sh)	Methanol	239

NOTE: - where two maxima are recorded, tentative assignments are discussed in text.

The electronic absorption maxima for the complexes $M(CO)_4L_2$ (M=Cr, Mo, W; L_2 = bmtt, bett) are presented in Table 10a. It appears from a comparison with the spectra for $W(CO)_4L_2$ complexes, where L_2 is a saturated, substituted diamine ligand[239] or L is a substituted pyridine ligand,[240] that the weak, low energy shoulder in the spectrum of $W(CO)_4$bett can be assigned as the first singlet⟶triplet transition. This transition is "buried" in the tail of the 368 nm maximum in the spectrum of $W(CO)_4$bmtt, while for the amine complexes the main visible maximum (corresponding to the ca 365 nm absorption in the thioether complexes) was assigned as the singlet ⟶ singlet transition.[240]

2.4 NUCLEAR MAGNETIC RESONANCE STUDIES

^{13}C nmr Spectra

Introduction

Carbon-13 nmr spectral studies on Group VIB carbonyl complexes have now firmly established that the extent of M⟶CO π-backbonding is one of the most important factors determining the ^{13}CO chemical shifts.[241] These studies have shown that as the π-acceptor ability of the substituent ligands decreases, the ^{13}CO resonances move progressively downfield. That is, the ^{13}CO resonances are deshielded by an increase in the electron population at M. These effects consequently enable excellent correlations to be observed between ^{13}CO chemical shifts and other physical measurements such as Cr-CO bond lengths,[241] IR stretching frequencies[241] and, for a series of $W(CO)_5L$ complexes, Cotton-Kraihanzel force constants.[242, 243]

Despite the advent of high resolution, pulse Fourier Transform techniques, there is a paucity of ^{13}C nmr data for both the monosubstituted and disubstituted Group VIB complexes of thioether ligands. This is primarily due to the often encountered problem of poor complex stabilities in the concentrated solutions that are required if the spectra are to be recorded in a reasonably short time.

The spectra of $[W(CO)_5]_2$bmtt, $W(CO)_4$bett and $Cr(CO)_4L_2$ (L_2=bmtt, bett) were recorded in this study despite some of the problems that were encountered with unstable solutions.

Results and Discussion

i) ^{13}CO Chemical Shifts

The cis and trans carbonyl groups (trans implies that the CO is trans to the ligand) are readily assigned as the latter are always deshielded with respect to the cis carbonyl groups.[244,245]

The results for these complexes are summarized in Table 11a and a characteristic spectrum is shown in Figure 10a. Some ^{13}CO chemical shift data for $W(CO)_5L$ complexes has been plotted as a function of their Cotton-Kraihanzel force constants (K_1 and K_2) in Figure 10b. Mann[243] has commented on the solvent dependence of both the IR spectra and the ^{13}CO chemical shifts and this has been taken into account in the compilation of the data.

Both graphs show the trends in the net basicities of ligands that are expected on the basis of previously established results. Thus, in terms of the ability of a ligand to place electronic charge onto $W(CO)_5$, it can be seen that phosphite ligands place the least charge and this can be related to these ligands' superior π-accepting ability (see Introduction). Although there is no other suitable data for $W(CO)_5L$ complexes of thioether ligands, the graphs suggest that bmtt has a net

TABLE 11a

^{13}CO CHEMICAL SHIFTS

COMPLEX	cis-$\delta\,^{13}$CO	trans-$\delta\,^{13}$CO	SOLVENT	REFERENCE
M=Cr				
$Cr(CO)_4$bmtt	215.1	226.8	$CDCl_3$	This Work
$Cr(CO)_4$bett	215.4	226.6	$CDCl_3$	This Work
$Cr(CO)_4L^{SMe}{}_2$	215.9	227.0	CD_2Cl_2	207
M=W				
$W(CO)_4$diphos	204.6	-	-	247
cis-$W(CO)_4[PEt_3]_2$	204.4	204.7	CH_2Cl_2	243
$W(CO)_4$bett	200.4	207.7	$CDCl_3$	This Work
$[W(CO)_5]_2$bmtt	196.9	199.9	$CDCl_3$	This Work

NOTES:
- Chemical shifts are ppm downfield from TMS,
- the ^{13}CO resonances for $Cr(CO)_6$ and $W(CO)_6$ are at 212.1 ppm[247] and 192.1 ppm[247] respectively,
- the data for some $M(CO)_5L$ complexes of thioether ligands (in various solvents) can be found in References 204 and 206 .

FIGURE 10a

^{13}C nmr - $Cr(CO)_4$bmtt in $CDCl_3$

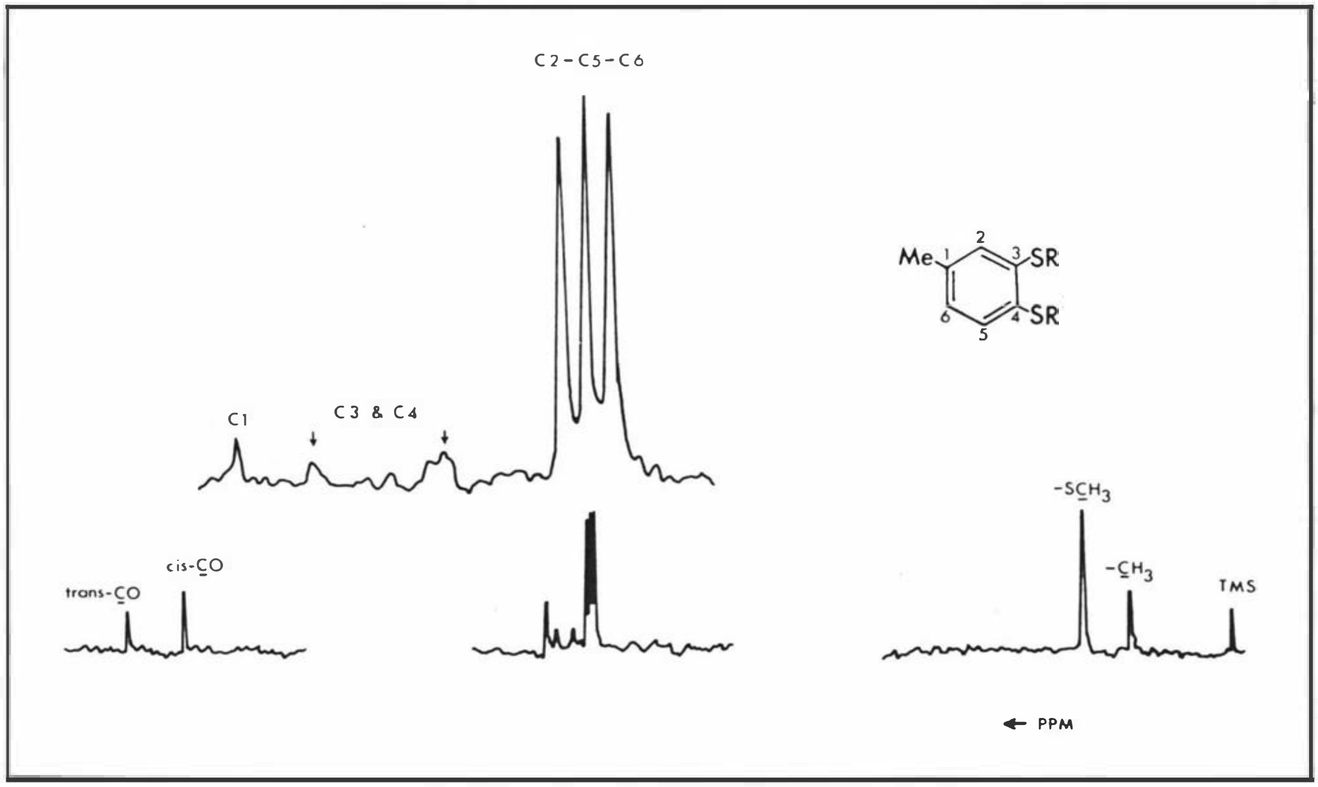
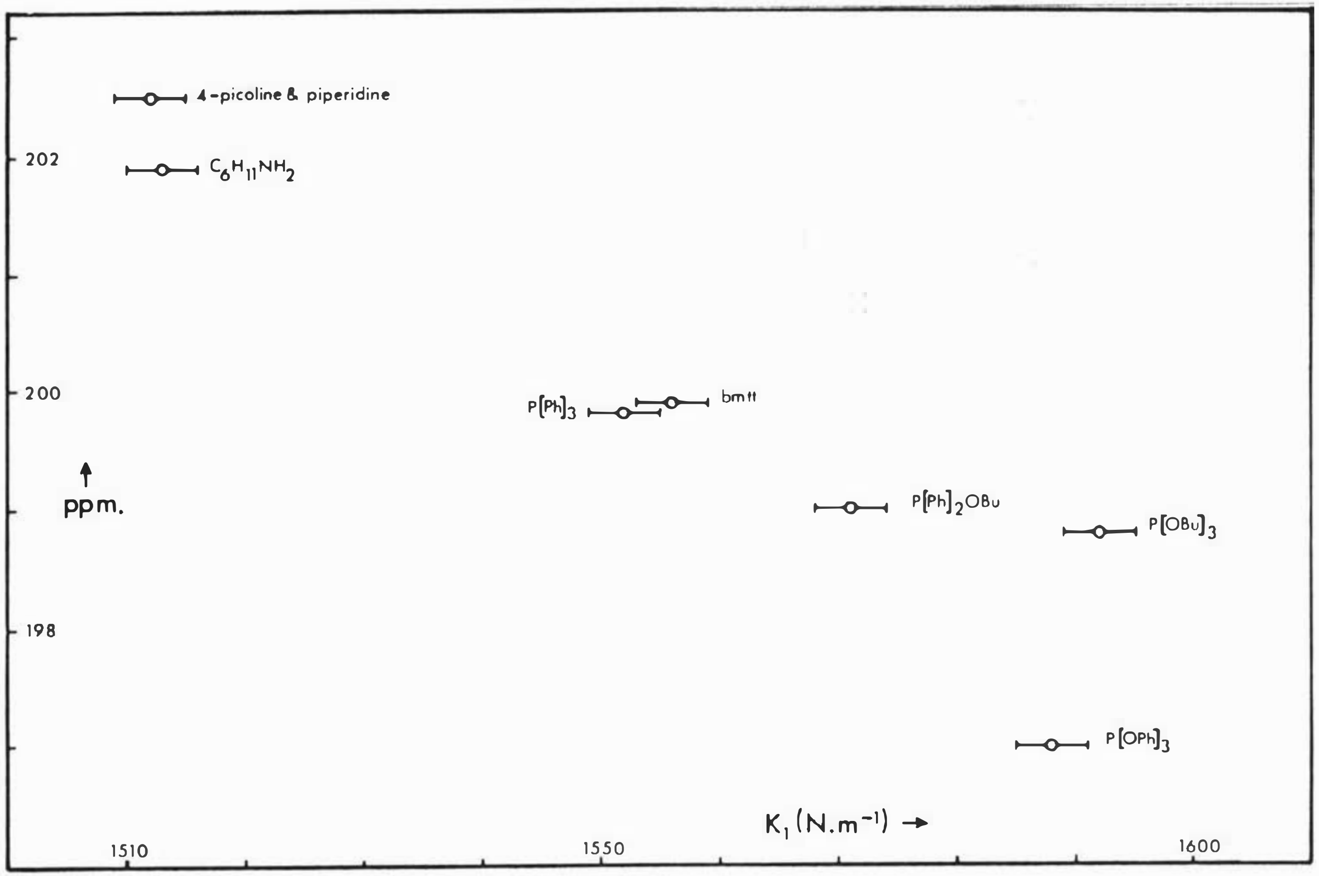


FIGURE 10b

trans-^{13}CO Chemical Shifts vs. trans-CO Force Constants

$[W(CO)_5]_n L$ Complexes

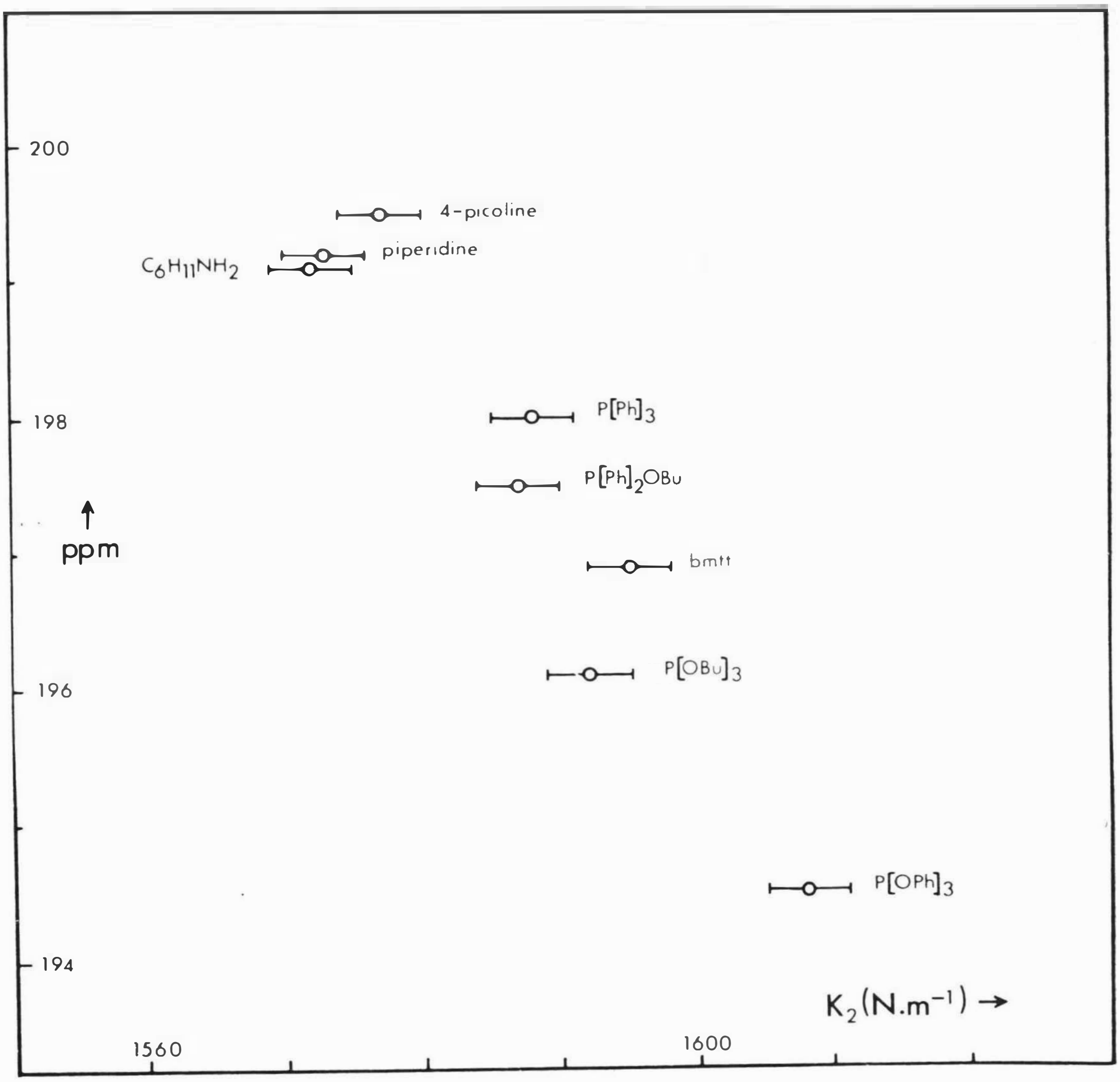


- n = 1 for all complexes except that of bmtt (n = 2)
- for literature references, see Figure 10c.

FIGURE 10c

cis-^{13}CO Chemical Shifts vs. cis-CO Force Constants

$[W(CO)_5]_nL$ Complexes



Ligand	Ref.(δ ^{13}CO)	Ref. (K_1 and K_2)
4-picoline	231	226
piperidine	231	226
$C_6H_{11}NH_2$	242	226
$P(Ph)_3$	242	226
$P(Ph)_2OBu$	242	226
bmtt	This work	This work
$P(OBu)_3$	242	226
$P(OPh)_3$	242	242

TABLE 11b

^{13}C CHEMICAL SHIFTS OF LIGANDS AND COMPLEXES

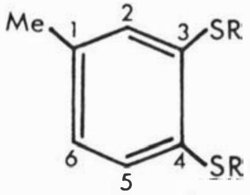
LIGAND/COMPLEX	$-SCH_3$	$-SCH_2\bar{C}H_3$	$-S\bar{C}H_2CH_3$	$-CH_3$	C1	C3,C4$^{\phi}$	C2,C5,C6$^{\phi}$
bmtt-in $CDCl_3$	16.11,16.76			20.98	136.07	133.22,137.93	126.49,126.98, 127.86
$Cr(CO)_4$bmtt-in $CDCl_3$	30.55,30.80			20.89	140.20	134.93,138.34	130.55,131.20 131.85
bmtt-in C_6D_6	15.75,16.48			20.94	135.87	134.41,138.79	126.62,127.51 128.15
bett-in $CDCl_3$		13.83,14.08	26.98,27.63	20.98	136.31	132.49,137.69	126.65,128.76 129.98
$Cr(CO)_4$bett-in $CDCl_3$		13.18†	41.35,41.51	20.89	140.20	134.60†	130.46,132.41 132.96
$W(CO)_4$bett-in $CDCl_3$		13.67†	44.19†	20.81			
bett-in C_6D_6		14.04,14.29	27.11,27.68	21.02	136.27	133.51,138.54	126.94,129.29 130.35

NOTES: - chemical shifts are ppm downfield from TMS

ϕ assignments are non-specific

† only one resonance was observed.

Ligand Carbon atoms are numbered as follows:



basicity similar to that of phosphorus ligands in that the electronic charge on $W(CO)_5$ is similar for both types of ligand.

The spectra of the $Cr(CO)_4L_2$ complexes (L_2=bmtt, bett) indicate that there is very little difference between the net basicities of bmtt, bett and 1,2-tetrakis(methylthio)ethylene and this is supported by the infrared spectra of the ligands' respective complexes.

ii) ^{13}C Chemical Shifts of the Ligands

The assignments and chemical shifts of the ^{13}C resonances for the uncoordinated and coordinated ligands are summarized in Table 11b. As expected on complexation, most of the ligand ^{13}C resonances, including the aryl ^{13}C atoms, shift downfield. Downfield shifts are not observed though, for the Ph-$\underline{C}H_3$ resonance of both ligands and for the $-SCH_2\underline{C}H_3$ resonance of bett.

The criteria on which the spectral assignments were based, are summarized in the Experimental section of the Appendices.

^1H nmr Spectra

Unlike the bridged-ligand complexes that were discussed in Chapter 1, the resonance absorptions of the alkyl side-chains move downfield on ligand complexation. This is consistent with a removal of electronic charge from the thioether donors. For the $M(CO)_4$bmtt complexes (M=Cr, Mo, W) the spectral resolution is sufficient to observe the inequivalence of the $-SCH_3$ protons. The ^1H chemical shifts are recorded in Table 12.

TABLE 12

^{1}H nmr DATA, M(CO)$_4$L$_2$ COMPLEXES OF bmtt, bett

COMPLEX	-SCH$_3$	-SCH$_2$CH$_3$	-SCH$_2$-	Ar-CH$_3$	Ar-H
bmtt	2.40,2.42			2.28	7.0
Cr(CO)$_4$bmtt	2.69,2.72			2.41	7.4
Mo(CO)$_4$bmtt	2.74,2.78			2.40	7.4
W(CO)$_4$bmtt	2.88,2.91			2.41	7.2
bett		1.30t(8)	2.89q(7)	2.35	6.9
		1.35t(8)	2.92q(7)		
Cr(CO)$_4$bett†		1.46t(8)	3.09q(7)	2.47	7.4
Mo(CO)$_4$bett		1.50t(8)	3.14t(7)	2.56	7.4
W(CO)$_4$bett		1.35t(8)	3.16q(7)	2.42	7.3

NOTES:
- spectra recorded in CDCl$_3$, chemical shifts are ppm downfield from TMS,
- t = triplet; q = quartet; coupling constants are in parentheses (Hz),
- chemical shifts for aryl protons (Ar-H) are the centres of the observed multiplets,

† complex decomposed.

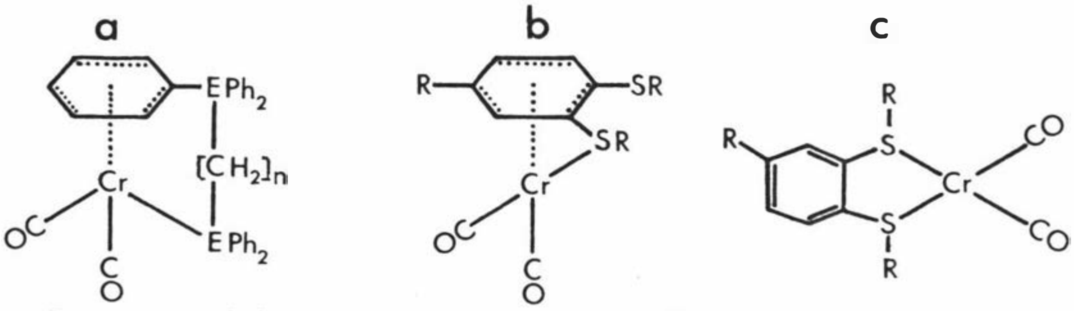
2.5 MASS SPECTRA

The mass spectral studies on Cr(CO)$_4$bmtt, Mo(CO)$_4$bmtt and W(CO)$_4$bmtt show that these complexes have a greater stability than $[W(CO)_5]_2$bmtt (Chapter 1). The expected parent molecular ions are observed for all three complexes but the presence of a very small quantity of $[W(CO)_5bmtt]^+$ was indicated for the sample of W(CO)$_4$bmtt. This molecular ion was also present in the mass spectrum of $[W(CO)_5]_2$bmtt (see Chapter 1).

An outstanding feature of the spectrum of Cr(CO)$_4$bmtt, is the absence of a peak for the ion $[Cr(CO)_3bmtt]^+$. The analogous ions are observed for the molybdenum and tungsten complexes. This phenomenon has been previously observed for chromium carbonyl complexes of ligands containing phenyl rings [234] and it was postulated that the absence of the ion $[Cr(CO)_3L]^+$

is due to the preferential formation of a complex with the structure shown in Figure 11a.

FIGURE 11



E = P or As, n = 1,2,3.

R = Me

A similar complex, possibly having one of the structures postulated in Figures 11b and 11c, may also explain the absence of the $[Cr(CO)_3bmtt]^+$ ion in the mass spectrum of $Cr(CO)_4bmtt$.

The spectra of $Mo(CO)_4bmtt$ and $W(CO)_4bmtt$ show ion peaks with masses corresponding to $Mo(CO)_7^+$ and $W(CO)_7^+$ respectively. While $W(CO)_4bmtt$ shows peaks which can be attributed to a $W(CO)_8^+$ ion, the analogous ion for $Mo(CO)_4bmtt$ is not observed. These ions have never been reported in the literature for other mass spectral studies of Group VIB carbonyl complexes.

SYNTHESES

The general photochemical method that is used in the synthesis of the Group VIB carbonyl complexes under consideration in Section II of this thesis, is described in the Appendices.

NOTE: In all preparations where solvent extractions are carried out, the extracts are filtered through Kieselguhr before continuing.

Tetracarbonyl(3,4-bis(methylthio)toluene)chromium(0)

After the addition of 3 mmole (0.566 g.) of ligand (dissolved in THF) to 3 mmole (0.660 g.) of irradiated $Cr(CO)_6$, the irradiation was continued for 75 minutes. The THF was removed (rotary evaporator) and excess $Cr(CO)_6$ was sublimed, *in vacuo*, from the residual oil. The IR spectrum (cyclohexane solution) of this oil showed the presence of both tetracarbonyl and pentacarbonyl species. Their separation was achieved on a silica-gel (100-200 mesh) column eluting with pentane and then benzene.

The tetracarbonyl complex (benzene fraction) was isolated by reducing the solvent volume and washing the resulting yellow crystals with cold pentane. They were recrystallized from pentane and air dried.

YIELD : 0.436 g.(42%)

A shorter irradiation time (e.g. 60 minutes) gave a reduced yield (0.373 g.)

Decacarbonyl-μ-(3,4-bis(methylthio)toluene)dichromium(0)

The solvent was removed *in vacuo* from the pentane fraction obtained in the preparation of $Cr(CO)_4$bmtt (above). The resulting impure crystals were washed with pentane to give a dry, yellow product, $[Cr(CO)_5]_2$bmtt.

YIELD : 0.040 g. (5%)

$[Cr(CO)_5]_2$bmtt is better synthesized by using a 2:1 ratio of $Cr(CO)_6$ to bmtt and stopping the irradiation after the addition of the ligand. On removing the THF, the residue was washed with pentane and the powdery, light yellow crystals were filtered off.

YIELD : 57%

Tetracarbonyl(3,4-bis(methylthio)toluene)molybdenum(0)

The ligand (3 mmole, 0.566 g.) was added to an irradiated solution of $Mo(CO)_6$ (3 mmole, 0.792 g.) and the irradiation was continued for a further 1.5 hours. IR spectra of solution samples taken after 10 and 60 minutes of irradiation, showed a reduction in the concentration of a pentacarbonyl complex and a corresponding increase in the concentration of a tetracarbonyl complex. On removing the THF and residual $Mo(CO)_6$ *in vacuo*, the residue was extracted into pentane and crystallized by concentrating and cooling the solution. The oil which remained after the pentane extraction, was purified on a silica-gel column using a benzene-pentane eluent (70:30). The second yellow band which came off the column contained $Mo(CO)_4$bmtt and this was crystallized on extraction into pentane, as outlined above.

YIELD : 0.346 g. (29%)

Tetracarbonyl(3,4-bis(methylthio)toluene)tungsten(0)

The ligand (2 mmole, 0.378 g.) was added to an irradiated solution of $W(CO)_6$ (2 mmole, 0.704 g.) in THF and the irradiation was continued for 105 minutes. On removing the THF and unreacted $W(CO)_6$, the residue was extracted into pentane. Both penta- and tetracarbonyl complexes were present in the extracts and these were separated on a silica-gel column with a pentane-benzene (70:30) eluent. When the two bands on the column were sufficiently separated, the benzene concentration was gradually increased until the second band was finally eluted with pure benzene. This band contained $W(CO)_4$bmtt which was recrystallized from a pentane solution.

YIELD : 0.161 g. (17%)

If, after adding the ligand, the irradiation time is decreased to about 75 minutes, the yield is 5% (0.044 g.).

Decacarbonyl-μ-(3,4-bis(methylthio)toluene)ditungsten(0)

The solvent was removed (in vacuo) from the solution containing the first band from the column in the preparation of $W(CO)_4$bmtt and pentane was added to the residual oil. Cooling the mixture precipitated light yellow, powdery crystals.

YIELD : 0.264 g. (32%)

Tetracarbonyl(3,4-bis(ethylthio)toluene)chromium(0)

After the addition of 3 mmole of bett (0.636 g.) to 3 mmole of irradiated $Cr(CO)_6$ (0.660 g.) in THF, the solution was irradiated for a further 45 minutes before the solvent and excess $Cr(CO)_6$ were removed in vacuo. The crude product, which contained a pentacarbonyl "impurity", was crystallized from pentane extracts of the residual crystals and oil. The crystals of $Cr(CO)_4$bett were filtered off and washed with cold pentane, which removed the impurity.

YIELD : 0.336 g. (30%)

Decacarbonyl-μ-(3,4-bis(ethylthio)toluene)dichromium(0)

About 15 minutes after adding 2 mmole of bett to an irradiated solution of $Cr(CO)_6$ (4 mmole), the THF was removed in vacuo. The residual, light yellow crystals were placed under vacuum for about 45 minutes, then washed with pentane and filtered.

YIELD : 0.427 g. (36%)

Tetracarbonyl(3,4-bis(ethylthio)toluene)molybdenum(0)

This complex was isolated from an attempt to synthesize $[Mo(CO)_5]_2$bett using a 2:1 ratio of $Mo(CO)_6$ to bett and the same method as for $[Cr(CO)_5]_2$bett. Considerable decomposition occurred during the pentane extractions however, giving $Mo(CO)_6$ and a brown material. These were filtered through Kieselguhr and the light yellow filtrates were concentrated then cooled to yield the pale yellow crystals of $Mo(CO)_4$bett. These were washed with cold pentane and vacuum dried.

YIELD : 0.138 g. (22%)

Tetracarbonyl(3,4-bis(ethylthio)toluene)tungsten(0)

A slight excess of bett (2.25 mmole) was used in an attempt to prevent the formation of $[W(CO)_5]_2$bett. The ligand was added to 2 mmole of irradiated $W(CO)_6$ and the irradiation was continued for 90 minutes.

After removing the THF, hexane extracts of the residue were filtered through Kieselguhr, the solvent removed and the residual brown oil (containing penta- and tetracarbonyl complexes) left under vacuum overnight. The complexes were separated on a silica-gel column using toluene-hexane (50:50) eluent. The second band on the column (eluted with neat toluene) contained $W(CO)_4$bett which was crystallized from a cyclohexane solution.

YIELD : 0.190 g. (19%)

In a second preparation where the solution was irradiated for 60 minutes after adding the ligand, the yield was only 5% (0.048 g.).

Decacarbonyl-μ-(3,4-bis(ethylthio)toluene)ditungsten(0)

The same method as for the preparation of $[Cr(CO)_5]_2$bett was used, with a 2:1 ratio of $W(CO)_6$ to bett. After the THF was removed, the residual oil was left to crystallize under vacuum for 2 hours. The crystals were washed with pentane and dried under vacuum.

YIELD : 0.643 g. (75%)

PREPARATION OF UNSTABLE C_6F_5SEt COMPLEXES

Pentacarbonyl(ethylthiopentafluorobenzene)chromium(0)

3 mmole of the ligand (0.685 g.) were added to 3 mmole of irradiated $Cr(CO)_6$ (0.660 g.) and the solution was left to react for 15 minutes. While the THF was being removed, the solution showed signs of decomposition and the residues from cyclohexane extracts of the reaction products are also unstable. The decomposition products are green.

Pentacarbonyl(ethylthiopentafluorobenzene)tungsten(0)

Using 2 mmole of ligand and 2 mmole of $W(CO)_6$ and the same preparative procedures as for the chromium complex, similar decomposition problems were encountered. The decomposition products are blue.

TABLE 13

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/°C	ANALYSES: Calc.(Found)/%		
			C	H	S
$[Cr(CO)_5]_2$bmtt	yellow	104-107	40.20 (40.39)	2.13 (2.39)	11.28 (11.45)
$[Cr(CO)_5]_2$bett	pale yellow	94-97	42.30 (42.53)	2.71 (2.93)	10.76 (10.45)
$[W(CO)_5]_2$bmtt	pale yellow	108-111	27.45 (27.88)	1.45 (1.95)	7.71 (8.86)
$[W(CO)_5]_2$bett	pale yellow	96-97	29.40 (30.09)	1.88 (2.07)	7.46 (8.72)
$Cr(CO)_4$bmtt	yellow	81-82	44.80 (44.93)	3.47 (3.53)	18.40 (18.71)
$Mo(CO)_4$bmtt	yellow	65-67	39.80 (40.09)	3.08 (3.18)	16.35 (16.25)
$W(CO)_4$bmtt	yellow	78-81	32.54 (31.48)	2.52 3.06)	13.36 (13.42)
$Cr(CO)_4$bett	pale yellow	72-74	47.86 (47.82)	4.28 (4.54)	17.04 (17.25)
$Mo(CO)_4$bett	pale yellow	66-69	42.86 (43.73)	3.84 (4.52)	15.25 (14.94)
$W(CO)_4$bett	pale yellow	86-88	35.47 (36.94)	3.17 (3.62)	12.62 (12.67)

CHAPTER 3

COMPLEXES OF MONODENTATE AND BIDENTATE SULPHUR-NITROGEN DONOR LIGANDS

The $M(CO)_4L_2$ complexes of 2-ethylthioethylamine (etea) and 2-(3,3-dimethyl-2-thiabutyl)pyridine (tbmp) are investigated in this Chapter together with the $[M(CO)_5]_2L$ complexes of etea and some $M(CO)_5L$ complexes of 2-methylthioaniline(mta), 2-methylmercaptobenzimidazole (mmbi), 2-methylthio-2-imidazoline (mti) and benzimidazole (bi).

The studies on the carbonyl complexes of etea and tbmp are the first to involve mixed sulphur-nitrogen donor, bidentate ligands. The complexes of benzimidazole have been previously reported[212] but these were prepared so that they could be characterized under the same conditionsas the $M(CO)_5L$ complexes, thereby simplifying the interpretation of the results for the mta, mti and mmbi ligands.

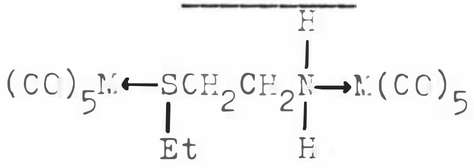
While the general syntheses of the $[M(CO)_5]_2$etea and $M(CO)_4L_2$ (L_2=etea, tbmp) complexes were similar to those that were described in the introductions to Chapter 1 and 2 respectively, the $M(CO)_5L$ complexes were synthesized by reacting the ligand with $M(CO)_5$THF in a 1:1 ratio.

3.1 INFRARED SPECTRA (CARBONYL STRETCHING VIBRATIONS)

i) $[M(CO)_5]_nL$ COMPLEXES (n = 1,2)

It was anticipated that the bridged-ligand complexes of 2-ethylthioethylamine (etea) would show split carbonyl-stretching absorptions due to bonding differences between the thioether and amine donors at the two $M(CO)_5$ centres (Figure 12).

FIGURE 12



$$(CO)_5M\leftarrow \underset{\displaystyle Et}{S}CH_2CH_2\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\rightarrow M(CO)_5$$

(M=Cr or W)

The spectra though, do not show these differences (Table 14a). It is apparent from this and other studies of mixed-donor Group VIB carbonyl complexes [248, 249] that despite quite large differences in the bonding properties of the donors, "averaged" spectra are observed. Thus for the $[M(CO)_5]_2$etea complexes (M=Cr, W), the carbonyl-stretching absorptions lie between the extremes observed for bridged-ligand complexes of dithioether ligands and diamine ligands[198] (Table 14a).

In the IR spectra of the $M(CO)_5L$ complexes (where L is 2-methylmercaptobenzimidazole, benzimidazole or 2-methylthio-2-imidazoline) that have been recorded in nitromethane solution, the B_1 mode is not generally observed. This appears to be a resolution phenomenon. A splitting of the E mode is also observed for most of these spectra and this can be related to the asymmetry of the ligands.[218]

The $M(CO)_5L$ complexes (M=Cr, Mo, W) of 2-methylthioaniline appear to be normal in cyclohexane.

ii) cis-$M(CO)_4L_2$ COMPLEXES

The spectra of the chelated-ligand complexes of

TABLE 14a

ν(CO) ABSORPTIONS FOR $[M(CO)_5]_nL$ COMPLEXES

COMPLEX	A_1(II)/cm^{-1}	B_1	E	A_1(I)	Solvent
$[Cr(CO)_5]_2$etea	2071(w)	1987(w)	1948(sh) 1940(s)	1926(m)	a
$[W(CO)_5]_2$etea	2076(w)	1988(m)	1945(s) 1933(s)	1927(sh)	a
$[Cr(CO)_5$mmbi$]$.0.5mmbi	2069(w)	n.o.	1938(vs) 1927(vs)	1883(s)	b
$W(CO)_5$mmbi	2074(w)	n.o	1932(sh) 1927(s)	1888(m)	b
$[Cr(CO)_5$bi$]$.0.5 bi	2071(m)	n.o.	1940(s-sh) 1935(vs)	1887(s)	b
$W(CO)_5$bi	2073(m)	n.o.	1927(sh) 1918(vs)	1878(m)	b
$Cr(CO)_5$mti	2069(m)	n.o.	1934(vs)	1889(m)	b
$Mo(CO)_5$mti	2070(w)	n.o.	1937(sh) 1932(vs)	1888(m)	b
$W(CO)_5$mti	2066(m)	n.o.	1924(vs) 1920(s-sh)	1880(m)	b
$Cr(CO)_5$mta	2071(m)	1984(w)	1945(vs)	1933(vs)	a
$Mo(CO)_5$mta	2080(w)	1987(m)	1951(s)	1934(s-sh)	a
$W(CO)_5$mta	2076(m)	1983(m)	1945(s-sh) 1941(vs)	1931(s-sh)	a

NOTES: - a = cyclohexane; b = nitromethane,

- w = weak; m = medium; s = strong; v = very;
  sh = shoulder
- n.o. = not observed.

TABLE 14b

ν(CO) ABSORPTIONS FOR $M(CO)_4L_2$ COMPLEXES

COMPLEX	A_1(I)/cm^{-1}	A_1(II)	B_1	B_2	SOLVENT
$Cr(CO)_4$etea	2017(w)	1905(m)	1889(s)	1870(m)	a
	2006(m)	1892(s-sh)	1881(s)	1848(s)	b
	2013(m)	1898(s)	1879(s)	1841(s)	c
$Mo(CO)_4$etea	2019(m)	1883(sh)	1901(s)	1845(s)	c
$W(CO)_4$etea	2018(m)	1881(s)	1894(s)	1843(s)	c
$Cr(CO)_4$tbmp	2014(m)	1909(m)	1896(s)	1871(m) 1866(sh)	a
$Mo(CO)_4$tbmp	2020(w)	1913(ms)	1906(s)	1876(m)	a
$W(CO)_4$tbmp	2015(w)	1905(m)	1894(s)	1874(m)	a

NOTES: - a = cyclohexane; b = toluene; c = chloroform.

2-ethylthioethylamine are normal (Table 14b) for cis-$M(CO)_4L_2$ complexes in chloroform.

In contrast to the spectra of the $M(CO)_4$etea complexes, $Cr(CO)_4$tbmp and $W(CO)_4$tbmp (tbmp=2-(3,3-dimethyl-2-thiabutyl)-pyridine) show a shoulder on the B_2 absorption, but the other modes are normal. The spectrum of $Mo(CO)_4$tbmp is also normal (Table 14b).

One possible reason for the appearance of the B_2 shoulder in the spectra of $Cr(CO)_4$tbmp and $W(CO)_4$tbmp, is that the t-butyl group can have two orientations with respect to the equatorial plane. That is, it can be either "up" or "down", to give two inequivalent conformational isomers.

3.2 FORCE CONSTANT CALCULATIONS

i) $[M(CO)_5]_nL$ COMPLEXES (n=1,2)

L=mmbi, mti : The force constant data can be used for the complexes $M(CO)_5L$ to determine whether the ligand is binding via the thioether donor or via one of the heterocyclic nitrogen donors. A comparison of the trans-carbonyl force constants for these complexes with those of $[M(CO)_5]_2$en (M=Cr, W) and $M(CO)_5$bi (M=Cr, W) where the ligands can only bind via nitrogen donors is found in Table 15. The results suggest that mmbi and mti bind to the metal via one of the heterocyclic nitrogens and not the thioether.

L=mta : A comparison of $Cr(CO)_5$mta with complexes containing thioether donors (Table 4) suggests that the ligand is bound via the thioether. However, similar comparisons for $W(CO)_5$mta (K_1=1526 ± 3 $N.m^{-1}$), imply that there may be W-N interactions in solution as K_1 is lower than normal for $W(CO)_5$thioether complexes. There is no evidence for this

TABLE 15

COTTON-KRAIHANZEL FORCE CONSTANTS

$[M(CO)_5]_nL$ COMPLEXES

COMPLEX	K_1 ($N.m^{-1}$)	K_2 ($N.m^{-1}$)
M=Cr		
$Cr(CO)_5mti$	1458	1578
$[Cr(CO)_5mmbi].0.5mmbi$	1455	1575
† $[Cr(CO)_5]_2en$	1451	1587
$Cr(CO)_5bi$	1443	1584
M=W		
$[W(CO)_5]_2bmtt$	1499	1592
$W(CO)_5mmbi$	1459	1575
$W(CO)_5mti$	1446	1564
† $[W(CO)_5]_2en$	1444	1576
$W(CO)_5bi$	1444	1567

NOTES:
- all spectra recorded in nitromethane solution,
- all errors are ± 5 $N.m^{-1}$ in K_1 and K_2,
- see Table 4 for mta complexes,
- K_1 is the force constant of the CO's trans to L and K_2 is the cis force constant,

† calculated from I.R. data, Ref. 198 .

suggestion though, in the ^{1}H nmr spectrum of this complex.

L=etea : It might be expected from the IR spectra that the trans-carbonyl force constants (K_1) for $[Cr(CO)_5]_2$-etea (K_1=1519 ± 3 N.m^{-1}) and $[W(CO)_5]_2$etea (K_1=1524 ± 3 N.m^{-1}) will have values at about the mean of those calculated from the thioether and amine donor data (Table 15) and this is what is observed.

ii) cis-$M(CO)_4L_2$ COMPLEXES

L=etea : $Cr(CO)_4$etea, like the bridged-ligand complexes $[M(CO)_5]_2$etea, has a K_1 (1366 ± 4 N.m^{-1}) at about the mean of the typical values for thioether and amine donors in cyclohexane solution (Table 9). The spectra for $Mo(CO)_4$etea and $W(CO)_4$etea could only be obtained in chloroform and were therefore unsuitable for comparison with other complexes.

L=tbmp : In contrast to $Cr(CO)_4$etea, $Cr(CO)_4$tbmp and $W(CO)_4$tbmp have trans-carbonyl force constants (K_1=1385 and 1379 ± 4 N.m^{-1} respectively) at values expected for thioether donors. This implies that the coordination of tbmp results in a lower electron density at M(C) than the coordination of etea. Such an effect may result from the lower basicity of the pyridyl donor of tbmp and/or enhanced M⟶L π-backbonding in the $M(CO)_4$tbmp complexes, as both would lead to an increase in K_1.

Detailed studies on $M(CO)_5L$ complexes (M=Cr, W) of amine donor ligands [226] have shown though, that changes in the basicity of the amine have little effect on K_1 and for $W(CO)_5L$ complexes of substituted pyridines, W⟶pyridyl π-backbonding also has no effect on the carbonyl stretching frequencies.[231, 237] The only other mechanism by which the electron density at M(O) can be decreased on coordination of tbmp, is an increase in M→thioether π-backbonding. The reason for such an increase is not readily apparent.

3.3 GENERAL INFRARED DATA

i) Complexes of 2-ethylthioethylamine ν(NH) Absorptions

The spectra were recorded for Nujol Mulls and then chloroform solutions to determine whether or not hydrogen bonding effects influence the frequencies observed in the mull spectra. The results show that there is little difference between the ν(NH) frequencies in the two media, except in the spectrum of the uncomplexed ligand (Table 16a).

Except in the case of $[W(CO)_5]_2$etea, the two ν(NH) absorptions do not undergo significant shifts to lower frequencies on complexation to M(O), where M is Cr, Mo and W. This is in contrast to the shifts that are observed for the same ligand on complexation to Cu(II) (See Section I, Chapter 5) and to the shifts (50 - 120 cm^{-1}) observed for some primary amines in their $W(CO)_5I$ and $W(CO)_4L_2$ complexes.[250] The ν(NH) frequencies for the etea complexes are very similar to those reported for the complexes $[M(CO)_5]_2$en (M=Cr, W).[198]

ii) Complexes of 2-methylthioaniline ν(NH) Absorptions

^{1}H nmr data suggests that the $-NH_2$ group is not involved in ligand-metal interactions in the $M(CO)_5$mta complexes and this is coupled with the observation that there are no significant red-shifts of the ν(NH) frequencies. (Table 16a). Hence although the IR spectra may seem to be a reliable basis for deciding that the $-NH_2$ group is not binding in each of the $M(CO)_5$mta complexes, the studies on the etea complexes (above) show that this is not so.

iii) Complexes of 2-methylmercaptobenzimidazole and benzimidazole.

a) ν(NH) Absorptions

There is little or no shift in the ν(NH) frequencies of the ligands on complexation (Table 16a). The observations refer to chloroform solutions of the free ligands and their $M(CO)_5L$ complexes (M=Cr, W) as the ν(NH) frequencies were not observed for Nujol Mulls of the free ligands. The implication is therefore, that Cr(0) and W(0) are not bound to the pyrrole nitrogen of mmbi, but a consideration of the etea complexes suggests that the interpretation of ν(NH) frequency "shifts" is not a reliable criterion in carbonyl complexes.

b) Heterocyclic Ring Absorptions

The characteristic absorptions (1700-1500 cm^{-1}) that are observed in Nujol Mulls of these complexes are presented in Table 16b and it can be seen that ligand coordination produces little or no change except for a splitting of the lowest frequency absorption in the benzimidazole complexes. The absorptions can probably be assigned as deformations of the plane of the ring nuclei, by analogy with the assignments that have been made for imidazole.[251] There will also be a weak δ(NH) absorption in this region.[151]

iv) Complexes of 2-methylthio-2-imidazoline.

a) ν(NH) Absorptions

There are no red-shifts in these absorptions (chloroform solution) on complexation of the ligand even though the force constant data and ^1H nmr spectra suggest N——M coordination. Instead, small shifts to higher frequencies are observed (Table 16a). These observations are in

TABLE 16a

ν(NH) ABSORPTIONS: $[M(CO)_5]_nL$ and $M(CO)_4L_2$ COMPLEXES

COMPLEX/LIGAND	$CHCl_3$ SOLUTION/cm^{-1}	NUJOL MULL/cm^{-1}
L = etea	3380(s)	3367(vs,br);3304(vs,br)
$[Cr(CO)_5]_2$etea		3363(m); 3322(m)
$[W(CO)_5]_2$etea	3347(vw); 3302(vw)	
$Cr(CO)_4$etea	3376(m); 3321(m)	3374(m), 3313(m)
$Mo(CO)_4$etea	3372(m); 3319(m)	3376(m); 3324(m)
$W(CO)_4$etea		3352(m); 3307(w)
L = mmbi	3460(m)	
$[Cr(CO)_5$mmbi$]$.0.5mmbi	3467(w)	3393(m)
$W(CO)_5$mmbi	3482(w)	3374(m)
L = bi	3485(s)	
$[Cr(CO)_5$bi$]$.0.5bi	3472(w)	3452(s); 3417(s)
$W(CO)_5$bi	3454(w)	3436(w); 3392(w)
L = mti	3431(m)	3093(br)
$Cr(CO)_5$mti	3452(m)	3452(w)
$Mo(CO)_5$mti	3460(m)	3428(w)
$W(CO)_5$mti	3474(w)	3440(m)
L = mta†	3461(s); 3364(s); [3192(w,br); 3079(m); 3030(m); 3001(m)]	
$Cr(CO)_5$mta†	3472(m); 3387(m); [3092(w)]	
$Mo(CO)_5$mta†	3380(br,s); [3070(m)]	
$W(CO)_5$mta†	3466(s); 3360(s); [3074(w)]	

NOTES: - br = broad,

† recorded as neat oils.

TABLE 16b

HETEROCYCLIC RING VIBRATIONS (1700 - 1500 cm^{-1})

COMPLEX/LIGAND	RING VIBRATIONS (cm^{-1}) - Nujol Mulls
L = mmbi	1622(w); 1592(w); 1498(s)
$[Cr(CO)_5$mmbi$]$.0.5mmbi	1621(w); 1592(w); 1496(m)
$W(CO)_5$mmbi	1617(w); 1595(m); 1494(s)
L = bi	1623(w); 1590(m); 1497(w)
$[Cr(CO)_5$bi$]$.0.5bi	1623(m); 1597(m); 1503(s); 1497(s)
$W(CO)_5$bi	1624(m); 1596(m); 1502(s); 1496(s)
L = mti†	1554(br)
$Cr(CO)_5$mti	1550(m)
$Mo(CO)_5$mti	1549(m)
$W(CO)_5$mti	1533(m)
L = tbmp	1593(s)
$Cr(CO)_4$tbmp	1602(w)
$Mo(CO)_4$tbmp	1604(w)
$W(CO)_4$tbmp	1600(w)

NOTE: † for mti and its complexes, the absorption is assigned as ν(C=N) - see text.

contrast to the significant shifts that are observed for the Cu(II) complexes of this ligand (this work) and in some M(II) complexes of other 2-substituted imidazolines.[152] Because extensive intermolecular hydrogen bonding lowers the free ligand ν(NH) frequency in Nujol Mulls, the complexes show large shifts to higher frequencies for this absorption.

b) ν(C=N) Absorption

In contrast to the Cu(II) complexes of this ligand, there is a negligible red-shift in this absorption on complexation to the zero-valent metals, Cr(0), Mo(0) and W(0) (Table 16b) and this effect may be due to these metals being less positively charged than Cu(II) in its complexes.

The absorption was assigned by analogy with the 2-substituted thiazolines.[98]

v) Complexes of 2-(3,3-dimethyl-2-thiabutyl)pyridine

Complexation of pyridyl ligands is usually accompanied by a blue-shift of the highest frequency, ring-stretching absorption (Section I, Chapter 2), but the shifts that are observed in Nujol Mulls of $M(CO)_4$tbmp (M=Cr, Mo, W) are not very significant (Table 16b). This absorption is not readily observed in the carbonyl complexes and this is due to it being "masked" by the broad and intense carbonyl stretching absorptions.

3.4 NUCLEAR MAGNETIC RESONANCE STUDIES

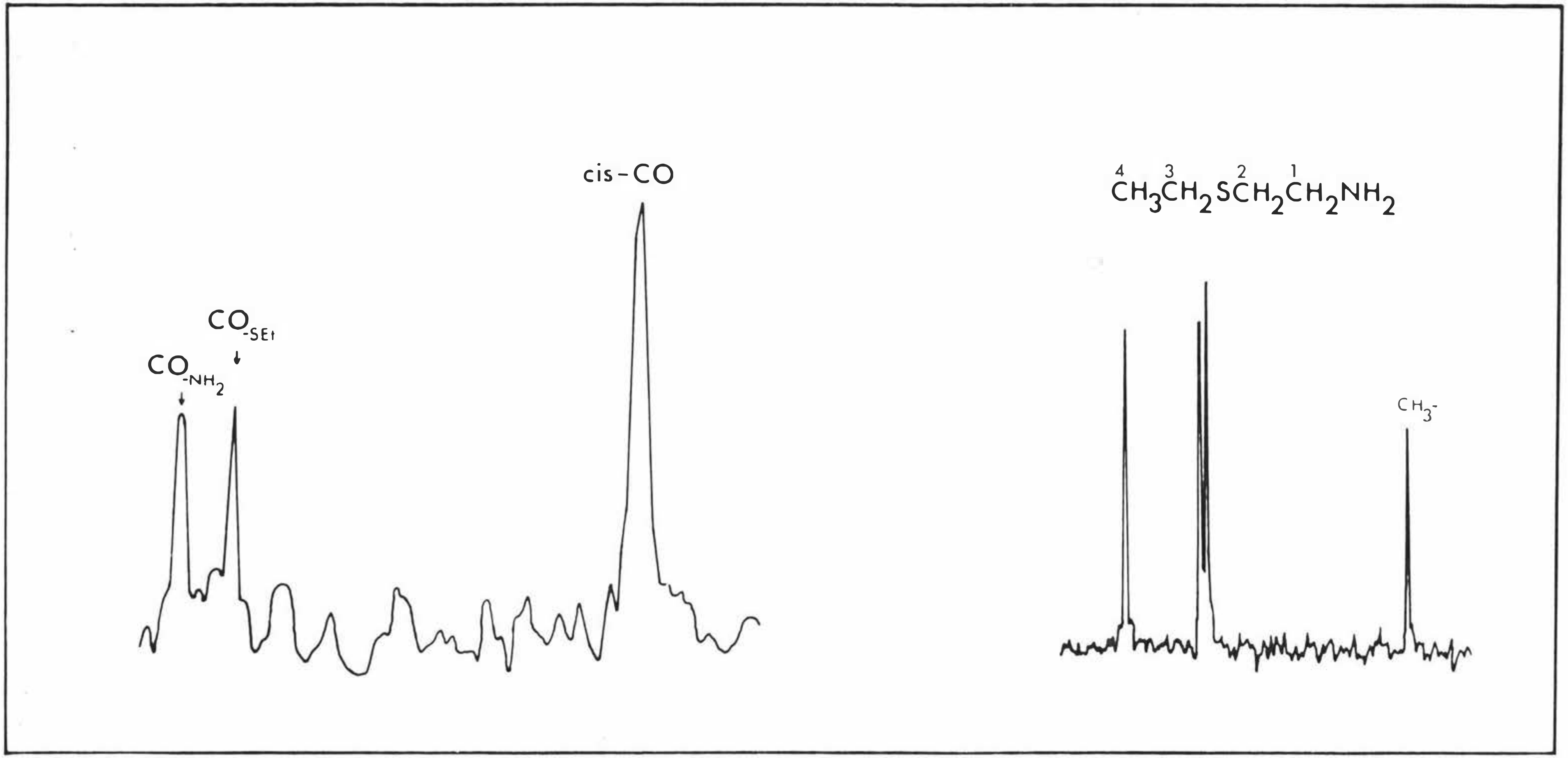
^{13}C nmr Spectra of $M(CO)_4$etea (M=Cr, Mo) and etea.

i) ^{13}CO Chemical Shifts

The outstanding feature of the spectra (Figure 13) is the appearance of two trans - ^{13}CO resonance peaks due to the inequivalence of the EtS- and $-NH_2$ donors in the complexes. The ^{13}CO resonances are thus assigned by

FIGURE 13

^{13}C nmr - Cr(CO)$_4$etea in C$_6$D$_6$



- unassigned resonances are C1, C2 and C3,
- subscripts -SEt and -NH$_2$ indicate *trans*-^{13}CO resonances.

recognising that π-backbonding to EtS- will result in a shielding of the CO group trans to this donor.

TABLE 17a

^{13}CO Chemical Shifts of $M(CO)_4$etea (M=Cr, Mo)

COMPLEX	cis-^{13}CO	^{13}CO trans to EtS-	^{13}CO trans to $-NH_2$
$Cr(CO)_4$etea	216.06	226.45	227.90
$Mo(CO)_4$etea	207.03	219.05	219.50

NOTES: - measured in C_6D_6

- ppm downfield from TMS

Similar spectra have been observed in the study of some $M(CO)_4L_2$ complexes (M=Cr, W) where L_2 is a carbene - thio ligand.[204]

ii) ^{13}C Chemical Shifts of the Ligand

Each of the four resonances that are observed for the free ligand can be readily assigned (Table 17b), but in the $M(CO)_4$etea complexes, the assignments are not obvious. Thus only the $-SCH_2\underline{C}H_3$ resonance has been assigned (Table 17c) and this appears to become slightly shielded on complexation.

TABLE 17b

^{13}C Chemical Shifts for $\overset{4}{C}H_3\overset{3}{C}H_2S\overset{2}{C}H_2\overset{1}{C}H_2NH_2$

SOLVENT	C1	C2	C3	C4
$CDCl_3$	35.67	40.86	25.44	14.73
C_6D_6	35.71	41.39	25.58	15.02

NOTES: - in $CDCl_3$, ^{14}N quadrupolar effects broaden the C1 and C2 resonances.[252]

- other assignments based on the spectrum of bett (Chapter 2), and on known spectra of primary amines such as $EtNH_2$.[253]

TABLE 17c

^{13}C Chemical Shifts for $M(CO)_4$etea

COMPLEX	C4	OTHER CARBONS
$Cr(CO)_4$etea	13.47	33.85, 34.41, 42.04
$Mo(CO)_4$etea	13.47	33.93, 34.90 42.37

NOTES: - measured in C_6D_6

- ppm downfield from TMS (and Table 17b)

^{13}C nmr Spectrum of $W(CO)_5$benzimidazole

The spectrum was recorded in $(CD_3)_2CO$ which meant that the trans- ^{13}CO resonance could not be resolved at about 205 ppm. The cis-^{13}CO chemical shift (198.85 ppm) can be compared with the analogous data for $W(CO)_5\overline{S(CH_2)_3SCH_2}$ (197 ppm)[204] and $W(CO)_5C_4H_6S$ (197.9 ppm)[206], where C_4H_6S is 2,5-dihydrothiophene, in the same solvent. The results are consistent with an increase in the electron population at tungsten, on replacing a thioether ligand with benzimidazole.

3.5 NUCLEAR MAGNETIC RESONANCE STUDIES

^1H nmr Spectra

i) Complexes of 2-ethylthioethylamine

When compared to the free ligand, both the methyl and methylene proton resonances have shifted downfield on the formation of $[Cr(CO)_5]_2$etea, but the $-NH_2$ resonance, which is quite strong in the uncomplexed ligand, was not observed (Table 18a). There is a broad absorption at about 2.0 ppm and this has the appearance of an exchange-broadened $-NH_2$ resonance, but the solution was decomposing and it is more likely that this resonance is due to a decomposition product.

TABLE 18a

^{1}H nmr DATA, COMPLEXES OF etea

COMPLEX	$-CH_2SCH_2CH_2-$	$-CH_3$	$-NH_2$
etea	2.35,2.47,2.58,2.70	1.25t(8)	4.66
$[Cr(CO)_5]_2$etea	2.52,2.71,2.82	1.41t(7)	-
$Cr(CO)_4$etea	*ca*2.5 (broad)	*ca*1.4(broad)	

NOTES: - satisfactory spectra were not recorded for the other complexes,

- spectra recorded in $CDCl_3$, chemical shifts in ppm downfield from TMS.

TABLE 18b

^{1}H nmr DATA, COMPLEXES OF mta

COMPLEX	$-SCH_3$	$-NH_2$
mta	2.33	4.21
$Cr(CO)_5$mta	2.65	*ca*4.2
$W(CO)_5$mta	2.89	*ca*3.7

NOTES: - spectra recorded under same conditions as above,

- for $Cr(CO)_5$mta, $-NH_2$ resonance weak, poorly resolved,
- both carbonyl complexes showed weak impurity peaks.

TABLE 18c

^{1}H nmr DATA, COMPLEXES OF mmbi

COMPLEX	$-SCH_3$	$-NH-$	Ar-H
mmbi	2.72	3.00	7.2
$[Cr(CO)_5$mmbi$]$.0.5mmbi	2.87	*ca*5.00(br)	7.5
$W(CO)_5$mmbi	2.91	3.44(br)	7.6

NOTES: - spectra recorded in $(CD_3)_2CO$, chemical shifts in ppm downfield from TMS,

- assignment of -NH- resonance confirmed for Cr complex by adding D_2O to solution. Resonance sharpened and moved upfield.

TABLE 18d

^{1}H nmr DATA, COMPLEXES OF mti

COMPLEX	$-SCH_3$	$-CH_2-$	$-NH-$
mti	2.49	3.67	3.97d(8)
$Cr(CO)_5$mti	2.44	3.57d(7),3.56d(7)	4.78
$Mo(CO)_5$mti	2.44	3.83d(7),3.59d(7)	4.84
$W(CO)_5$mti	2.46		

TABLE 18e

^{1}H nmr DATA, COMPLEXES OF tbmp

COMPLEX	$-CH_3$	$-CH_2S-$	α-H
tbmp	1.36	3.94	8.55d(6)
$Cr(CO)_4$tbmp†	1.30	4.08	> 9
$Mo(CO)_4$tbmp	1.33	4.12	8.97d(5)
$W(CO)_4$tbmp†	1.33	4.28	> 9

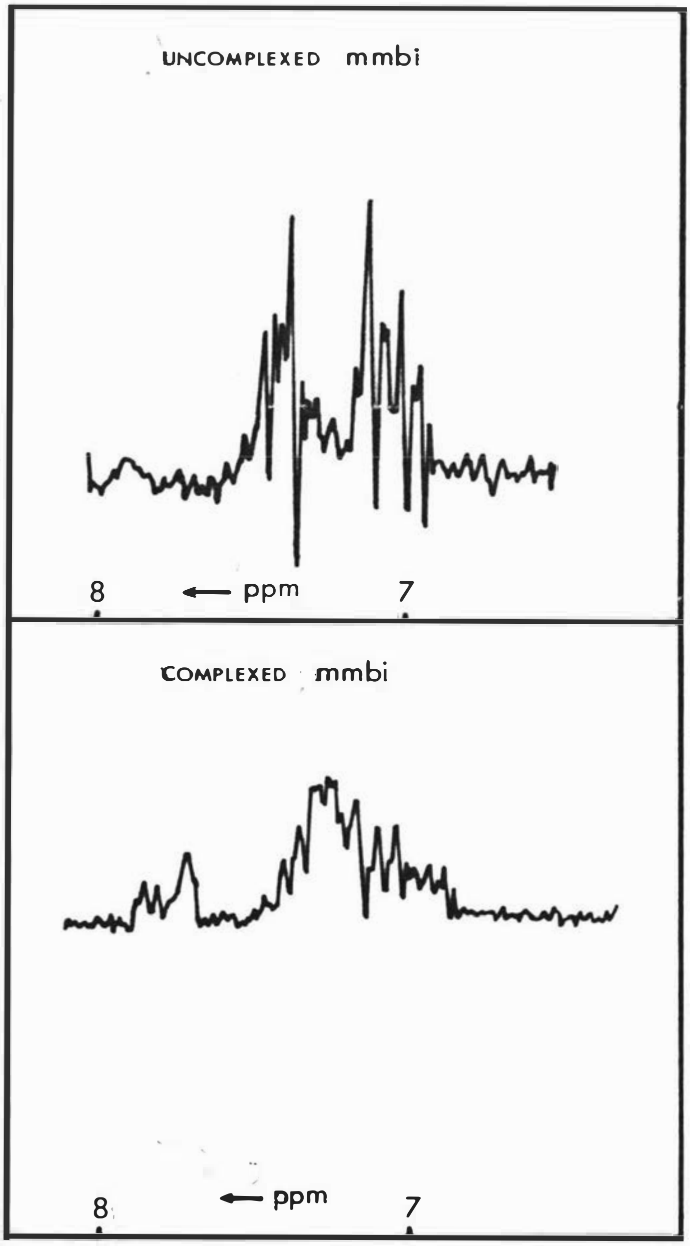
NOTES(Tables 18d, 18e):

† solutions decomposing

- all spectra recorded in $CDCl_3$, chemical shifts are ppm downfield from TMS,
- d = doublet; coupling constants are in parentheses(Hz).

FIGURE 14

^{1}H nmr - Aryl Protons of mmbi



- spectra recorded in $(CD_3)_2CO$.

The $-NH_2$ resonances were not observed for the $[M(CO)_5]_2L$ complexes (M=Cr, W) of ethylenediamine and 1,12-diaminododecane, either.[198]

ii) Complexes of 2-methylthioaniline

This ligand shows downfield shifts in the $-SCH_3$ resonance, of 0.32 ppm and 0.56 ppm for $Cr(CO)_5$mta and $W(CO)_5$mta respectively (Table 18b). On complexation of this ligand, the $-NH_2$ resonance has moved upfield and it is considerably weaker and broader than in the free ligand spectra. The evidence thus suggests that mta is binding via the thioether donor only.

iii) Complexes of 2-methylmercaptobenzimidazole

$Cr(CO)_5$mmbi and $W(CO)_5$mmbi also show downfield shifts in the $-SCH_3$ resonance of the ligand (0.15 ppm and 0.19 ppm respectively) however the larger downfield shifts of the -NH- resonance (ca 2.00 ppm and 0.44 ppm respectively) indicate that the ligand is probably complexed via one of the heterocyclic nitrogens (Table 18c). This conclusion is also supported by the asymmetrical pattern (Figure 14) of the aryl-ring proton absorptions (and at least two of the peaks move downfield) in the complexes. The free ligand, in contrast, shows a symmetrical pattern (Figure 14). A similar asymmetry is also observed for the complexes of benzimidazole.

iv) Complexes of 2-methylthio-2-imidazoline

The non-existence of any M-S interactions in the complexes of mti, is conclusively established by a comparison of the spectrum of the free ligand with the spectra of these complexes (Table 18d). While the $-SCH_3$ resonance is not significantly affected, the -NH- resonance moves 0.81 ppm and 0.87 ppm downfield for M=Cr and M=Mo respectively.

The -NH- resonance was not observed for M=W and this may be the result of exchange broadening effects and solubility problems.

For the free ligand, the methylene protons' resonance is a single peak but on complexation, four peaks are observed where M=Cr and Mo. This implies that the methylene protons have become inequivalent through metal complexation to one of the nitrogen donors.

The ^{1}H nmr data thus supports the suggestion from the force constant calculations that 2-methylthio-2-imidazoline binds to the zero-valent metals, Cr(0), Mo(0), and W(0), via one of the heterocyclic nitrogen donors and not the thioether substituent.

v) Complexes of 2-(3,3-dimethyl-2-thiabutyl)pyridine

In Table 18e, it can be seen that on the formation of the chelated-ligand complexes $M(CO)_4$tbmp, downfield shifts in the $-CH_2S-$ resonance and the resonance of the proton ortho to the pyridyl nitrogen, result. There are no significant shifts in the t-butyl protons' resonance.

3.6 ELECTRONIC SPECTRA

$[M(CO)_5]_nL$ Complexes (n=1,2)

The spectra are assigned similarly to those of the bridged-ligand bmtt and bett complexes (Chapter 1). In the complexes of mmbi, bi and mti though, $M \longrightarrow \pi^*(L)$ charge transfer is also possible and in the tungsten complexes of these ligands this absorption has been tentatively assigned.

i) L=etea, n=2.

Even though there are two distinctive $M(CO)_5L$ chromophores in these bridged-ligand complexes, the spectra are quite normal and there is no evidence of differences between the thioether and amine donors. The point to note from the spectra is that the 1e ⟶ $2a_1$ charge transfer transition of both complexes (M=Cr,W) lies in the region more appropriate for amine donors than thioether donors.

The spectra and their assignments are shown in Tables 19a (M=Cr) and 19b (M=W) respectively and a comparison of the 1e ⟶ $2a_1$ charge transfer transitions of the $[M(CO)_5]_nL$ complexes that are the subject of this chapter, together with other data from the literature, can be found in Tables 6a and 6b respectively (Chapter 1).

ii) L=mta, mmbi, mti (n=1)

L=mta: The 1e ⟶ $2a_1$ charge transfer absorptions for $Cr(CO)_5mta$ and $W(CO)_5mta$ are similar to those of $[Cr(CO)_5]_2bmtt$ and $[W(CO)_5]_2bmtt$ (see Chapter 1) respectively and these observations provide additional evidence for a $CH_3S \rightarrow M$ bonding mode in the complexes. The spectra for the $M(CO)_5mta$ complexes (M=Cr, Mo, W) and the tentative assignments that have been made, are shown in Tables 19a (M=Cr), 19b (M=W) and 19c (M=Mo) respectively.

L=mmbi: The similarities between the spectra of $Cr(CO)_5mmbi$ and $W(CO)_5mmbi$, and their respective, analogous complexes of benzimidazole (Tables 19a, 19b), support the infrared and nuclear magnetic resonance data for nitrogen ⟶ M(0) bonding in the complexes of mmbi. Further weight to this evidence is lent by the assignment of a $W \rightarrow \pi^*(L)$ charge transfer transition at about 330 nm for both $W(CO)_5mmbi$ and $W(CO)_5bi$. This medium intensity absorption is also observed for $W(CO)_5mti$, but not for $W(CO)_5mta$ or any of the bridged-ligand complexes of bmtt, bett and etea. This assignment is supported by the assignment of a similar

TABLE 19a

ELECTRONIC SPECTRA - $[Cr(CO)_5]_nL$ COMPLEXES

COMPLEX	ABSORPTION(nm)	ϵ (l.mol.$^{-1}$cm^{-1})	ASSIGNMENT
$[Cr(CO)_5]_2$etea	*ca* 256	26660	
	332(sh)	3538	
	412	4528	1e → $2a_1$/d-d
$Cr(CO)_5$mta	244		
	302		
	437		1e → $2a_1$/d-d
$[Cr(CO)_5$mmbi$]$.0.5mmbi	406	3124	1e → $2a_1$/d-d
$[Cr(CO)_5$bi$]$.0.5bi	259	16212	
	271(sh)	14622	
	279	12318	
	405	2616	1e → $2a_1$/d-d
$Cr(CO)_5$mti	256	21529	
	407	2908	1e → $2a_1$/d-d

TABLE 19b

ELECTRONIC SPECTRA - $[W(CO)_5]_nL$ COMPLEXES

COMPLEX	ABSORPTION(nm)	ϵ ($l.mol.^{-1}cm^{-1}$)	ASSIGNMENT
$[W(CO)_5]_2$etea	ca 260	19971	
	291(sh)	5058	
	390	4620	$1e \rightarrow 2a_1$
	397(sh)	4547	d—d (s—s)
	430(sh)	905	d—d (s—t)
$W(CO)_5$mta	ca 250		
	ca 295		
	304		
	392		
$W(CO)_5$mmbi	257	21818	
	288	11405	
	331(sh)	1959	$d \rightarrow \pi^*(L)$
	392	3140	$1e \rightarrow 2a_1$/d-d(s-s)
	423(sh)	826	d—d (s—t)
$W(CO)_5$bi	258	18125	
	268(sh)	10417	
	279	7917	
	281	4333	
	324	1604	$d \rightarrow \pi^*(L)$
	395	2799	$1e \rightarrow 2a_1$/d-d(s-s)
	426(sh)	792	d—d (s—t)
$W(CO)_5$mti	258	20516	
	283(sh)	6242	
	336	1621	$d \rightarrow \pi^*(L)$
	398	3331	$1e \rightarrow 2a_1$/d-d(s-s)
	432(sh)	1040	d-d (s-t)

TABLE 19c

ELECTRONIC SPECTRUM OF $Mo(CO)_5$mta

ABSORPTION(nm)	ϵ ($l.mol.^{-1}cm^{-1}$)	ASSIGNMENT
243	ca 15037	
309	ca 4889	
ca385	ca 350	$1e \rightarrow 2a_1$/d-d

NOTES: (For Tables 19a, 19b, 19c)

- all spectra were recorded for Abs. EtOH solutions,
- sh = shoulder; extinction coefficients are approximate,
- (s—s) denotes a singlet→singlet transition,
- (s—t) denotes a singlet→triplet transition,
- solution of $Mo(CO)_5$mta was decomposing.

TABLE 20

ELECTRONIC SPECTRA FOR $M(CO)_4L_2$ COMPLEXES

	L_2 = etea		L_2 = tbmp	
METAL	ABSORPTION(nm)	ϵ(l.mol.$^{-1}$cm^{-1})	ABSORPTION	ϵ
Cr	244	16711	341	5578
	338	4578	372	5167
	425	1393		
Mo	ca 242	15615	303	8080
	ca 264	16577	362	5678
	305	8942		
	391	1673		
W	ca 260	12586		
	301	5916		
	390	1284		
	410(sh)	535		

NOTES: - all spectra were recorded for Abs. EtOH solutions,

- sh = shoulder; extinction coefficients are approximate.

absorption for $W(CO)_5$pyridine at 334 nm.[231]

L=mti: The spectra of $Cr(CO)_5$mti and $W(CO)_5$mti (Tables 19a and 19b) suggest that the thioether substituent of this ligand, like mmbi, does not participate in $L \rightarrow M(CO)$ bonding. It is probable that $Mo(CO)_5$mti (Table 19c) is similar to its chromium and tungsten analogues.

cis-$M(CO)_4L_2$ COMPLEXES (L_2=etea, tbmp)

The spectra are recorded in Table 20, but as outlined in Chapter 2, specific assignments can not be made as yet. It is interesting to observe though, that the visible maxima for the etea complexes (M=Cr, Mo) are at lower energies than the same absorptions for the tbmp complexes. The visible maxima of the latter complexes are very similar to those of the bmtt and bett chelated-ligand complexes that were discussed in Chapter 2.

3.7 REACTIVITY STUDIES

COMPLEXES OF 2-ETHYLTHIOETHYLAMINE

These studies investigate the stability of $[W(CO)_5]_2$etea under reflux conditions and the stability of etea towards displacement by triphenylphosphite from $[W(CO)_5]_2$etea and $W(CO)_4$etea. The experiments were monitored by infrared spectroscopy.

i) Reflux $[W(CO)_5]_2$etea in cyclohexane

After about 5 minutes of refluxing, the conversion to the chelated-ligand complex is almost complete, although even after 15 minutes, a small amount of a pentacarbonyl complex is still present. The identity of this pentacarbonyl complex is not clear. The spectra are dominated by an intense absorption, due to $W(CO)_6$, at 1986 cm^{-1}.

Hence $[W(CO)_5]_2$etea $\longrightarrow$ $W(CO)_6$ + $W(CO)_4$etea, under gentle reflux conditions.

ii) Reflux $[W(CO)_5]_2$etea in presence of excess $P(OPh)_3$

In cyclohexane solution after 5 hours of refluxing, the initially yellow solution is almost colourless. The interpretation of the infrared spectra (Figure 15) is not as readily apparent as for the analogous experiment with $[W(CO)_5]_2$bett (Chapter 1).
The following points can be noted though:

a) there is no apparent thermal conversion of $[W(CO)_5]_2$etea to $W(CO)_4$etea as observed in the above experiment. In the reaction of $[W(CO)_5]_2$bett with $P(OPh)_3$, some of the chelated-ligand complex was formed initially (Chapter 1).

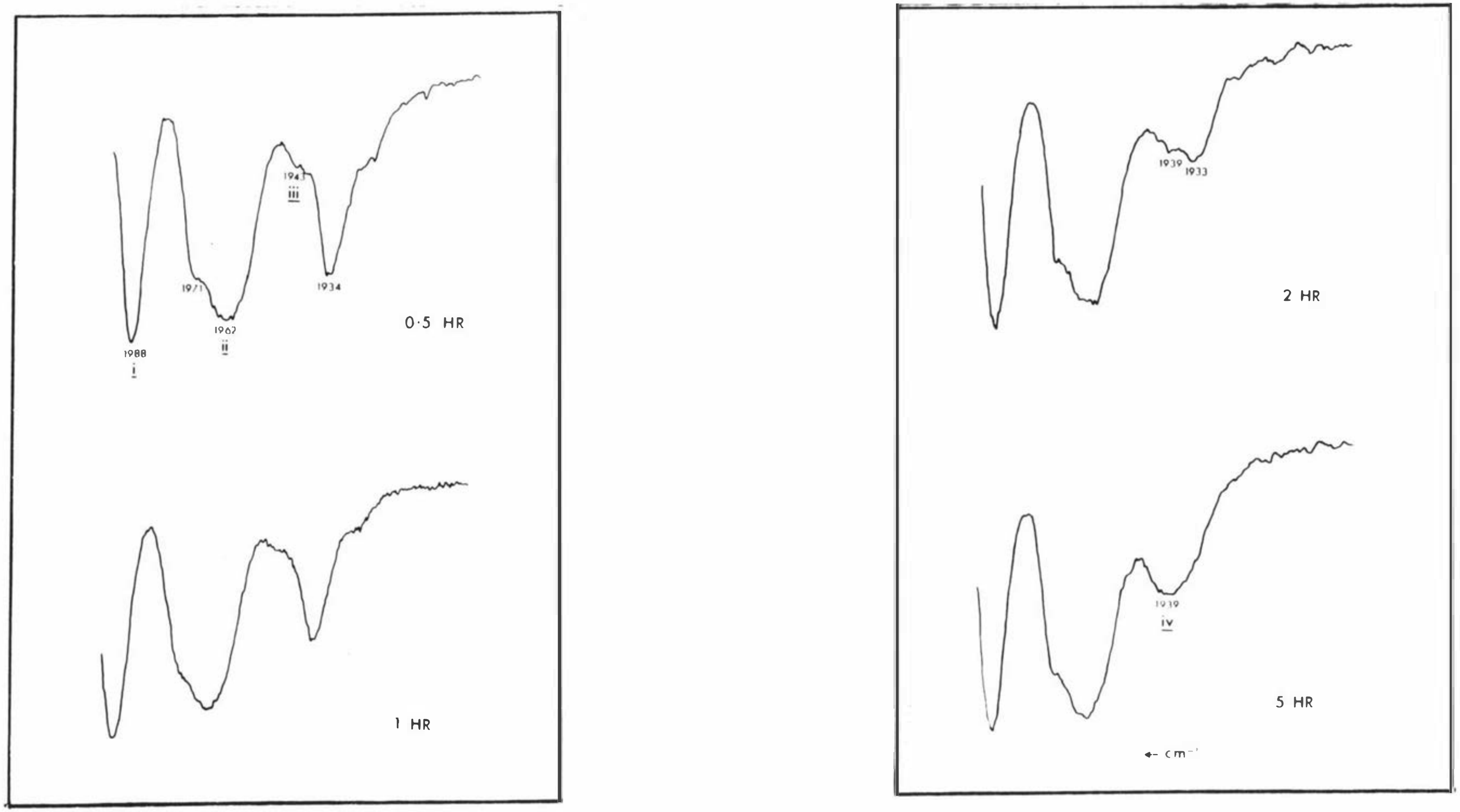
b) the changes in the strong absorption at about 1934 cm^{-1} during the refluxing, suggest that in the initial spectra the species that is responsible for this absorption is different than the species that gives rise to the absorption after 5 hours. The latter species appears to be cis-$W(CO)_4[P(OPh)_3]_2$ (see below) while the former could be an "intermediate".

iii) Reflux $W(CO)_4$etea in presence of excess $P(OPh)_3$

In both cyclohexane and benzene, the conversion of $W(CO)_4$etea to cis-$W(CO)_4[P(OPh)_3]_2$, in the presence of a ten-fold excess of triphenylphosphite, can be followed relatively easily by infrared spectroscopy. For the cyclohexane solution, the presence of cis-$W(CO)_4[P(OPh)_3]_2$ was indicated after only five minutes of refluxing. The changes over a period of 30, 40 and 60 minutes can be followed in

FIGURE 15

IR Spectra - Reflux $[W(CO)_5]_2$etea With Excess $P(OPh)_3$



Key to Figure 15

Species	Identity
i	$W(CO)_6$
ii	$W(CO)_5P(OPh)_3$
iii	$[W(CO)_5]_2$etea
iv	*cis*-$W(CO)_4[P(OPh)_3]_2$

Key to Figure 16

Species	Identity
i	$W(CO)_4$etea
ii	*cis*-$W(CO)_4[P(OPh)_3]_2$
iii	$W(CO)_6$

Both reflux experiments were carried out in cyclohexane.

FIGURE 16

IR Spectra - Reflux W(CO)$_4$etea With Excess P(OPh)$_3$

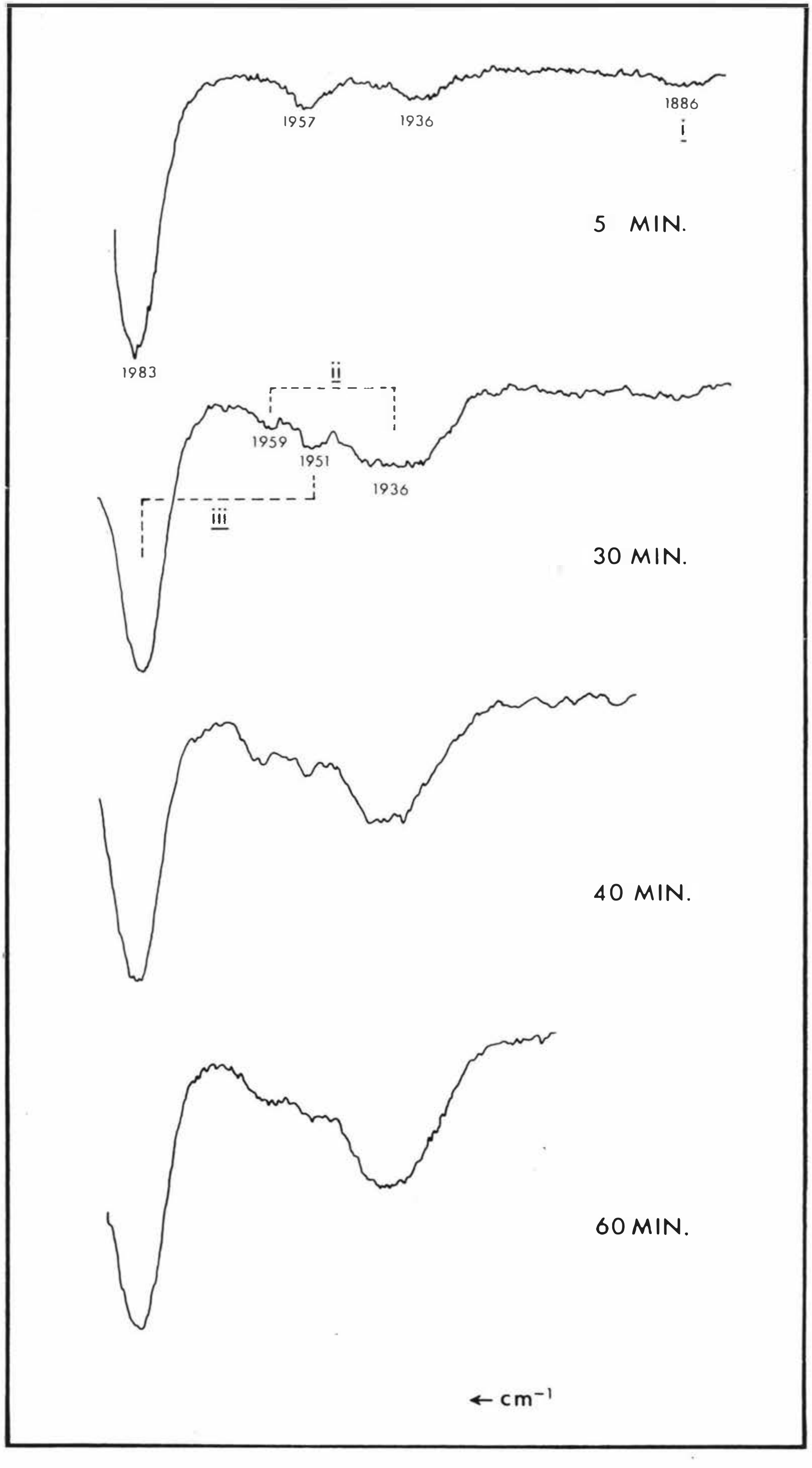


Figure 16 and it can be seen that the absorption at 1936 cm^{-1} is quite broad in comparison to the narrow band that was observed (Figure 15) in the initial stages of refluxing $[W(CO)_5]_2$etea with $P(OPh)_3$.

In an experiment where a slightly greater than 1:1 ratio of $P(OPh)_3$ to $W(CO)_4$etea was refluxed in cyclohexane, a similar conversion was observed. These experiments do not provide any insight though, into the nature of the postulated "intermediate" that was "observed" on refluxing $[W(CO)_5]_2$etea and excess $P(OPh)_3$ in cyclohexane.

COMPLEXES OF mta AND mti

Attempts were made to isolate the HBr salts of $Cr(CO)_5$mta, $W(CO)_5$mta and $Cr(CO)_5$mti, but although reactions were observed, the products were unstable and could not be characterized.

3.8 MASS SPECTRA OF $M(CO)_5$mta (M=Cr, Mo, W)

Although these complexes could not be isolated analytically pure, the mass spectra of the oils that were isolated from the reactions of $M(CO)_5$THF with mta provide additional evidence for the identity of the principal components of these oils.

The identities of the complexes $Cr(CO)_5$mta and $Mo(CO)_5$mta were confirmed by the detection of the molecular ions $[Cr(CO)_5mta]^+$ and $[Mo(CO)_5mta]^+$, while the mass spectrum of $W(CO)_5$mta shows only a weak feature that can be attributed to $[W(CO)_5mta]^+$. A stronger feature is observed at $^m/_e$ = 435 and this corresponds to $[W(CO)_4mta]^+$. It appears then, that volatilisation and electron bombardment provide sufficient energy to convert $W(CO)_5$mta to $W(CO)_4$mta, but this could only be achieved to a very limited extent by refluxing

$W(CO)_5$mta in cyclohexane.

There are no peaks in the spectra of $Mo(CO)_5$mta and $W(CO)_5$mta that can be attributed to $[M(CO)_7]^+$ (M=Mo, W) or $[W(CO)_8]^+$ in the latter spectrum.

SYNTHESES

The same general photochemical method that is used for the syntheses that were described in Chapter 2, is also used here.

1) COMPLEXES OF 2-ETHYLTHIOETHYLAMINE

Decacarbonyl-μ-(2-ethylthioethylamine)dichromium(0)

The ligand (2 mmole, 0.210 g.) was added to an irradiated solution of 4 mmole of $Cr(CO)_6$ (0.880 g.). After allowing the solution to react for 10 minutes, the solvent was removed in vacuo. Excess $Cr(CO)_6$ was sublimed from the yellow residue overnight and then the residue was extracted into benzene. The solution was concentrated, cooled and cyclohexane was added to precipitate an oil that contained both tetra- and pentacarbonyl complexes. The solvent was removed from the supernatant and a crystalline pentacarbonyl complex was precipitated from a cyclohexane solution of the residue. The $[Cr(CO)_5]_2$etea was recrystallized from benzene by the addition of cyclohexane. $[Cr(CO)_5]_2$etea was also precipitated from a cold benzene solution of the above oil, on adding cyclohexane.

Both samples were washed with cold cyclohexane after filtering and dried under vacuum.

YIELD : 0.177 g. (18%)

Decacarbonyl-μ-(2-ethylthioethylamine)ditungsten(0)

1 mmole of the ligand (0.105 g.) was added to an irradiated solution of 2 mmole of $W(CO)_6$ (0.704 g.). The solution was allowed to react for 10-15 minutes before the solvent was removed in vacuo. Excess $W(CO)_6$ was sublimed from the residue, which was subsequently extracted into benzene. The yellow crystals of $[W(CO)_5]_2$etea precipitated from a

benzene-cyclohexane solution that had been left at 4°C overnight. After filtering, these were washed with cold cyclohexane then dried under vacuum.

YIELD : 0.312 g. (50%)

Tetracarbonyl(2-ethylthioethylamine)chromium(0)

After the addition of 3 mmole of etea (0.316 g.) to the irradiated solution of 3 mmole of $Cr(CO)_6$ (0.660 g.), the irradiation was continued for a further 90 minutes. The THF and excess $Cr(CO)_6$ were removed *in vacuo* and the crystalline residue was extracted into benzene. The solution was concentrated until the onset of precipitation and then cyclohexane was added and the mixture cooled. The yellow precipitate was filtered off and washed with cyclohexane.

YIELD : 0.510 g. (63%)

Tetracarbonyl(2-ethylthioethylamine)molybdenum(0)

The same procedure as for $Cr(CO)_4$etea was followed using 3 mmole of etea (0.316 g.) and 3 mmole of $Mo(CO)_6$ (0.792 g.). $Mo(CO)_4$etea was precipitated out of a concentrated benzene solution by adding a small quantity of cyclohexane and then cooling the solution.

YIELD : 0.667 g. (71%)

Tetracarbonyl(2-ethylthioethylamine)tungsten(0)

Pale yellow $W(CO)_4$etea was synthesized by the same procedure as $Cr(CO)_4$etea and $Mo(CO)_4$etea. 2 mmole of etea (0.210 g.) and 2 mmole of $W(CO)_6$ (0.704 g.) were used.

YIELD : 0.581 g. (72%)

2) COMPLEXES OF 2-(3,3-DIMETHYL-2-THIABUTYL)PYRIDINE

Tetracarbonyl[2-(3,3-dimethyl-2-thiabutyl)pyridine]-chromium(0)

The ligand (2 mmole, 0.363 g.) was added to the irradiated $Cr(CO)_6$ (2 mmole, 0.440 g.) and the irradiation continued for 90 minutes. The solvent was removed *in vacuo*, the residue extracted into benzene, then the solution concentrated and n-hexane added to crystallize the yellow complex. The $Cr(CO)_4$tbmp was recrystallized from hot n-hexane containing a small amount of benzene and the needle-like crystals were filtered off and dried under vacuum.

YIELD : 0.316 g. (46%)

Tetracarbonyl [2-(3,3-dimethyl-2-thiabutyl)pyridine]-molybdenum(0)

2 mmole of ligand (0.363 g.) and 2 mmole of $Mo(CO)_6$ (0.528 g.) were used as for $Cr(CO)_4$tbmp. The tbmp/$Mo(CO)_6$ /THF solution was irradiated for only 60 minutes and then $Mo(CO)_4$tbmp was isolated and recrystallized as for $Cr(CO)_4$tbmp.

YIELD : 0.492 g. (63%)

Tetracarbonyl [2-(3,3-dimethyl-2-thiabutyl)pyridine]-tungsten(0)

The initial procedure was the same as for $Cr(CO)_4$tbmp using 2 mmole of tbmp and 2 mmole of $W(CO)_6$ (0.704 g.). The removal of the THF left an oily residue that contained a black decomposition product. This was removed by adding n-hexane to the benzene extract then filtering the cloudy suspension through Kieselguhr. The orange filtrate was concentrated and filtered then hexane was added. The solution was cooled to precipitate $W(CO)_4$tbmp which was recrystallized from benzene as for $Cr(CO)_4$tbmp and $Mo(CO)_4$tbmp.

YIELD : 0.248 g. (26%)

3) COMPLEXES OF 2-METHYLTHIO-2-IMIDAZOLINE

Pentacarbonyl(2-methylthio-2-imidazoline)chromium(0)

3 mmole of mti (0.349 g.) were added to 3 mmole of irradiated $Cr(CO)_6$ (0.660 g.) when the THF was removed and

the residue extracted into benzene-pentane. This solution was concentrated to about 2 cm^3 and pentane was added to precipitate yellow $Cr(CO)_5$mti. The product was filtered, washed with pentane and recrystallized from THF.

YIELD : 0.534 g. (58%)

Pentacarbonyl(2-methylthio-2-imidazoline)molybdenum(0)

In this reaction, 3 mmole of mti and 3 mmole of $Mo(CO)_6$ were used as in the preparation of $Cr(CO)_5$mti. The residue that remained after removing the THF was unstable in acetone, does not extract into benzene-pentane and in pure benzene, it has a low solubility. It was however, extracted into benzene, the solution filtered through Kieselguhr, concentrated and filtered again. The solution was concentrated further to about 10 cm^3, cooled and pentane was added to precipitate light yellow $Mo(CO)_5$mti. The product was filtered, washed with pentane and dried before recrystallizing from THF.

YIELD : 0.382 g. (36%)

An unsuccessful attempt was made to convert $Mo(CO)_5$mti to $Mo(CO)_4$mti by refluxing the pentacarbonyl complex in THF for an hour. There was no infrared evidence for the formation of any $Mo(CO)_4$mti.

Pentacarbonyl(2-methylthio-2-imidazoline)tungsten(0)

This was isolated from an unsuccessful attempt to synthesize the bridged-ligand complex $[W(CO)_5]_2$mti using 2 mmole of $W(CO)_6$ (0.704 g.) and 1 mmole of mti (0.116 g.). The solution was allowed to react for 5 minutes after adding the ligand to the irradiated $W(CO)_6$ solution and then the solvent was removed. The pentane-insoluble residue was extracted into hexane-benzene (50:50). The solvent was removed (in vacuo) from the extract, the residue dissolved in acetone and the mixture filtered to remove excess $W(CO)_6$. An impure product was isolated from this acetone solution and so it was purified on a silica-gel column, using an acetone eluent. The column fraction was taken to dryness and the residue put under vacuum for 24 hours. An infrared spectrum showed that the $W(CO)_6$ had been removed from the $W(CO)_5$mti.

4) COMPLEXES OF 2-METHYLMERCAPTOBENZIMIDAZOLE

Pentacarbonyl(2-methylmercaptobenzimidazole)chromium(0). 0.5 [2-methylmercaptobenzimidazole]

A THF solution of the ligand (3 mmole, 0.493 g.) was added to 3 mmole of irradiated $Cr(CO)_6$ (0.660 g.). The solvent was removed, the residue extracted into acetone and the solution concentrated. A precipitate which appeared dissolved on adding benzene. This solution was filtered concentrated and petroleum ether added to precipitate a yellow powder which was filtered and washed with benzene.

YIELD : 0.656 g. (75%)

Pentacarbonyl(2-methylmercaptobenzimidazole)tungsten(0)

A 1:1 ratio of mmbi to $W(CO)_6$ was used as for the chromium complex. After the THF was removed, the residue was extracted with benzene and then the benzene insoluble residue was extracted into acetone. While the benzene extracts contained both pentacarbonyl and tetracarbonyl complexes, the acetone soluble fraction consisted mainly of $W(CO)_5$mmbi. The impure product was recrystallized twice from acetone solutions by the addition of cyclohexane.

An attempt was made to convert a sample of $W(CO)_5$mmbi to $W(CO)_4$mmbi by irradiating it in THF for 2 hours, but this was unsuccessful.

5) COMPLEXES OF BENZIMIDAZOLE

$Cr(CO)_5bi$ and $W(CO)_5bi$ were first reported by Beck, Weis and Wieczorek [212] who synthesized the complexes using the same photochemical techniques that have been described herein (see Appendices). The preparations that were used for this work differ in content though and in the synthesis of the chromium complex, $[Cr(CO)_5bi]\cdot 0.5bi$ was isolated instead of $Cr(CO)_5bi$ as reported by Beck *et al*.

Pentacarbonyl(benzimidazole)chromium(0).0.5[benzimidazole].

3 mmole of the ligand (0.354 g.) in THF were added to an irradiated solution of 3 mmole of $Cr(CO)_6$ (0.660 g.) The THF was removed, the yellow crystalline residue extracted into benzene and the solution concentrated. An impure product was precipitated by adding cyclohexane to the benzene solution. It was therefore dissolved in acetone, the solution was filtered and cyclohexane-pentane added. A yellow precipitate appeared when the solution was cooled and this was filtered, washed with cyclohexane and pentane, then dried *in vacuo*.

YIELD : 0.581 g. (78%)

There is little change in the analyses for this complex on further recrystallization from THF.

Pentacarbonyl(benzimidazole)tungsten(0)

The same procedure as for $[Cr(CO)_5bi]\cdot 0.5bi$ was initially followed, using 2 mmole of ligand (0.236 g.) and 2 mmole of $W(CO)_6$ (0.704 g.). Yellow crystals were precipitated by adding cyclohexane to a concentrated benzene solution of the residue. These were filtered, washed with pentane and recrystallized from benzene.

YIELD : 0.725 g. (82%) - before recrystallization

6) SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF 2-METHYLTHIOANILINE

The analytically pure complexes M$(CO)_5$mta (M=Cr,Mo,W), could not be isolated because of their reluctance to form crystalline products and because they rapidly decompose on silica-gel columns. Their existence and nature was however, inferred from IR, ^{1}H nmr and mass spectral studies (this chapter) and the investigations that are described in the following sections.

Pentacarbonyl(2-methylthioaniline)chromium(0)

After the ligand (3 mmole, 0.418 g.) had been added to an irradiated solution of $Cr(CO)_6$ (3 mmole, 0.660 g.), the THF was removed and the green-yellow residual oil was extracted into n-hexane. A yellow oil deposited on removing the solvent from these extracts. The oil was "dried" for 20 hours under vacuum, but the analyses approximate those required for $[Cr(CO)_5mta].0.5(C_6H_{14})$

Calculated for $[Cr(CO)_5mta].0.5(C_6H_{14})$:	C 48.12%;	H 4.30:	N 3.74
Found :	48.90 ;	4.03;	3.69

An unsuccessful attempt was made to synthesize $Cr(CO)_4$mta by irradiating $Cr(CO)_5$mta in THF.

Pentacarbonyl(2-methylthioaniline)molybdenum(0)

The same method as for the chromium complex was followed using 3 mmole of the ligand and 3 mmole of $Mo(CO)_6$ (0.792 g.). A brown precipitate separated with the yellow oil, but it was carefully removed by dissolving in hexane. The presence of some $Mo(CO)_6$ was indicated by the IR spectrum of the yellow oil.

Pentacarbonyl(2-methylthioaniline)tungsten(0)

This was prepared by the same method as for the chromium and molybdenum complexes using 2 mmole of mta (0.279 g.) and 2 mmole of $W(CO)_6$ (0.704 g.). A cloudy, yellow oil was isolated from the n-hexane extracts.

In a second preparation, a light yellow solid (MP. 70 - 72^{o}) was isolated and this returned Carbon and Hydrogen analyses corresponding to those required for $[W(CO)_5mta]$.0.25(hexane).

Calculated for $[W(CO)_5mta]$.0.25(hexane): C 33.45%; H 2.59
Found : 33.15 ; 2.75

Further characterization of $W(CO)_5$mta

i) After 10 minutes of refluxing $W(CO)_5$mta with a ten-fold excess of $P(OPh)_3$, all of the mta had been replaced by $P(OPh)_3$. An IR spectrum of the reaction products in chloroform provides good evidence for this conclusion.

Reaction Products :2084(s);1995(sh);1967(sh); 1952(vs)
Literature $W(CO)_5P(OPh)_3$(Ref 291):2088(s);1997(sh);1968(sh); 1955(vs)

The observed formation of $W(CO)_5P(OPh)_3$ is in itself, good evidence for the existence of a $W(CO)_5$mta complex.

ii) $W(CO)_5$mta was refluxed in a cyclohexane and this forced the formation of a small quantity of a tetracarbonyl complex, but the intensities of the IR absorptions after 8 hours of refluxing were the same as they were after 1 hour.

TABLE 21

MISCELLANEOUS PHYSICAL DATA

COMPLEX	COLOUR	M.P/^{o}C	ANALYSES: Calc.(Found)/%			
			C	H	N	S
$[Cr(CO)_5]_2$etea	yellow	72-75	34.37 (34.27)	2.27 (2.95)		6.55 (6.12)
$[W(CO)_5]_2$etea	yellow	83-84	22.34 (22.55)	1.47 (1.65)		4.26 (4.99)
$Cr(CO)_4$etea	yellow	114-117	35.69 (35.76)	4.12 (4.09)		11.91 (12.38)
$Mo(CO)_4$etea	yellow	117-118	30.68 (30.52)	3.54 (3.58)		10.24 (10.18)
$W(CO)_4$etea	pale yellow	150-151	23.95 (23.21)	2.76 (2.91)		7.99 (8.47)
$Cr(CO)_4$tbmp	yellow	125-127	48.69 (48.98)	4.38 (4.67)	4.06 (3.94)	
$Mo(CO)_4$tbmp	yellow	134-136	43.19 (43.59)	3.88 (3.91)	3.60 (2.59)	
$W(CO)_4$tbmp	yellow	169-170	35.24 (35.57)	3.17 (3.29)	2.94 (2.89)	
$Cr(CO)_5$mti	yellow	dec. > 100	35.07 (35.38)	2.62 (2.68)	9.09 (9.09)	
$Mo(CO)_5$mti	pale yellow	dec.125	30.69 (30.84)	2.29 (2.36)	7.96 (8.94)	
$W(CO)_5$mti	yellow-orange	dec.167	24.56 (24.83)	1.83 (2.22)	6.37 (6.78)	
$[Cr(CO)_5$mmbi$]$.0.5mmbi	yellow	> 230	46.57 (46.60)	2.76 (3.17)	9.59 (9.22)	
$W(CO)_5$mmbi	pale yellow	167-169	31.98 (32.03)	1.65 (1.56)	5.74 (5.71)	
$[Cr(CO)_5$bi$]$.0.5bi	pale yellow	dec.104	50.42 (49.93)	2.46 (2.85)	11.38 (11.25)	
$W(CO)_5$bi	yellow	146-150	32.61 (32.91)	1.37 (1.27)	6.34 (5.91)	

GENERAL DISCUSSION

AND

CONCLUSIONS

THIOETHER INTERACTIONS
WITH
ZERO-VALENT METALS

A) ARYL THIOETHER AND ALKYL THIOETHER LIGANDS

The $[M(CO)_5]_2L$ complexes (where M = Cr, W and L = bmtt, bett) that were characterized in this study are the first examples of bridged-ligand, Group VIB metal carbonyl complexes of dithioether-substituted, benzene-related ligands. This type of complex was not reported in an earlier study on the Group VIB metal carbonyl complexes of 1,2-bis(methylthio)benzene.[195] The formation of both bridged-ligand and chelated-ligand ($M(CO)_4L_2$ where M = Cr,Mo, W and L_2 = bmtt, bett) complexes demonstrates the flexibility of these ligands towards transition metal coordination. Similar behaviour is observed for other dithioether ligands (such as the $RS(CH_2)_nSR$ ligands; see Table 1).

i) Interpretation of Electronic Spectra

The electronic spectra of the $[M(CO)_5]_nL$ complexes of the aryl thioether ligands bmtt (n=2), bett (n=2), m-bmtb (n=2) and mta (n=1), are consistent with the M-S (thioether) bonding being weaker than in analogous complexes of alkyl thioether ligands such as $RSCH_2CH_2SR$ (where R = t-Bu, Et). Similar differences between the bridged-ligand complexes of $RSCH_2CH_2SR$ where R is p-XC_6H_4 (X = NO_2,Cl,H,Me,OMe,NMe_2) [194] and where R is t-Bu[194] are also apparent on examining the electronic spectral data for those complexes.

The electronic spectral results suggest that, in general, aryl thioether ligands [and phosphine sulphides such as $SPMe_3$ and $SP(Me_2\phi)$] have net σ-donor/ π-acceptor bonding characteristics similar to those of heterocyclic and alkyl amine ligands.

The electronic 1e ⟶ $2a_1$ C.T. transition (see Chapter 1, Section II) of $Cr(CO)_5SPMe_3$ occurs at energies similar to those of the $[Cr(CO)_5]_nL$ complexes of aryl thioether ligands (see Table 6, Section II) such as bmtt, bett, pte, nte (all n=2) and mta (n=1). This suggests that the overall strengths of the individual Cr-S bonds in all of these complexes are similar, and that the Cr-S bond(s) will be comparable in length to the Cr-S bond (2.510(2) Å) of $Cr(CO)_5SPMe_3$.[227] That is, they should be longer than in $Cr(CO)_5S(Et)CH_2Ph$[203] (2.458(2) Å), for which the 1e ⟶ $2a_1$ C.T. transition energies are similar to those of the $[Cr(CO)_5]_nL$ (n=1 or 2) complexes of other alkyl thioether ligands (see Table 6, Section II). Similar predictions are applicable to the $[W(CO)_5]_nL$ complexes of aryl thioether ligands.

In the absence of knowledge about the electronic spectra of $M(CO)_4L_2$ complexes (see Chapter 2, Section II), it can not be said with any certainty that similar predictions apply to these complexes. That is, it can not be argued that the bonding behaviour of a specific bidentate ligand (e.g. bmtt,bett,o-bmtb,dto) will necessarily be similar in both its bridged- and chelated-ligand complexes. For example, in its chelated-ligand complexes, a ligand may act as a better π-acceptor[221] (compared to its bridged-ligand complexes), simply because there is one less carbonyl group competing for the metals π-bonding, d-electrons. This means that although aryl dithioethers may exhibit weakened M-S bonding in their $[M(CO)_5]_2L$ complexes (compared to alkyl dithioethers), this may not be apparent in their chelated-ligand complexes. This point is evident from a comparison of the crystal structures of $W(CO)_4$o-bmtb[195] and $W(CO)_4(t\text{-}BuS(CH_2)_nSt\text{-}Bu)$[200] where n=2 and 3. In fact, for the former complex, the W-S bonds (mean 2.52(2) Å) may actually be slightly shorter that in the latter complexes (n=2, mean W-S = 2.562(5) Å and n=3, mean W-S = 2.578(5) Å.). However, the differences are not statistically significant and there is the possibility that steric interactions may have an effect on the W-S bonding in the latter complexes.

ii) Force Constant Calculations

The information provided by the force constant calculations for the complexes of thioether ligands other than C_6F_5SEt is more difficult to interpret. For the chromium complexes (Tables 4 and 9b) there do not appear to be any major differences between the net π-acceptor/ σ-donor bonding characteristics of the sulphur atoms in alkyl thioether ligands (e.g. dto, bms, $S(Et)CH_2Ph$, $S(Et)_2$) and aryl thioether ligands (e.g. bmtt, bett, o-bmtb, mta, $S(Ph)_2$) where RS- is adjacent to an aromatic π-orbital system. However, for the tungsten complexes (Tables 4 and 9b) there do appear to be some differences, especially in the $W(CO)_4L_2$ complexes. The aryl thioether ligands generally appear to be better π-acceptors and/or weaker σ-donors. It is not clear why such differences are more significant in the tungsten complexes. Factors such as energy differences between the M(O) d-orbitals and the acceptor/donor orbitals on the sulphur atoms, will be important in determining net $M \xrightarrow{\sigma/\pi} S$ overlap.

iii) General Conclusions

Over all, the results of these spectroscopic studies [and those of other authors][194,198] tend to suggest that aryl thioether ligands are poorer σ-donors and, in general, may act as better π-acceptors (particularly in chelated-ligand complexes) than alkyl thioether ligands. These conclusions are in agreement with the recently published results for a study on the electronic spectra of some Pt(II) and Pd(II) complexes of aryl thioether and alkyl thioether ligands.[177]

The poorer σ-donor ability of aryl thioether ligands probably arises from delocalisation of the sulphur lone-pair electrons onto adjacent π-orbital systems (i.e., n_S/π conjugation). These effects are enhanced by the presence of electron-withdrawing substituents. Photoelectron spectroscopic studies for ligands such as 1,4-bis(methylthio)-benzene, methylthiobenzene and 2-methylthionaphthalene[187,188,265] have shown this delocalisation to be real. It can also be used to explain the photoelectron spectra of bmtt, bett and m-bmtb (see Chapter 7, Section I).

It was concluded (This Work) from the spectroscopic properties of the Pt(II) and Pd(II) complexes of 1,2-bis(pentafluorophenylthio)ethane and ethylthiopentafluorobenzene (Pt(II) only), that the π-component of the M-S (thioether) bonding is probably of only minor importance to its net strength. Other workers have come to similar conclusions[249,266] and further support for these conclusions is lent by the studies on the $M(CO)_5I$ complexes of C_6F_5SEt. Hence although it is apparent from force constant calculations that the π-component of the M-S bonding (M = Cr, W) in these complexes is significantly greater than for other thioether ligands, a decrease in $S \rightarrow M$ σ-donation (due to electronegativity effects) results in the complexes being quite unstable.

This study has shown that substituent effects can influence the π-acceptor/ σ-donor properties of thioether ligands. The effects are manifested in the spectroscopic and chemical properties (e.g. the unstable nature of the $M(CO)_5C_6F_5SEt$ complexes) of their Group VIB metal carbonyl complexes.

B) MIXED (THIOETHER)S-N LIGANDS

The bridged and chelated ligand complexes of etea and the chelated-ligand complexes of tbmp, are the first examples of these types of Group VIB metal carbonyl complex involving sulphur-nitrogen donor ligands. Similar bridging and chelating roles have been observed in the metal carbonyl complexes of phosphorus-nitrogen (e.g. 2-(diphenylphosphinoamino)pyridine [248]) and phosphorus-sulphur ligands (e.g. $(Ph)_2PCH_2CH_2SMe$ [249]).

In the infrared spectra of the $[M(CO)_5]_2$etea complexes, averaged carbonyl stretching absorptions are observed. That is, there is no splitting of the carbonyl stretching absorptions as a result of bonding differences between the S(thioether) and N donors at the respective $M(CO)_5L$ centres. The infrared spectra for the complexes of 2-(diphenylphosphinoamino)pyridine and $(Ph)_2PCH_2CH_2SMe$ are similar in this respect.

For the ligands mti and mmbi, these studies have provided conclusive evidence for the preference of M-N interactions (over M-S interactions) in their $M(CO)_5I$ complexes. In transition metal complexes of imidazole and benzimidazole, the ligand almost invariably binds via the pyridine nitrogen and not the pyrrole nitrogen (-NH-).[153] The latter will only bind if the proton is removed. There is no reason to suspect that mti and mmbi are any different in this respect. There is no indication, from the spectroscopic results, that M-S(thioether) interactions exist in the complexes of mti and mmbi with the zero-valent Group VIB metals. These results are thus in general agreement with the interpretation of the spectroscopic data for the Cu(II) complexes of these ligands. (Cu(II)/mti complexes, see Chapter 5, Section I; Cu(II)/mmbi complexes, Ref. 148) and for a Co(II) complex of mti (Chapter 5, Section I).

From a consideration of the Pearson classification of acids and bases,[6] it may be intuitively expected that Cu(II) would prefer to bind to one of the heterocyclic nitrogens of mti and mmbi. Similar reasoning would suggest that the "soft" zero-valent metals (Cr(O), Mo(O), W(O)) would prefer to bond to the "soft" thioether sulphur in these ligands. That this expectation is not observed may suggest that:

i) Steric considerations are important in determining the nature of the M(O)-I interactions where I is mti and mmbi. However, molecular model studies do not provide any evidence to support this suggestion.

ii) Pyridyl N is a "softer" base than thioether S. Although this can be legitimately infered from the results of the carbonyl studies, the studies on the Cu(II) complexes of mti and mmbi do not support this suggestion.

iii) π -backbonding to the carbonyl groups of $M(CO)_5$ may cause M(O) to act more as an "intermediate" acid and therefore, to prefer M(O)-N interactions on the formation of $M(CO)_5L$ (L = mti, mmbi).

In contrast to mti and mmbi, it is apparent from the spectroscopic data for the $M(CO)_5$mta complexes, that mta prefers to bind via the thioether sulphur donor only. Chelated-ligand complexes of mta could not be isolated, even though their presence was indicated in reflux and mass spectral studies.

The $-NH_2$ group's reluctance to participate in bonding to zero-valent Cr, Mo and W can be attributed to the low basicity of the aniline amino group. Aniline is a weaker base (due to electron delocalisation) than heterocyclic amines such as pyridine[267] and imidazole.[153] Dennenberg and Darensbourg[237] have previously commented on the unstable nature of $Cr(CO)_5$aniline in solution, which precluded further attempts to purify the complex.

Hence, even the extra stability that is usually imparted by chelation (see Introduction, Section I) does not appear to readily induce M(O)-amine interactions in mta.

C) BONDING CHARACTERISTICS OF DIFFERENT LIGAND TYPES

Before crystallographic data became available for Group VIB metal carbonyl complexes of thioether ligands, it was assumed[129] that the π-acceptor ability of thioether sulphur is similar to that of related phosphine ligands. However a comparison[199] of the structures of complexes such as $Cr(CO)_4$diphos (diphos = 1,2-bis(diphenylphosphino)ethane)[268] and $Cr(CO)_4$dto (dto = 3,6-dithiaoctane)[199] indicated that thioethers have a lower π-acidity than phosphine ligands. In the former complex the Cr-P bonds (mean, 2.360(2) Å) are significantly shorter than the Cr-S bonds (mean, 2.418(1) Å) of $Cr(CO)_4$dto, even though phosphorus is considered to have a greater covalent radius (1.10 Å)[22] than sulphur (1.04 Å).[22] The similarity of the cis and trans Cr-CO bondlengths in the respective complexes (Table 22) implies that the net electron densities at the respective chromium atoms are similar. The same argument applies to $Cr(CO)_5P(Ph)_3$ and $Cr(CO)_5S(Et)CH_2Ph$. Thus if phosphine ligands such as diphos and $P(Ph)_3$ are better π-acceptors than thioethers such as dto and $S(Et)CH_2Ph$, they must also be better σ-donors.[199]

TABLE 22

STRUCTURAL DATA FOR Cr(O) COMPLEXES

COMPLEX	cis-Cr-CO	trans-Cr-CO	Cr-L	REFERENCE
$Cr(CO)_6$	1.909(3)			269
	1.914(2)			264
$Cr(CO)_5P(OPh)_3$	1.896(5)	1.861(4)	2.309(1)	270
$Cr(CO)_5P(Ph)_3$	1.880(4)	1.844(4)	2.422(1)	270
$Cr(CO)_5S(Et)CH_2Ph$	1.88(1)	1.859(7)	2.458(2)	203
$Cr(CO)_5SPMe_3$	1.900(4)	1.815(8)	2.510(2)	227
$Cr(CO)_4$diphos	1.884(7)	1.831(7)	2.360(2)	268
$Cr(CO)_4$dto	1.887(3)	1.832(3)	2.418(1)	199
$Cr(CO)_4I_2^{SMe}$	1.886(9)	1.833(7)	2.379(2)	207
$Cr(CO)_3$(3NH-pd)		1.816(5)	2.185(4)	271

- 3NH-pd = 3-Azapentane-1,5-diamine
- all bondlengths are Angstroms.

Alkyl amine ligands do not have any π-acidity at all.[232] This is reflected in the short trans-Cr-CO bonds (Table 22) of $Cr(CO)_3$(3NH-pd). In the Group VIB metal carbonyl complexes, an increase in M → L π-interactions results in an increase in the M-CO bondlengths. This effect is particularly evident in the trans-M-CO bonding (see Table 22 for Cr complexes)

In contrast to the alkyl amine ligands, aromatic heterocyclic amines have π^*-orbitals that are capable of participating in π-bonding with filled d-orbitals on M(O).[237] The effects of these π-interactions have been observed in a variety of studies (kinetics,[237] photoelectron[232] and ^{13}C nmr[231,232] spectral studies, thermodynamic studies [231]) and they can be shown to influence the W-pyridine stretching frequencies in a series of $W(CO)_5$(4R-pyridine) complexes.[231] However, (in contrast to P and S ligands) these π-interactions have not been observed to have any significant influence on $\nu(CO)$,[231,237] $\nu(W-C)$[231] and $\delta(WCO)$[231] frequencies, and ^{13}CO nmr chemical shifts.[231]

The results of the spectroscopic investigations that have been presented in this thesis, when considered in conjunction with the work of other authors, allow various types of phosphorus, sulphur and nitrogen donor ligands to be placed in the following general order of decreasing M(C)-I interactions:

phosphite > phosphine > alkyl thioether > aryl thioether ~ phosphine sulphur ~ pyridyl N ~ alkyl 1^{ry}amine > aryl 1^{ry}amine.

This series is derived primarily from the electronic spectroscopic data for $[M(CO)_5]_nI$ complexes (n = 1 or 2).

In terms of decreasing π-acceptor ability, the general ligand sequence:

phosphite > phosphine > aryl thioether > alkyl thioether > phosphine sulphide ~ pyridyl N,

is consistent with crystallographic and infrared spectroscopic data.

Spectroscopic and crystallographic investigations into the nature of the Group VIB metal carbonyl complexes of thioether ligands, have thus provided a valuable insight into the bonding behaviour of these ligands. The comparison of relevant data with that for analogous complexes of phosphorus and nitrogen donor ligands, has been of particular importance to the interpretation of the results of these studies.

THE ROLE OF STERIC INTERACTIONS IN THE COMPLEXES OF tbmp, tbmq, I, etea AND mti

1) COMPLEXES OF tbmp

The crystallographic and spectroscopic studies on the M(II) (M = Cu, Co, Ni) and Cu(I) complexes of tbmp, have shown that their structural and behavioural diversity is broad and complex. A comparison with the complexes of other bidentate ligands, suggests that part of this diversity may be attributed to the influence of the bulky t-butyl groups that are attached to the coordinated sulphur atom.

i) On examination of the crystal structure of $[Cu(tbmp)Br_2]_2$ (Chapter 1, Section I), the t-butyl groups appear to be responsible for blocking the approach of a sixth ligand to the remaining coordination site on each Cu(II). The complex therefore, exists as discrete dimers. Crystallographic studies on complexes such as $Cu(aep)Cl_2$[272] (aep = 2-(2-aminoethyl)pyridine), $Cu(amp)Br_2$[25] (amp = 2-(aminomethyl)pyridine) and $Cu(en)Cl_2$[87] (en = ethylenediamine), where the ligands' amino groups are unsubstituted show that Cu(II) prefers to adopt a tetragonal polymeric geometry. In order to do this, infinite chains of planar CuN_2X_2 units, bridged by halide ions, are formed. Livingstone <u>et al</u>, in their work on 2-(methylthiomethyl)pyridine (mmp),[15] concluded that $Cu(mmp)Cl_2$ and $Cu(mmp)Br_2$ also have tetragonal polymeric structures.

ii) The electronic and far-infrared spectroscopic studies provide good evidence for the preference of <u>cis</u>-octahedral structures in the $M(tbmp)_2X_2$ complexes (M=Cu(II), Co(II), Ni(II). Molecular model studies provide support for these conclusions and show that two isomers are equally possible:

a) two sulphurs cis, two X^- cis, two nitrogens trans;

b) two sulphurs cis, two X^- cis, two nitrogens cis.

A structure in which the two sulphurs are cis and the two nitrogens are cis, but the two anions are trans, is ruled out by the molecular models. A trans tetragonal structure (2S trans, 2N trans, $2X^-$ trans), as adopted by complexes such as $Cu(mtea)_2(ClO_4)_2$[33] (mtea = 2-methylthioethylamine), $[Cu(en)_2X.H_2O]X$[89,91,97] ($X = Cl^-$, Br^-) and $Cu(aep)_2(ClO_4)_2$[40], does not appear to be possible for the $M(tbmp)_2X_2$ complexes either. There would be excessive steric interactions between the t-butyl groups of one ligand and carbon 6 on the pyridyl ring of the second ligand, if this structure was adopted. The M(II) complexes therefore assume a cis-octahedral configuration in preference to undergoing tetrahedral distortions. These would effectively reduce steric interactions, too.

In contrast to tbmp, Livingstone et al[15] report that mmp, on the basis of model studies, is able to coordinate in a trans square planar configuration.

2) COMPLEXES OF tbmq

This ligand can be considered to be disubstituted tbmp in that two R groups (the second aromatic ring) have been added to carbons 5 and 6. The effect of this "substitution" is quite dramatic. For Cu(II), only the distorted tetrahedral $Cu(tbmq)X_2$ ($X = Cl^-$, Br^-) species could be isolated in pure form. Although there was some indication that a $Cu(tbmq)_2(ClO_4)_2$ complex can be formed (Chapter 6, Section I), there was no evidence for the formation of 2:1 species with chloride and bromide anions. In contrast to the

$[Cu(tbmp)Br_2]_2$ complexes, $Cu(tbmq)Cl_2$ and $Cu(tbmq)Br_2$ are probably monomeric in the solid state. Thus tbmq can be compared with 2-methyl-8-methylthio-quinoline(mmtq) which also forms distorted tetrahedral complexes[14] of this type. On the other hand, the magnetic moments (μ = 1.79-1.93) for the 1:1 complexes of 8-methylthioquinoline[13] appear to be normal for square planar Cu(II). If the complexes of mmtq tried to adopt a planar structure, the 2-methyl group would interact with the other ligands in the equatorial plane.[12] Similar steric effects can explain the distortions in $Cu(tbmq)Cl_2$ and $Cu(tbmq)Br_2$. However, the calculation of $g_{\parallel} / |A_{\parallel}|$ ratios for the latter complexes (see Chapter 6, Section I), indicated that the distortions are not severe and their structures can be best described as being flattened tetrahedral.

3) COMPLEXES OF I

Molecular models suggest that the three potential binding sites (imine N, thioether S, ketone O) of this ligand can not assume a planar configuration about a coordinating metal ion. Therefore, tetrahedral distortions must occur and this is indicated in the spectroscopic data. Brodie and Otsuka in their study of some related disubstituted camphorquinone ligands,[162] suggested that the wide ligand bite will also be an important factor in forcing a tetrahedral geometry on the metal ion.

It was inferred from the infrared data for the $CuI(ClO_4)_2.acetone.xH_2O$ (x = 0.2) complexes (Chapter 6, Section I) that the ketone oxygen of I is coordinated to Cu(II). The crystal structure analysis[163] for a Cu(II) complex of the monosubstituted imine formed by 3-hydroxymethylenecamphor and phenylalanine, showed that this oxygen can bind to Cu(II). It is relevant to note that in the latter complex, the "square planar" CuO_3N chromophore has undergone slight tetrahedral distortions.

4) COMPLEXES OF etea and mti

In contrast to the $Cu(tbmp)_2X_2$ complexes, the analogous complexes of etea, and $Cu(mti)_4Cl_2$, (Chapter 5, Section I) exhibit trans coordination of the anions. The observation of two $\sigma(S) \rightarrow Cu(II)$ charge transfer absorptions in the electronic spectra of $Cu(etea)_2(ClO_4)_2$ and $Cu(etea)_2(BF_4)_2$ was interpreted as indicating that the coordinated -SEt groups are cis to each other. However, it could not be decided from the reflectance spectra, whether or not the chloride and bromide complexes have similar structures. For 2-methylthioethylamine (mtea), the analogous perchlorate complex has been shown[33] to have a trans-tetragonal structure (the -SMe groups are trans) and only one $\sigma(S) \rightarrow Cu(II)$ charge transfer absorption is evident in its mull spectrum.[47]

The apparent preference of $Cu(mti)_4Br_2$ for cis anion coordination, suggests that with four mti ligands in the equatorial plane, there are steric reasons as to why both bromide ions can not bind in the axial positions. For the smaller chloride ions, however, axial coordination does take place.

The studies on the transition metal complexes that have been reported in Section I of this thesis, have shown that apparently simple systems, on close examination, can exhibit remarkably varied structural and chemical behaviour. For studying the Cu(II) complexes, the sensitivity of electron spin resonance spectroscopy has been especially useful in interpreting their behaviour in various solvents.

Of particular importance to the interpretation of the spectroscopic data for the complexes of tbmp, tbmq and I, has been the comparison of the complexes of etea and mti. In general, the complexes that these latter ligands form, are similar to those which have been well characterized for ethylenediamine and imidazole.

These studies have thus shown that the synthesis of structurally distorted (quite apart from normal Jahn-Teller distortions) Cu(II) complexes can be readily achieved by the use of simple, but suitably designed ligands.

THIOETHER INTERACTIONS
WITH
Cu(I) AND Cu(II)

An understanding of thioether sulphur/zero-valent metal bonding, can be extended to consider the possible characteristics of thioether sulphur interactions with other metals, such as copper in its +1 and +2 oxidation states.

i) $Cu^{n+} \longrightarrow S$(thioether) π-interactions

In the Pearson classification of acids and bases,[6] Cu(I) is classed as a "soft" acid and Cu(II) as an "intermediate" acid. Also, the studies with the zero-valent Group VIB metals (see above) have shown that thioether sulphur is capable of participating in partial π-bonding interactions with the d-orbitals of "soft" metal atoms. Hence it is anticipated that $Cu^{n+} \longrightarrow S$(thioether) π-backbonding will be more acceptable to copper in its +1 oxidation state, that it will be to copper in its +2 oxidation state.

An examination of the crystallographic data for Cu(II) and Cu(I) complexes of thioether ligands (see Chapter 1 and 3, Section I) enables some pertinent comparisons:

a) the mean equatorial Cu(II)—S(thioether) bondlength (Range, 2.303(1) - 2.488(3) Å) for all of the crystal structures that have been reported (Table 4b), is 2.342(2) Å. This corresponds to the predicted Cu(II)-S single bond of ca 2.34 Å (see Chapter 1).

b) The mean Cu(I)—S(thioether) bondlength (Range, 2.276(2) - 2.345(1) Å) for all of the crystal structures that have been reported (Table 16, Section I) is 2.315(3) Å. The predicted Cu(I)—S single bond is ca 2.39 Å.

It is apparent therefore, that the average Cu(II)—S (thioether) bond represents an essentially single bond. In the cases where the Cu(II)—S bonds are shorter, for example in Cu(14-ane-S_4)(ClO_4)$_2$,[9] (the mean Cu(II)—S is 2.303(1) Å) there may be some Cu(II)⟶S π-donation. However, in general, there appears to be little evidence to suggest that Cu(II)⟶S π-donation is a normal feature of Cu(II)-thioether complexes. In contrast, the Cu(I)—S bonds in Cu(I)-thioether complexes are consistently shorter than the predicted single bond value; the average difference being ca 0.07 Å.

In accordance with the predicted behaviour (see above), the crystallographic data (in agreement with the conclusions of Baker and Norris[10]) provides strong evidence for the existence of Cu(I)⟶S(thioether) π-bonding. Seff and his co-workers have also provided crystallographic evidence for Cu(I)⟶S π-interactions, from their studies on the complexes of disulphide ligands.[110]

ii) Bondlength Differences Between Oxidation States

a) Cu^{n+}— S Bonds

In $[Cu(tbmp)Br_2]_2$, where both ligands are chelated (see Chapter 1, Section I), the Cu(II)—S bonds (2.353(5) and 2.351(6) Å) are identical to the Cu(I)—S bond (2.358(4) Å) of the chelated ligand in Cu(tbmp)$_2$Br (Chapter 3, Section I). These results are in general agreement with the comparative crystallographic studies of Baker and Norris,[10] Rorabacher et al[7,9] and Brubaker et al.[11] In each of these studies it was found that on changing the Cu oxidation state, there is little change in the Cu^{n+}— S(thioether) bondlengths, despite the slightly greater covalent radius of Cu(I) (1.35 Å) compared to Cu(II) (1.30 Å). Baker and Norris suggested that the similarities can be attributed to a greater π-component in the Cu(I)--S (thioether) bonding. The results for $[Cu(tbmp)Br_2]_2$ and $Cu(tbmp)_2Br$ are in agreement with this conclusion.

However, on comparing "model" complexes where a specific ligand has changed its structural role (for example chelated vs monodentate), large differences in the Cu^{n+}—S bondlengths may be observed. This point is illustrated in the structures of $Cu(tbmp)_2Br$ and $[Cu(tbmpH)Br_2]_2$ (Chapter 3, Section I). Where tbmp is monodentate in these complexes, the Cu(I)-S bonds are significantly shorter (2.304(3) and 2.276(2) Å resp.) than the Cu^{n+}—S bonds for the chelated tbmp ligands of $Cu(tbmp)_2Br$ (n = 1, Cu(I)-S = 2.358(4) Å) and $[Cu(tbmp)Br_2]_2$ (n = 2, Cu(II)-S = 2.353(5), 2.351(6) Å). Hence care should be taken in making such comparisons.

b) <u>Cu^{n+}— N Bonds</u>

Although the Cu(I)-N(pyridyl) bond (2.11(1) Å) in $Cu(tbmp)_2Br$ appears to be slightly longer than the Cu(II)-N(pyridyl) bonds (mean, 2.06(2) Å) of $[Cu(tbmp)Br_2]_2$, the difference (0.05(2) Å) is not statistically significant. Neither is there any significant difference between the means of the Cu(I)-N(pyridyl) bonds (mean, 2.03(1) Å) and the Cu(II)-N(pyridyl) bonds (mean, 2.021(8) Å) for the complexes in Tables 16 and 4c (see Section I). The predicted Cu(I)-N and Cu(II)-N single bonds are ca 2.09 Å and ca 2.04 Å (Chapters 3 and 1, Section I) respectively.

In general, there is no indication that Cu(II)→N(pyridyl) π-donation is significant. In contrast however, the crystallographic data suggests that some Cu(I)—N(pyridyl) π-donation may occur in the Cu(I) complexes of substituted pyridine ligands. Support for this possibility is provided by the studies (see earlier discussion) on the Group VIB metal carbonyl complexes of substituted pyridine ligands. Thus Cu(I)→N(pyridyl) π-donation (from the Cu(I) d-orbitals into the empty π^*-orbitals of the ligand) would generally account for the similarities in the Cu(I)—N and Cu(II)—N bondlength data.

FLEXIBILITY OF Cu^{n+}— S(thioether) INTERACTIONS

It is apparent from the foregoing discussion, that thioether sulphur interactions with Cu(II) and Cu(I) are remarkably flexible:

i) low M.W. complexes of thioether ligands exhibit widely varying structural and chemical behaviour,

ii) geometry and oxidation changes are easily accommodated,

iii) crystallographic studies have shown that Cu(II)—S(thioether) bondlengths vary over a greater range (2.303(1)-2.607(2) Å; see Table 4b, Section I) than Cu(II)—N(pyridyl) bondlengths (*ca* 1.980(6)-2.16(1) Å; Table 4c).

Because a wide variety of active site geometries and varying degrees of "site-structure rigidity" [276] will be encountered in different biological systems such as the copper proteins, this flexibility (or plasticity) implies that methionine thioether sulphur is an ideal inner coordination sphere ligand.

STRUCTURAL CHANGES IN COPPER PROTEINS

i) General Discussion

It is apparent from the above evidence that the biologically relevant donor groups, thioether sulphur (as in methionine) and pyridyl nitrogen (as in histidine), are capable of participating in π-bonding with a "soft" metal such as Cu(I). This capability can explain the general observation (for "model" complexes) that there is little or no change in Cu^{n+}— S(thioether) and Cu^{n+}— N(pyridyl) bondlengths on changing the Cu^{n+} oxidation state. These structural features are therefore of direct relevance to the redox role of the Cu^{n+} ion in the copper proteins. In these proteins, electron transfer would be facilitated if structural changes (both bonding and geometric) are minimised.[10]

A distorted tetrahedral Cu(II) geometry is not energetically favoured as ligand-field stability is maximised for square planar, four-coordinate Cu(II).[276] Thus in the proteins where Cu(II) has a distorted tetrahedral geometry, site-structure rigidity[276] (imposed on Cu(II) by the protein) must overcome the tendency for Cu(II) to adopt a square planar structure and therefore allow oxidation state changes to proceed without severe geometry changes.

Earlier, (Chapter 1, Section I) it was argued that tetrahedral distortions in the geometry of a Cu(II) complex (containing coordinated thioether sulphur and pyridyl nitrogen) do not appear to affect the Cu(II)—S and Cu(II)—N bonding either. This is despite the expectation[276] that changes in the Cu(II)—L bondlengths may arise from geometric distortions, as observed in the flattened tetrahedral and square planar forms of $CuCl_4^{2-}$.[277]

ii) Conclusions

The crystallographic data for "model" Cu^{n+} (n = 1,2) complexes containing thioether sulphur and pyridyl nitrogen as ligands, suggests that in proteins such as plastocyanin[5] (and possibly azurin[278]) where methionine and histidine form part of the distorted tetrahedral, inner coordination sphere, oxidation state changes will be accompanied by little or no change in the Cu^{n+}—L (n = 1,2) bondlengths. This is not likely to be altered by the presence of coordinated cysteine thiolate sulphur (as in plastocyanin) as it too, is capable of participating in π-bonding with Cu(I).

On the other hand, oxidation state changes for a protein such as Cu-Zn superoxide dismutase (if indeed they do occur) may be accompanied by rearrangements in the geometry of the active site.[7] In the oxidised protein, Cu(II) has a distorted square planar N_4 environment.[8] That this is an unfavourable geometry for Cu(I) is evidenced by the structural differences that are almost invariably observed in crystallographic studies of low M.W. complexes. However in most "model" complexes, Cu(II) and Cu(I) are not subject to the same constraints that may be imposed by the site-structure rigidity of a protein.

THE ORIGIN OF THE 600 nm. ABSORPTION IN "MODEL" COMPLEXES AND THE "BLUE" PROTEINS

Before the crystal structure of poplar-leaf plastocyanin became known, several studies had implicated Cu(II)/cysteine thiol and/or Cu(II)/methionine thioether interactions as being responsible for the intense ($\epsilon \sim 4000$ l.mol.$^{-1}$cm^{-1}) optical absorption that is observed near 600 nm [4] in the "blue" copper proteins.

i) Cu(II)-thiol Interactions

Although the complex reactions between mercaptides and Cu(II) have been studied intensively,[279] few systems exhibit the stability that would enable Cu(II) complexes of coordinated thiolate sulphur to be isolated.

Three examples which have been successfully characterized crystallographically are the complex Cu(I)/Cu(II) clusters formed by D-penicillamine ($HSC(CH_3)_2CHNH_2COOH$)[280,281] and β,β-dimethyl cysteamine ($HSC(CH_3)_2CH_2NH_2$),[282] and a trigonal bipyramidal CuN_4S complex formed by the addition of o-mercaptobenzoic acid to a Cu(II) complex of the macrocycle, [rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazocyclotetradecane].[283]

The Cu(I)/Cu(II) clusters both have intense absorptions at about 518 nm. (ϵ =4250 and 3400 resp.) and these have been assigned as $\sigma(S^-) \longrightarrow$ Cu(II) charge transfer transitions.[282] A poorly resolved absorption at ca 590 nm for the CuN_4S complex was assigned as a d-d transition.

The reaction of thiolates with Cu(II) complexes will often result in intensely blue, but usually unstable (e.g., the reaction of t-butyl thiolate with $Cu(tbmp)_2(ClO_4)_2$:- Chapter 2, Section I) Cu(II)/thiolate species being formed.[80,135,284]

In most cases, an intense absorption, that can be assigned as a $\sigma(S^-) \longrightarrow$ Cu(II) charge transfer transition,[80] is observed at about 600 nm. The reactions of Cu(II) with ligands such as imidotetraphenyldithiodiphosphinate,[166] N-(2-thiophenyl)pyridine-2-aldimine[285] and 3-ethoxybutan-1,2-onebis(thiosemicarbazone)[286] also result in these intense absorptions being observed.

ii) Cu(II)-thioether Interactions

Despite the rapid growth in the number of spectroscopically and crystallographically characterized Cu(II) complexes of coordinated thioether sulphur, very few exhibit the electronic absorption that is characteristic of "blue" copper. In those that do,[36,69,81] the absorptions are not as intense as those observed for the Cu(II)/thiolate complexes that were discussed above. The work of Schugar and his co-workers[47] enables these absorptions to be assigned as $\pi(S) \longrightarrow Cu(II)$ charge transfer transitions.

iii) <u>General Discussion</u>

Early work by Gray and his colleagues[276,287] resulted in the ca 600 nm absorption, of plastocyanin and other "blue" copper proteins, being assigned to $\sigma(S^-) \longrightarrow Cu(II)$ charge transfer (arising from cysteine/Cu(II) binding). Considerable support for their assignment has come from the characterization of "model" Cu(II)/thiolate complexes (see above) and recent Raman spectroscopic investigations.[288]

However, as a result of this Raman work, Ferris et al concluded that $\pi(S) \longrightarrow Cu(II)$ charge transfer may also make a minor contribution to the intensity of the 600 nm absorption in the "blue" proteins where methionine also appears to be coordinated.

As the intense $\pi(S) \longrightarrow Cu(II)$ absorptions that can be produced by thioether coordination are observed only rarely, the conditions enabling these transitions to take place, are therefore, not readily attainable in most small molecule systems. Braithwaite, Rickard and Waters[69] have concluded that the degree of copper-sulphur orbital overlap is an important factor in enabling these transitions to be observed However, as noted in the early work of Rorabacher et al,[81,289] the geometry of the Cu(II) chromophore is not important. Hence, of the various structurally divergent complexes that have been investigated in this thesis, only one [Cu(tbmq)Cl_2; see Chapter 6, Section I] showed an absorption (reflectance spectrum only) that can be assigned as a $\pi(S) \longrightarrow Cu(II)$ charge transfer transition.

APPENDIX I

i) LIGAND SYNTHESES

3,4-bis(methylthio)toluene and 3,4-bis(ethylthio)-toluene

Although 3,4-bis(methylthio)toluene has previously been prepared and used in reactions with metal salts,[261] its preparation was not reported.

General Procedure: For both ligands, 10 cm^3 (0.086 mole) of toluene-3,4-dithiol were dissolved in about 100 cm^3 of Abs.EtOH. To this, a slight excess of Na (4.0 g.) was slowly added while the solution was being stirred and the respective alkyl iodides (11 cm^3 of MeI, 14 cm^3 of EtI) were then slowly added. After the solutions had been refluxed for about an hour, they were left to stand overnight.

i) 3,4-bis(methylthio)toluene (bmtt)

On shaking the solution that had been left to stand, white crystals precipitated. These were filtered, washed with distilled water and a further quantity of distilled water was added to the filtrate to precipitate a second crop. The two crops of crystals were dried under vacuum filtration (with N_2 passing over them). They were then combined and recrystallized from Abs.EtOH. A further crop was isolated after the filtrate was concentrated *in vacuo* and cooled at 0°C.

YIELD: 13.883 g. (87%)

ii) 3,4-bis(ethylthio)toluene (bett)

Deionised water (200 cm^3) was added to the solution that had been left to stand overnight. An oil which precipitated after this solution had been cooled, was extracted into ether. After the cloudy, aqueous-ethanol fraction had been concentrated <u>in vacuo</u>, further ether extractions were carried out until the aqueous phase was clear. The ether extracts were then combined, concentrated and dried with anhydrous Na_2CO_3 before the ether was removed <u>in vacuo</u>. The oil was distilled to give the colourless ligand.

YIELD: 8.090 g. (44%)

<u>Other Ligands</u>

The syntheses of ethylthiopentafluorobenzene and 2-(3,3-dimethyl-2-thiabutyl)pyridine are described in Appendix I, Section I, together with the preparations of 2-ethylthioethylamine and 2-methylthio-2-imidazoline. Benzimidazole, 2-methylmercaptobenzimidazole and 2-methylthioaniline were used as supplied.

ii) DISTILLATION OF LIGANDS

The microdistillations were carried out as described in the Appendices to Section I.

TABLE 23

LIGAND PROPERTIES AND ANALYTICAL RESULTS

LIGAND	APPEARANCE	M.P/B.P/Other	ANALYSES:Calc.(Found)/%
bmtt	white solid	38 °C	φ C 57.40, H 6.41, S 33.12 (57.48) (6.41) (33.12)
bett	colourless oil	120-122° [<u>ca</u> 20 mm.Hg]	C 62.20, H 7.58, S 30.20 (62.52) (7.56) (30.28)

<u>NOTES</u>: φ calculated for $[C_9H_{12}S_2] . 0.25(H_2O)$

- mass spectra indicated that bmtt loses a methyl group and then the two sulphurs. This implies that a methyl group is being transferred; i.e. ligand rearrangement is occurring.[254] This does not occur in 1,2-bis(methylthio)benzene.[255]

iii) METHYLATION OF bmtt

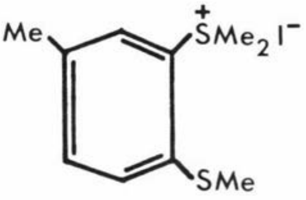
In the presence of a large excess of methyl iodide, an acetone solution of bmtt (0.944 g.) was left to stand for four weeks at 4 °C, under nitrogen. An almost plastic residue (0.122 g.) was isolated from the solution. The ^1H nmr spectrum ($CDCl_3$ solution) suggests that there is a mixture of the two species shown below.

^1H nmr SPECTRUM; METHYLATION OF bmtt

COMPLEX	-SMe	$-\overset{+}{S}(CH_3)_2$	$Ar-CH_3$	Ar-H
bmtt	2.40, 2.42		2.28	7.0
bmtt/MeI products	2.66, 2.69	3.60, 3.85	2.53, 2.60	7.75

NOTE: - chemical shifts are ppm downfield from TMS

- chemical shifts for aryl protons (Ar-H) are the centres of the observed multiplets.



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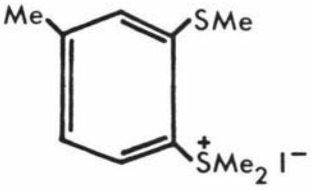


APPENDIX II

i) GENERAL SYNTHESIS OF CARBONYL COMPLEXES

The Group VIB metal carbonyl complexes that are described in this thesis were synthesized using the Strohmeier photochemical technique[256]. Although other more direct, methods can be used, the Strohmeier method has the following advantages:

- thermally unstable complexes can be formed,
- the products are often more pure and are formed in better yields,
- less time is needed (compared with thermal substitution reactions) for the preparation of complexes.

For all of the syntheses that were described in Section II, a mixture of the parent hexacarbonyl ($M(CO)_6$, M = Cr, Mo, W) and tetrahydrofuran (THF) is irradiated for about one hour in an atmosphere of oxygen-free, dry dinitrogen. The THF is deoxygenated with dinitrogen before irradiating. The irradiation results in the formation of $M(CO)_5THF$, in two steps:

1) $M(CO)_6 \xrightarrow[\text{1 HOUR}]{h\nu} [M(CO)_6]^* \longrightarrow [M(CO)_5] + CO$

"excited"
intermediate

2) $[M(CO)_5] + THF \longrightarrow M(CO)_5THF$

The irradiation is stopped at this point and the ligand is added to the solution. This results in an exchange reaction (3);

3) $M(CO)_5THF + \text{Ligand} \longrightarrow M(CO)_5\text{Ligand} + THF$

and the individual complexes are isolated as described in the relevant Chapters.

NOTE: - in all cases where solvents were removed *in vacuo*, a rotary evaporator was used. Where complexes or residues were dried *in vacuo* an evacuated (*ca* 2-5 mm. Hg) drying line was used. The sublimation of excess $M(CO)_6$ was also carried out on this line.

ii) CHARACTERIZATION OF UNSTABLE C_6F_5SEt COMPLEXES

The existence of the unstable $M(CO)_5C_6F_5SEt$ complexes (M = Cr, W) was inferred from IR studies on the products of the preparations that are described in Chapter 2. IR spectra (2100-1850 cm^{-1}) were recorded for freshly extracted (and filtered) cyclohexane solutions. The carbonyl stretching frequencies are reported in Table 3. A ^1H nmr spectrum (see below) which was recorded for a freshly extracted $CDCl_3$ solution (filtered under N_2) of the $Cr(CO)_5THF/C_6F_5SEt$ reaction products, supports the IR evidence for the existence of an unstable $Cr(CO)_5C_6F_5SEt$ complex.

^1H nmr SPECTRA (in $CDCl_3$)

COMPLEX	$-SC\bar{H}_2CH_3$	$-SCH_2C\bar{H}_3$
C_6F_5SEt	2.96q(7)	1.29t(7)
$Cr(CO)_5C_6F_5SEt$	*ca* 3.1 m	*ca* 1.3 m

NOTES: - m = multiplet; t = triplet; q = quartet,
- chemical shifts are ppm downfield from TMS,
- coupling constants are in parentheses (Hz),

iii) REACTIVITY STUDIES; EXPERIMENTAL DETAILS

Where it was possible, either cyclohexane or n-hexane were used as solvents for the following reasons:

- only moderate reflux temperatures (75° and 69° C respectively) are required,

- the carbonyl complexes are more stable in these solvents,
- superior IR spectral resolution is achieved.

All reactions were carried out under an atmosphere of oxygen-free, dry dinitrogen and IR spectra were recorded only for the ν(CO) region.

a) Reflux $[W(CO)_5]_2$bett in n-hexane

About 50 mg. of the complex were dissolved in 80 cm^3 of n-hexane.

b) Reflux $[W(CO)_5]_2$bett with excess Triphenylphosphine

A 6:1 ratio of Ph_3P (0.079 g.) to the carbonyl complex (0.043 g.) was used. The solvent was cyclohexane.

c) Reflux $[W(CO)_5]_2$bett with excess Triphenylphosphite

$[W(CO)_5]_2$bett (0.1 mmole, 0.086 g.) was refluxed for 2 hours (in cyclohexane) with 1 mmole of $P(OPh)_3$ (0.310 g.). Samples were removed for IR analysis after refluxing for 5, 20, 30, 60 and 120 minutes respectively.

d) Reflux $[W(CO)_5]_2$etea with excess Triphenylphosphite

The carbonyl complex (0.065 mmole, 0.050 g.) was refluxed (in cyclohexane) with a ten-fold excess of $P(OPh)_3$ (0.202 g.). Samples were removed for IR analysis after 0.5, 1, 2 and 5 hours respectively.

e) Reflux $W(CO)_4$etea with excess Triphenylphosphite

$[W(CO)_5]_2$etea (0.065 mmole, 0.050 g.) was refluxed in cyclohexane to convert it to $W(CO)_4$etea. A ten-fold excess of $P(OPh)_3$ (0.202 g.) was then added and the refluxing was continued. Samples were removed for IR analysis after 5, 30, 40 and 60 minutes.

In benzene, $W(CO)_4$etea (0.20 mmole) was refluxed with 2 mmole of $P(OPh)_3$ over a period of 8 hours.

APPENDIX III

i) INSTRUMENTS AND RECORDING OF SPECTRA

Infrared spectra were recorded on a Beckman IR-20 spectrophotometer and calibrated with polystyrene film. To record the spectra of solutions, 0.5 mm. NaCl cells were used.

Electronic Spectra were recorded on a Shimadzu MPS-5000 spectrophotometer, using 10 mm. quartz cells. The spectra were recorded immediately after the preparation of each solution.

^{1}H nmr spectra were recorded using a JEOL C-60HL High Resolution NMR spectrometer. Tetramethylsilane (TMS) was used as an internal standard for all spectra.

Decomposition problems were often encountered and these were minimised, or even eliminated, by filtering each solution under N_2.

Resonances were assigned for both the ligands and their complexes by a consideration of integrated peak areas, expected spin-spin coupling effects and symmetry effects (for bmtt and bett).

^{13}C nmr spectra (proton decoupled) were recorded on a JEOL JNM-FX60 Fourier Transform spectrometer, using TMS as an internal standard. Each carbonyl solution was filtered before use.

Relatively high concentrations (ca 50-100 mg.cm^{-3}) of the carbonyl complexes were used in order to minimise the data collection time. For each complex, the ligand resonances were recorded first. For the ^{13}CO resonances 1-2 mg. of the inert, paramagnetic, relaxation reagent

$Cr(acac)_3$[257] were added to the solutions to give a ratio of about 1:100 $Cr(acac)_3$:substrate.[258] The resulting decreased relaxation times enabled the data to be collected in a shorter time (ca 30 minutes).

The longer spin-lattice relaxation times (T_1) of non-protonated carbon atoms[258] enable the substituted aryl carbon atoms (C1, C3, C4; see Table 11b) of bmtt and bett to be easily distinguished from the other (C2, C5, C6) aryl carbon atoms. The former have relatively low intensities. C1 has been tentatively assigned by comparison with the spectra of some n-methylthiotoluene (n = 2,3,4) ligands.[259]

Mass spectra were recorded on an A.E.I. MS9 instrument.

ii) SOLVENTS

a) Spectroscopic Investigations: All solvents were of Spectroscopic Grade. Nitromethane was stored over molecular sieves.

b) Preparative Work: All hydrocarbon solvents were redistilled before use.

Acetone was A.R. grade.

Tetrahydrofuran was dried with anhydrous calcium chloride before it was distilled over Na wire. Cuprous chloride was added to the solution being distilled to destroy explosive peroxides. Care was also taken to ensure that the solution being distilled did not drop below a volume of about 200 cm^3.

APPENDIX IV

MISCELLANEOUS REACTIONS

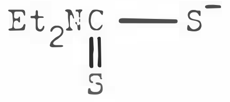
i) Reaction of tetraethylthiuramdisulphide with $Cr(CO)_6$

On adding the ligand to irradiated $Cr(CO)_6$ (in THF) there is immediate discolouration and decomposition gradually occurs through several stages. A stable carbonyl-free, violet complex (probably $Cr(Et_2Dtc)_3$) was isolated from benzene extracts.

	M.P/°C	IR/cm^{-1}	REF.
Violet complex	253-255	1487	This work
$Cr(Et_2Dtc)_3$	250(dec)	1542-1480 Φ	M.P;Ref. 262 I.R;Ref. 263

Φ Band in this region due to $\nu(C=N)$ mode of the $>C=\overset{+}{N}R_2$ canonical form for dithiocarbamoto complexes.

- Et_2Dtc is



$Et_2N\underset{\underset{S}{\|}}{C}-S^-$

ii) Reaction of 1,4,8,11-tetrathiacyclotetradecane (TTP) with $W(CO)_6$

In an attempt to synthesize a bridged-ligand complex, 1 mmole of TTP (0.268 g.) was added to 2 mmole of irradiated $W(CO)_6$ (0.703 g.) in THF. The mixture had to be irradiated for 30 minutes to dissolve most of the ligand and then it was filtered. A pale yellow precipitate (M.P 56-62°; Yield: 0.130 g.) was isolated from acetone extracts of the reaction products.

The relative concentrations of the penta-and tetra-carbonyl species of this solid are unaffected by attempts to separate the species on a silica-gel column.

Although the carbon and hydrogen analyses are close to those expected for $W_2(CO)_9TTP$, the sulphur analysis is too low.

Calculated for $W_2(CO)_9$TTP:	C 25.69%;	H 2.27;	S 14.44
Found :	25.55	2.45	11.96 also 12.06

The highest peak in the mass spectrum of the "complex" is $[W(CO)_6]^+$; the ligand is observed intact.

<u>IR Spectrum</u> (nitromethane solution)

ν(CO) assigned to $W(CO)_4$: <u>ca</u> 2019(w) cm^{-1}

ν(CO) assigned to $W(CO)_5$: 2079(w); 1975(vw); 1940(s).

ν(CO) unassigned : 1916(ms); 1906(ms); 1872(m); 1862(m); 1848(m).

iii) <u>Reactions of $M(CO)_6$ (M=Mo, W) with fpte</u>

Attempts were made to synthesize $M(CO)_4$fpte and $[W(CO)_5]_2$fpte respectively (fpte = 1,2-bis(pentafluorophenylthio)ethane) by the normal methods. However there was no evidence for the formation of any complexes with this ligand.

APPENDIX V

FORCE CONSTANT CALCULATIONS
FOR
CARBONYL COMPLEXES

The general solutions for the approximate secular equations given by Cotton and Kraihanzel[216] are outlined below. For these equations:

K_1 is force constant of CO's trans to the substituent ligand (L)

K_2 is force constant of CO's cis to L.

K_i is an interaction constant.

$\lambda = \nu^2 \times 0.058890$ where ν is frequency (cm^{-1}) of absorption.

$\mu = 0.14576$

Force constants calculated from these equations have units of dyne cm^{-1}. To convert to $N.m^{-1}$, multiply K by 10^{-3}.

i) Solution for C_{4v} $M(CO)_5L$ complex, using $A_1(I)$, B_1 and E modes

$$K_1 = \left[\left(\frac{4\mu^2 K_i^2}{\mu K_2 + 4\mu K_i - \lambda_{a'}}\right) + \lambda_{a'}\right] / \mu$$

where $K_2 = \lambda_{B_1}/\mu$ and $K_i = (\mu K_2 - \lambda_E)/2\mu$

NOTE: To simplify the equations, $A_1(I)$ is written as a'

and $A_1(II)$ is written as a''

ii) Solution for C_{4v} $M(CO)_5L$ complex, using $A_1(I)$, $A_1(II)$ and E modes

$$K_1 = \left(-b + \sqrt{b^2 - 4ac}\right)/2a$$

where $a = -10\mu^2$ [Hence $2a = -0.424918$]

$b = 11\mu\alpha - 2\lambda_E\mu$ [$\alpha = \lambda_{a'} + \lambda_{a''}$]

$c = 2\alpha\lambda_E - 9\alpha\lambda_{a'} + 9\lambda_{a'}^2 - \lambda_E^2 - \alpha^2$

Using K_1, then:

$$K_2 = (2\lambda_E - \mu K_1 + \alpha)/3\mu$$

and $K_i = (\mu K_2 - \lambda_E)/2\mu$

iii) Solution for C_{2v} $M(CO)_4L_2$ complex, using $A_1(I)$, B_1 and B_2 modes

$$K_2 = \left(-b - \sqrt{b^2 - 4ac}\right)/2a$$

where $a = 2\mu^2$

$b = \mu(3\lambda_{B_2} - 4\lambda_{B_1} - 4\lambda_{a'})$

$c = \lambda_{a'}(2\lambda_{B_1} + \lambda_{B_2} + \lambda_{a'}) + \lambda_{B_1}(2\mu - \lambda_{B_2})$

Using K_2, then:

$$K_i = (\mu K_2 - \lambda_{B_1})/2\mu$$

and $K_1 = (\lambda_{B_2} - \mu K_i)/\mu$

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