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METAL COORDINATION STUDIES

OF

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A thesis presented in partial
fulfilment of the requirements
for the degree of Doctor of
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NIGEL GRANT LARSEN

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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(C), Mo(C), W(C)) 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, $\text{Cu}(\text{tbmp})_n\text{X}_2$ ($n=1$, $\text{X}=\text{Cl}^-$, Br^- ; $n=2$, $\text{X}=\text{BF}_4^-$, ClO_4^- , Cl^- , Br^-), $[\text{Cu}(\text{tbmp})_2\text{X}]\text{BF}_4$ ($\text{X}=\text{Cl}^-$, Br^-), and the Cu(I) complexes, $\text{Cu}(\text{tbmp})_n\text{Br}$ ($n=1,2$) and $\text{Cu}(\text{tbmpH})\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^-).

Crystallographic studies are reported for $\text{Cu}(\text{tbmp})\text{Pr}_2$, $\text{Cu}(\text{tbmp})_2\text{Br}$ and $\text{Cu}(\text{tbmpH})\text{Br}_2$.

$\text{Cu}(\text{tbmp})\text{Br}_2$ crystallizes as discrete, non-centrosymmetric dibromo-bridged dimers ($[\text{Cu}(\text{tbmp})\text{Pr}_2]_2$), 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 thioether sulphur atoms (mean Cu(I)-S = 2.331(4) Å) and a pyridyl nitrogen (Cu(I)-N = 2.11(1) Å).

Cu(tbmpH)Br₂ forms centrosymmetric dimers ([Cu(tbmpH)Br₂]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)₂X₂ complexes are cis-octahedral in the solid state, whereas the [Cu(tbmp)₂X]BF₄ complexes are tetragonal pyramidal.

An unstable deep blue species is formed by the addition of t-butyl thiolate to Cu(tbmp)₂X₂, where X is ClO₄⁻ or BF₄⁻. The displacement of tbmp (by pyridine) from Cu(tbmp)₂X₂ (X = Cl⁻, BF₄⁻) is also discussed.

With Co(II) and Ni(II), the cis-octahedral M(tbmp)₂X₂ (X=Cl⁻, Br⁻) and M(tbmp)₂(ClO₄)₂.nH₂O (n = 1,2) complexes have been characterized.

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

ii) Complexes of 2-ethylthioethylamine (etea)

The tetragonal complexes $\text{Cu(etea)}\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-$), $\text{Cu(etea)}_2\text{X}_2$ ($\text{X} = \text{BF}_4^-, \text{ClO}_4^-, \text{Cl}^-, \text{Br}^-$) and $[\text{Cu(etea)}_2\text{Cl}]\text{BF}_4$ have been characterized and the displacement of etea from $\text{Cu(etea)}_2(\text{ClO}_4)_2$ (by pyridine), is discussed.

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

In the reactions of mti with $M(\text{II})$, the tetragonal complexes $\text{Cu(mti)}_4\text{X}_2$ ($\text{X} = \text{BF}_4^-, \text{Cl}^-, \text{Br}^-$) were successfully synthesized, together with a tetrahedral complex, $\text{Co(mti)}_3\text{Cl}_2$. In the latter, one mti molecule appears to remain uncomplexed.

With $\text{Cu(mti)}_4(\text{BF}_4)_2$, 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, $\text{Cu(tbmq)}\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-$) and the Cu(I) complexes, $\text{Cu(tbmq)}\text{Br}$, $\text{Cu(tbmqH)}\text{Br}_2$ and $\text{Cu(tbmq)}_2\text{ClO}_4$, were synthesized. In contrast to tbmp and etea, tbmq does not form the six-coordinate complexes, $\text{Cu(tbmq)}_2\text{X}_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-$).

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

Although I is susceptible to hydrolysis, the successful isolation and characterization of the pseudo-tetrahedral $\text{CuI}(\text{ClO}_4)_2 \cdot \text{acetone} \cdot x\text{H}_2\text{O}$ ($x = 0, 2$) complexes was achieved from acetone solutions. A ^1H nmr line broadening experiment indicates that $\text{Cu(II)}/\text{S}(\text{thioether})$ interactions take place under hydrophobic conditions.

vi) Complexes of 1,2-bis(pentafluorophenylthio)ethane (fp_{te}) and ethylthiopentafluorobenzene (C₆F₅SEt)

In order to determine the effects of the electro-negative pentafluorophenyl substituents, the spectroscopic data for cis-PtCl₂fp_{te}, cis-PdCl₂fp_{te} and trans-PtCl₂(C₆F₅SEt)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 fp_{te} (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 (bm_{tt}) and 3,4-bis(ethylthio)toluene (be_{tt})

The bridged-ligand complexes, [M(CO)₅]₂bm_{tt} and [M(CO)₅]₂be_{tt} (M=Cr, W), and the chelated-ligand complexes, M(CO)₄bm_{tt} and M(CO)₄be_{tt} (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 bm_{tt} and be_{tt}, 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 C₆F₅SEt (see above), with which unstable M(CO)₅C₆F₅SEt (M=Cr, W) complexes were synthesized.

Reactivity studies are reported for [W(CO)₅]₂be_{tt} and the mass spectra of [W(CO)₅]₂bm_{tt} and the M(CO)₄bm_{tt}

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

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

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

Both the bridged-ligand $[\text{M}(\text{CO})_5]_2\text{etea}$ (M=Cr, W) and the chelated-ligand $\text{M}(\text{CO})_4\text{etea}$ (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, $\text{Cr}(\text{CO})_4\text{etea}$ and $\text{Mo}(\text{CO})_4\text{etea}$ (the carbonyl complexes showing two distinct trans- ^{13}CO resonances) and reactivity studies for $[\text{W}(\text{CO})_5]_2\text{etea}$ and $\text{W}(\text{CO})_4\text{etea}$, 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 $\text{M}(\text{CO})_5\text{L}$ 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 $\text{W}(\text{CO})_5\text{mta}$, by triphenylphosphite.

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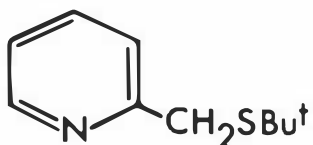
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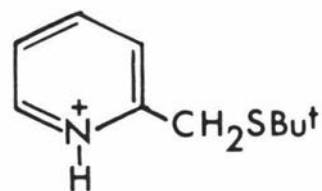
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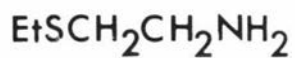
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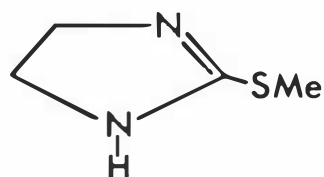
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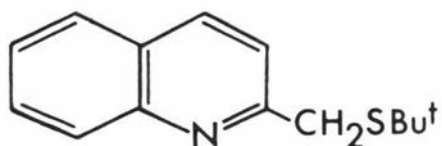
tbmpH⁺



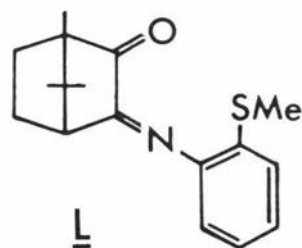
etea



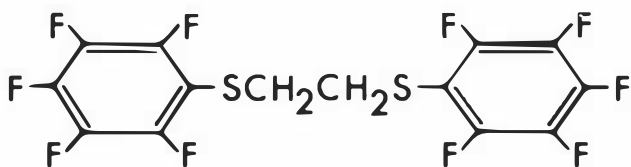
mti



tbmq



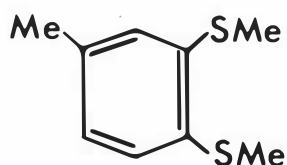
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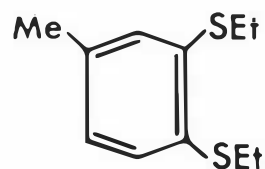
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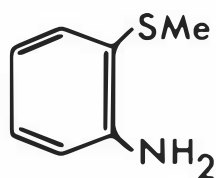
C₆F₅SEt



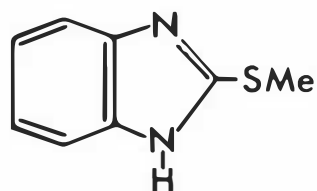
bmtt



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 ₆ F ₅ SEt	=	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

I ²	= bis(N,N-dimethylacetamido)thioether
I ³	= 1,4,8,11-tetrathiacyclotetradecane
I ⁴	= 2-methylthioethylamine
I ⁵	= [3,3'-ethylenedithiobis(o-phenyleneimino-methylidyne)bis(pentane-2,4-dionato)] ²⁻
I ⁶	= tricyclo[17.5.5.5 ^{7,13}]tetraaza-1,7,13,19-dioxa-4,16-tetrathia-10,22,27,32-tetratriacontane
I 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 ₆ acac	= [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 ₂ S ₂	= bis(2-pyridyl)disulphide
py ₂ Et ₂ S ₂	= bis[2-(2-pyridyl)ethyl]disulphide
pea	= [2-(2-pyridyl)ethyl] bis[2-(ethylthio)ethyl]amine

tal-i-C ₃ H ₇	=	N-(2-thenylidene)isopropylamine
C ₈ H ₈	=	cyclooctatetraene
DPFA	=	bis(diphenylphosphino)acetylene
tal-CH ₃	=	N-(2-thenylidene)methylamine
(Me ₂ N) ₂ Et ₂ S 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
n-te	=	1,2-bis(p-nitrophenylthio)ethane
dad	=	1,12-diaminododecane
2,9-dtd	=	2,9-dithiadecane

CHAPTER 2

diphos	=	1,2-bis(diphenylphosphino)ethane
I_2^{SMe}	=	1,2-tetrakis(methylthio)ethylene
I_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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