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(0), Mo(0), W(0)) 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 $Cu(tbmp)_2Br$, each Cu(I) ion is bound by a terminal bromine (Cu(I)-Br = 2.426(2) Å), two thicether 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 $Cu(tbmp)_2X_2$ complexes are cis-octahedral in the solid state, whereas the $[Cu(tbmp)_2X]BF_4$ complexes are tetragonal pyramidal.

An unstable deep blue species is formed by the addition of t-butyl thiolate to $Cu(tbmp)_2X_2$, where X is ClO_4^- or BF_4^-. The displacement of tbmp (by pyridine) from $Cu(tbmp)_2X_2$ ($X = Cl^-$, BF_4^-) is also discussed.

With Co(II) and Ni(II), the cis-octahedral $M(tbmp)_2X_2$ ($X=Cl^-, Br^-$) and $M(tbmp)_2(ClO_4)_2.nH_2O$ (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 ^1H 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 ^1H 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 ^1H 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 $[M(CO)_5]_2$bmtt, $M(CO)_4$bett (M=Cr, W), $Cr(CO)_4$bmtt and the ligands. The ^{13}CO chemical shifts for $[M(CO)_5]_2$bmtt and the $M(CO)_5L$ 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.

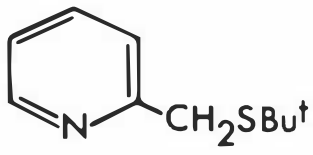
iii) Complexes of 2-methylthioaniline (mta), 2-methylmercapto-benzimidazole (mmbi) and 2-methylthio-2-imidazoline (mti)

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.

CONTENTS

LIGANDS AND ABBREVIATIONS



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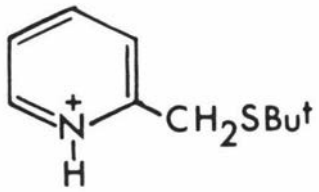
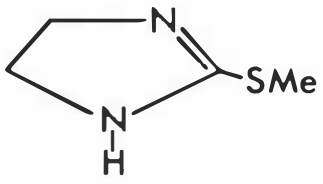


tbmpH$^+$

$EtSCH_2CH_2NH_2$

etea



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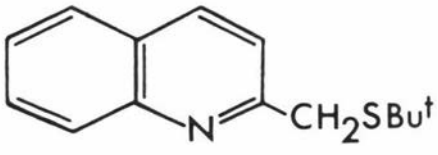

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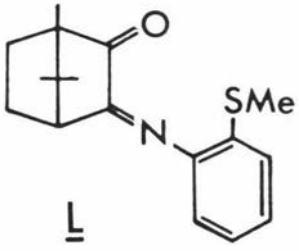

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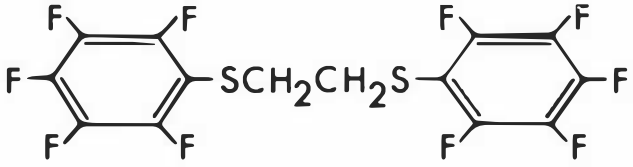

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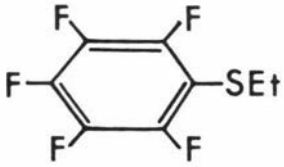
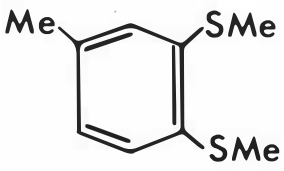


C_6F_5SEt



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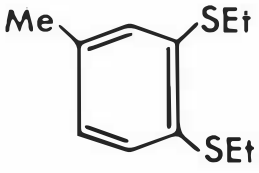
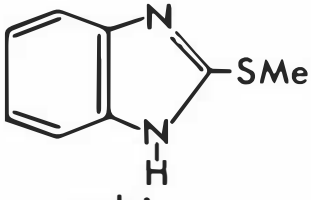


bett

mta



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

α-pic = 2-methylpyridine (α-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^o = 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-phenyleneimino-methylidyne)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$]^-$

L^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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