COMPLEXES OF TRANSITION METALS WITH N-, S- AND O- DONOR LIGANDS

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ABSTRACT

Complexes of the ambidentate ligands dimethyl sulphoxide and pyridine-2-thiol have been prepared and characterised by infra-red, ^1H nuclear magnetic resonance and electronic spectroscopy and by magnetic susceptibility measurements.

Dimethyl sulphoxide complexes of ruthenium(II) and rhodium(III) are shown to have both S- and O- bonded dimethyl sulphoxide in the same molecule. Exchange reactions of the complexes have been studied by ^1H nuclear magnetic resonance spectroscopy; the utility of 'shift' reagents, such as tris(heptafluoro-dimethyl octanedienato) Europium(III), in resolving the ^1H nuclear magnetic resonance spectrum is indicated.

Replacement of the coordinated dimethyl sulphoxide by various ligands affords a convenient route to some new ruthenium(II) complexes. These complexes have been characterised by the usual spectroscopic techniques and by elemental analysis.

Complexes of pyridine-2-thiol with a large number of metals have been prepared. They are shown to be almost all sulphur bonded by infra-red and electronic spectroscopy. The mid infra-red criterion for determining the mode of bonding of ligands containing the thioamide linkage is critically discussed.

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To my Parents

To my Wife

CONTENTS

ABBREVIATIONS

i.r.	infra-red
n.m.r.	nuclear magnetic resonance
e.s.r.	electron spin resonance
g.l.c.	gas-liquid chromatography
X_g	gram susceptibility
X'_M	molar susceptibility, corrected for diamagnetism of ligands
μ_{eff}	effective magnetic moment
B.M.	Bohr magneton
Dq	crystal field splitting parameter
B	Racah parameter
β	$\frac{\text{B in complex}}{\text{B in free ion}}$

Me	methyl
Et	ethyl
t-Bu	tertiary butyl
dien	$NH_2C_2H_4NHC_2H_4NH_2$
$(C_2H_5)_4$dien	$(C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$
fod	heptafluoro-dimethyloctanedienato
PySH	pyridine-2-thiol
py	pyridine
bipy	2,2'-bipyridyl
phen	1,10-phenanthroline
MBTH	mercaptobenzthiazole

1 kK = 1000 cm^{-1}

CHAPTER 1

GENERAL INTRODUCTION

A. Ambidentate ligands

Ambidentate ligands are those with more than one mode of coordination. In this thesis, coordination compounds containing dimethyl sulphoxide (Me_2SO) and pyridine-2-thiol (PySH) as ligands are studied. These ligands are ambidentate, as Me_2SO can bond through either its sulphur or oxygen atoms, and pyridine-2-thiol can bond through its sulphur or nitrogen atoms, or both if it functions as a chelating monoanion. The behaviour of an ambidentate ligand is of interest mainly for the information its coordination behaviour yields on the nature of the metal-ligand bond.

The complexing behaviour of an ambidentate ligand with a particular metal can often be predicted using either Ahrland, Chatt and Davies' idea of class (a) or class (b) behaviour,[1] or Pearson's extension of this idea to 'hard' and 'soft' acids and bases.[2] These theories recognise the great difference between the coordination affinities of the first and second elements from Groups Vb, VIb and VIIb of the Periodic Table, i.e. N and P, O and S, F and Cl. The class (a) acceptors form their stablest compounds with the first ligand atom of each group, whereas the class (b) acceptors favour the second (or subsequent) ligand atom. Most metals in their common oxidation states show class (a) behaviour while class (b) behaviour is shown by the heavier metals of Group VIII.

In Pearson's notation, class (a) metals are 'hard' and class (b) metals 'soft'. Since ligand atoms of the first row such as N, O and F are also classified as 'hard' whereas P, S and Cl are 'soft' the

general rule suggested is that 'hard' acids bind strongly to 'hard' bases while 'soft' acids bind strongly to 'soft' bases.

However, the coordination behaviour of a particular ligand can be considerably influenced both by steric factors and electronic effects, such as the presence or absence of π-acceptor ligands, for example. Electronic influences are obviously important in such simple ligands as SCN^-, $SeCN^-$, CN^- and NO_2^- and as the identity of the ligating atom can often be inferred by simple i.r. criteria, these ligands have been extensively studied.[3] For example, when SCN^- bonds through its nitrogen atom as -N = C = S, the C - S vibration is reported to be between 780 - 860 cm^{-1}, whereas in -S - C ≡ N, the S-bonded form, the C - S vibration is in the region 690 - 720 cm^{-1}.[4,5]

Similar ideas can be applied to many simple ligands and unambiguous assignment of the mode of bonding made, assuming that the particular vibration of interest can be identified. As the ligands become more complicated, unambiguous assignment of the bonding atom generally becomes more difficult and criteria which are of specific rather than general utility must be adopted.

B. <u>Me_2SO as a ligand</u>

The ready commercial availability of Me_2SO has led to much study of this ligand in both organic and inorganic chemistry. Me_2SO is used widely as a solvent[6] and as a mild oxidising agent[7] in organic chemistry. The first comprehensive study of Me_2SO as an ambidentate ligand was carried out by Cotton and Francis.[8] Since then the reactions of most of the elements of the Periodic Table with Me_2SO have been studied; the literature has been comprehensively reviewed up until 1968.[9,10]

Although a complete normal coordinate analysis of Me_2SO[11] indicated that the S - O stretching vibration in the molecule derived at least half its potential energy from associated methyl rocking modes, the change in ν (SO) on coordination of Me_2SO to a metal is now a standard method of determining the mode of coordination. The considerable double bond character of the sulphoxide group in Me_2SO[12] can be considered to come from the superposition of $p\pi \rightarrow d\pi$ bonding (from O to S) upon the $S \rightarrow O$ sigma bonding i.e. the molecule is best formulated as a resonance hybrid:

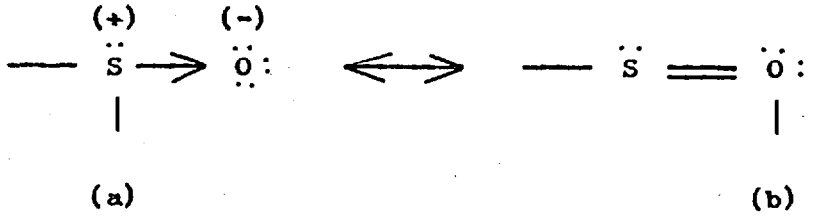


Fig. 1.1

Coordination of oxygen to a metal should thus lessen the $p\pi - d\pi$ back bonding, lower the S - O bond order and decrease ν (SO). Conversely, coordination of sulphur should increase the $p\pi - d\pi$ bonding and raise ν (SO). This is equivalent to coordination through oxygen stabilising (a) and coordination through sulphur stabilising (b).

In early studies, virtually all complexes showed a decrease in ν (SO) when compared with that of the free ligand at 1055 cm^{-1}. Such complexes included those of the first row transition metals, aluminium, zinc, tin, lead and heavier metals such as uranium or thorium when heavily solvated with Me_2SO. Preliminary studies indicated bonding to palladium in the complex $PdCl_2(Me_2SO)_2$ through the sulphur as ν (SO) occurred at 1120 cm^{-1}. Unambiguous assignment of ν (SO) is difficult because of the proximity of methyl rocking modes but use of $(CD_3)_2SO$ in addition to

$(CH_3)_2SO$ and comparison of i.r. spectra allows a complete assignment of bands to be made; $PdCl_2(Me_2SO)_2$ and the related complex $PtCl_2(Me_2SO)_2$ both show an increase of ca. 60 cm^{-1} in ν (SO) and were considered to be the first examples of S-bonded Me_2SO. An X-ray determination of the structure of $PdCl_2(Me_2SO)_2$ confirmed that bonding was indeed through the sulphur and that the complex was the planar trans isomer.[13] This is presumably more stable than the cis isomer as in the latter case considerable methyl interaction would cause some steric hindrance. Thus although most metals studied have been of class (a) character and would have been expected to bond with oxygen, there is a steric factor to be considered when the metal is of class (b) character and sulphur coordination is a possibility. The heavier metals of Group VIII come into this category and it is amongst these elements i.e. ruthenium, rhodium, palladium, osmium, iridium and platinum that sulphur bonding of the Me_2SO is to be expected. In addition, there is evidence of sulphur bonding amongst the actinides thorium and uranium in the salts $Th(ClO_4)_4.6Me_2SO$ and $UO_2(ClO_4)_2.4Me_2SO$; again there is an indication of the importance of steric as well as electronic factors. $Th(ClO_4)_4.12Me_2SO$ has two ν (SO) values, 1044 cm^{-1} and 946 cm^{-1}, assigned to lattice and O-bonded Me_2SO respectively. On heating to ca. 190°C the complex loses six Me_2SO molecules and ν (SO) moves to 1144 cm^{-1} and 1113 cm^{-1}, indicating a change of donor atom from oxygen to sulphur; the change is probably influenced by steric considerations.[14] A similar change from oxygen to sulphur bonding is suggested in the thermal decomposition of $UO_2(ClO_4)_2.5Me_2SO$ to $UO_2(ClO_4)_2.4Me_2SO$.[15]

Until recently, complexes of Me_2SO with the heavier Group VIII metals had been little studied but recent interest has resulted in a

large number of complexes of these elements being characterised. A study of the ruthenium complex $[Ru(NH_3)_5Me_2SO]^{2+}(ClO_4)_2$ has questioned the value of the ν (SO) criterion of the mode of bonding.[16] In this complex, studies involving deuteriated as well as non-deuteriated ligands show that ν (SO) is at 1045 cm^{-1}. This is essentially unchanged from that of free Me_2SO but a crystal structure of the complex[17] shows sulphur bonding of the Me_2SO molecule, although an S - O distance of 1.527 Å is considerably longer than the S - O distance in other S-bonded species (c.f. $PdCl_2(Me_2SO)_4$, which has an S - O distance of 1.476 Å.[13])

However, an additional criterion involving the ^1H n.m.r. spectrum of the methyl protons of Me_2SO in such complexes has been proposed;[18-20] the diamagnetism of the complexes generally means that well-resolved ^1H n.m.r. spectra can be obtained. In S-bonded Me_2SO the methyl protons are substantially deshielded (i.e. occur further downfield) when compared with the free ligand or with O-bonded Me_2SO. For example, in the O-bonded Me_2SO complexes of tin or lead, there is little change in the positions of the methyl resonances and no M- ^1H spin coupling is apparent.[21,22] If other sulphoxides apart from Me_2SO are used, the same conclusions are reached if the protons on the α-carbon atom are considered.

In contrast, the S-bonded complexes of platinum(II) and palladium(II) show substantial deshielding corresponding to a downfield shift of ca. 1 p.p.m. with respect to free Me_2SO. M- ^1H spin coupling is also apparent in the platinum(II) complexes.

If this criterion is applied to the complex $[Ru(NH_3)_5Me_2SO]^{2+}(ClO_4)_2$, the correct ligating atom, sulphur, can be identified, as the methyl protons are deshielded to the extent that a downfield shift of 0.58 p.p.m. is observed.[16]

Care must be exercised in the interpretation of spectra observed as some solvents used (e.g. pyridine) exchange rapidly with the bound sulphoxide and yield a signal due only to the uncomplexed ligand. With $PdCl_2(Et_2SO)_2$, the only suitable solvent, pyridine, gave rapid exchange, but a spectrum in the absence of free sulphoxide could be obtained by addition of slightly less than the calculated amount of Et_2SO to $PdCl_2(C_6H_5CN)_2$. The shift of the methyl protons indicated sulphur coordination.[20]

The ^1H n.m.r. criterion would be expected to be of particular utility when linkage isomerism in the same complex occurs, as integration of S-bonded against O-bonded protons should indicate the number of S- and O-bonded molecules present in the complex. The first example of this kind of linkage isomerism was noted in the complexes $[Pd(Me_2SO)_4]^{2+}X_2$ ($X = ClO_4^-$, BF_4^-),[23] where the isomerism was postulated after an examination of i.r. spectra of both deuteriated and non-deuteriated complexes. Extension of this work to platinum(II) and to other alkyl sulphoxides has led to the isolation of totally S-bonded, mixed site and totally O-bonded sulphoxide complexes.[24]

It now seems clear that in palladium(II) and platinum(II) complexes, at least, in the absence of any steric limitations, sulphur is the preferred donor atom. Thus $PtCl_2(Me_2SO)_2$ and $PdCl_2(Me_2SO)_2$ are both S-bonded, as are corresponding complexes with the considerably more sterically hindered sulphoxide, diisoamyl sulphoxide, IASO. However, while $[ML_4]^{2+}X_2$ (M = Pd, Pt; L = Me_2SO, IASO; $X = ClO_4^-$, BF_4^-) contain mixed coordination sites when $L = Me_2SO$, the complexes when L = IASO are completely oxygen bonded.[24] This can be rationalised as an 'enforced' coordination to an unfavourable atom, oxygen, because of the extreme steric pressure which results in the complex if the sulphoxide attempts to coordinate through its sulphur atom. Similarly, the ^1H n.m.r.

spectra of the complexes $[Pt(Me_2SO)_4]^{2+}X_2$ ($X = ClO_4^-$, BF_4^-) indicate both sulphur and oxygen donor atoms, with the oxygen bonded molecules being more labile than the sulphur bonded ones, as might be expected.

In S-bonded complexes such as $PdCl_2(Me_2SO)_2$ or $PtCl_2(Me_2SO)_2$ strong in-plane metal - sulphur bonding should occur. This is reflected in the large change in ν (SO) and an empirical correlation between the strength of the metal - sulphur bonding and the change in ν (SO) seems to be possible. In the complex $AuCl_3(Me_2SO)$, recently prepared by the interaction of Me_2SO and $AuCl_3$ in chloroform, ν (SO) moves to 1198 cm^{-1},[25] suggesting a strong Au-S bond. This shift of 143 cm^{-1} to higher frequency is the highest yet discovered in Me_2SO complexes. However, since ν (SO) derives at least half of its potential energy from associated methyl rocking modes, anything more than a very general correlation of bonding strength with change in ν (SO) is open to question. Examination of the change in ν (SO) on complexation of various sulphoxides to manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II) has shown that little significance can be attached to it, especially as a measure of the metal - oxygen bond strength.[26]

Palladium and platinum complexes with Me_2SO as ligand have been most extensively studied amongst the metals of Group VIII. However, some iridium complexes with Me_2SO have also been prepared[27,28] and have been shown to be sulphur bonded[29] although no preparative details were given. The preparation of cis-and trans-$IrCl_3(pyridine)_2Me_2SO$ has been reported,[30] but no spectroscopic data were given.

If possible, it is best that both i.r. and ^1H n.m.r. criteria for S- or O-bonding be examined before an assignment of the ligating atom is made. One other obvious method available is the identification of an M - O or M - S vibration in the far i.r. region. However, associated

ligand modes which are also present, and coupling of these modes to the M - O or M - S stretching vibration often render such assignments meaningless. Both ν (MO) and ν (MS) have been assigned in some mixed site complexes of alkyl sulphoxides,[24] but the large range over which metal - oxygen or metal - sulphur vibrations occur means that there is difficulty in initially assigning bands in this region to ν (MO) or ν (MS); the use of far i.r. spectroscopy in determining the mode of bonding of a sulphoxide is thus very limited.

C. Ligands containing both N and S donor atoms

It is notable that amongst ambidentate ligands, those which can, in principle at least, coordinate through nitrogen or sulphur are especially well-studied. As mentioned earlier, simple ligands such as NCS^- have attracted extensive interest, primarily as it is easy to determine the nature of the coordinating atom from an examination of the infra-red spectrum.

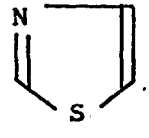
Even with simple ligands, when electronic effects in determining the nature of the bonding atom are expected to be dominant, steric effects cannot be neglected entirely. In NCS^-, the ligand is linear when bonding through nitrogen but bent when coordinating through sulphur. The greater steric requirement of the latter case is shown by an examination of the related complexes $[Pd(dien)SCN]^+$ and $[Pd(C_2H_5)_4\,dien\,NCS]^+$.[31] The greater steric hindrance brought about by changing dien to $(C_2H_5)_4$ dien results in a change of coordinating atom of SCN^- from sulphur to nitrogen in an attempt to relieve some of the steric pressure. Other ligands may also affect the bonding of an ambidentate ligand by electronic effects. Sulphur coordination can be stabilised by acceptance of electron density from non-bonding d orbitals on the metal (d_{xz}, d_{xy} and d_{yz}) into empty sulphur d orbitals. When other π-acceptors are present

they can compete with the sulphur atom for this $d\pi - d\pi$ bonding and thus reduce the stabilisation derived from sulphur bonding. This explains why the change from M - S to M - N bonding when two SCN^- groups in $[M(SCN)_4]^{2-}$, (M = Pd, Pt), are replaced by triethylphosphine is not observed on their replacement by ammonia.[32] In most cases, it is difficult to judge whether the coordination behaviour stems from electronic or steric effects; it is probably a combination of the two in most complexes. With more complex ligands, simple criteria such as the change in frequency of a particular vibrational mode are rarely definitive and careful use of the available spectroscopic techniques is generally necessary. Comparative studies with ligands containing only one donor atom are useful and nitrogen coordination in thiazole (Fig. 1.2, (a)) complexes of cobalt(II), nickel(II), copper(II) and zinc(II) has been suggested by comparison of the spectra of the complexes with those of the analogous pyridine complexes.[33] No ambidentate behaviour was noted, probably because of the importance of the resonance form of thiazole which puts a positive charge on the sulphur.

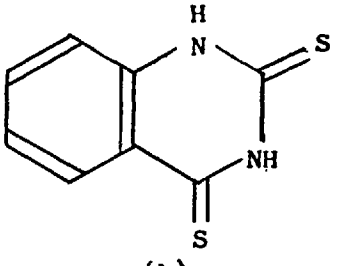
Ligands with the thioamide linkage, -CS - NH-, can have three modes of coordination as they can bond through sulphur, nitrogen or both as a chelating anion. Such chelating behaviour was noted in complexes of quinazoline (1H, 3H)-2,4-dithione, (Fig. 1.2, (b)), where stoichiometry and infra-red data were definitive.[34] In contrast, complexes of ε-thiocaprolactam, (Fig. 1.2, (c)), were sulphur bonded,[35] the criteria being a comparison with the electronic spectra of other sulphur donors, such as thiourea and N,N dimethyl thioacetamide, and the change in frequency of ν (C=S) on coordination.

This assignment of sulphur as the donor atom in these complexes has since been questioned by Singh and Rivest,[36] who suggested that

thiazolidine complexes of cobalt(II), (Fig. 1.2, (d)) were nitrogen bonded, and that ε-thiocaprolactam complexes should be similar. They based their assignment on a detailed analysis of the changes in frequency on coordination of vibrations in the thioamide region. However, vibrations in this region do not consist of individual ν (C=S) or ν (C-N) modes but can be interpreted as showing four bands, 'thioamide bands I, II, III and IV' [37,38] all involving the -CS - NH moiety. It appears that assignments of the donor atom based on shifts in frequency of those 'thioamide bands' are dubious, as it is often difficult to differentiate these bands from other vibrations, such as ring modes, which occur in the same region.



(a)



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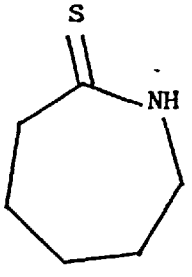
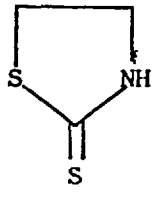


(c)



(d)

Fig. 1.2.

Later work on the complexing of thiazolidine thione[39] suggested that sulphur was the donor atom, mainly from a study of the far i.r. spectra of the complexes prepared. This conclusion is in accord with the behaviour of all ligands containing a thioamide group whose coordination behaviour has been studied.

Difficulties also arise when hydrogen bonding occurs in the ligand and is absent in the complexes, as shifts in the so-called diagnostic vibrational modes on coordination are then not definitive, even if they are correctly assigned, unless care is taken to remove such effects; the use of dilute solution spectra is recommended.[36]

The large variation in force constants of metal - sulphur bonds means that far i.r. criteria based on identifying ν (M-N) or ν (M-S) is of dubious utility. In cobalt(II) complexes of 2,2' dithiodipyridine, bands in the region 220 - 250 cm^{-1} in the far i.r. spectrum were assigned to metal - nitrogen stretches[40] without additional evidence, despite studies on the sulphur bonded cobalt(II) complexes of thiourea[41] and thioacetamide[42] which indicated that the metal - sulphur vibrations come in the same region. Working with the same ligand, Keeton and Lever[43] postulated nitrogen bonding as electronic spectra yielded Dq and B values comparable with those of known nitrogen bonded complexes. The usefulness of electronic spectroscopy in such studies is shown by the large number of different stereochemistries of copper(II) with the above ligand which can be differentiated.[44]

D. Conclusions

The methods used to identify the ligating atom in complexes of ambidentate ligands depend very much on the exact nature of the ligand. The standard technique of using changes in frequency of prominent ligand modes on coordination to a metal is dubious, because

(i) in general, the bands are not pure vibrations but contain a great deal of the character of other neighbouring bands,

(ii) hydrogen bonding and other effects can introduce frequency shifts unrelated to the identity of the coordinating atom,

(iii) it is often very difficult to assign a particular ligand mode correctly, particularly if the region is complicated by the presence of other vibrations.

As data on far i.r. and electronic spectroscopy accumulates, it will be easier to interpret results by comparison with previous work and these techniques have the advantage of giving a more direct way of examining the nature of the coordinating atom.

CHAPTER II

SPECTROSCOPIC STUDIES ON SOME Me_2SO COMPLEXES

A. Introduction

As outlined in Chapter I, the spectroscopic study of Me_2SO complexes has been of value in elucidating the mode of bonding of this ambidentate ligand. The criterion for S- or O-bonding, involving the shift in ν (SO) on coordination has been shown to require careful examination as explained earlier, but this criterion, together with ^1H n.m.r. studies on diamagnetic complexes, is usually definitive. As discussed, mixed S- and O- coordination sites have been discovered in Me_2SO and other sulphoxide complexes of palladium(II) and platinum(II)[24] but little or no investigation has been attempted with the related elements ruthenium and rhodium with coordinated sulphoxides.

The far i.r. spectrum of $RhCl_3(Me_2SO)_3$ has been studied but no conclusions were drawn as to the mode of bonding.[45] However, the possibility of both S- and O-bonded Me_2SO being present has been suggested, on somewhat tenuous evidence.[46]

It was therefore considered opportune to prepare some simple halo complexes of ruthenium and rhodium and to investigate them in some detail using conventional, far i.r. and ^1H n.m.r. spectroscopy.

B. Ruthenium

(i) Reaction of ruthenium trichloride with Me_2SO

Although commercial ruthenium trichloride, '$RuCl_3.3H_2O$', is essentially non-stoichiometric, consisting of both Ru(III) and Ru(IV) aquo and hydroxy species,[47] its interaction with refluxing Me_2SO proved reproducible and proceeded cleanly to give yellow $RuCl_2(Me_2SO)_4$.

During the course of these studies, Rempel et al. reported the preparation of the same complex by the prolonged interaction of $RuCl_3.3H_2O$ with Me_2SO under hydrogen at 80°C.[48] Various methods of isolating the complex in high yield were attempted, the most successful being precipitation with acetone after concentration of the solution under reduced pressure. On re-concentration, the filtrate deposited more complex, and a total yield (based on ruthenium) of 80% was consistently obtained. Further non-stoichiometric orange crystals could be isolated from the reaction mixture; these had S:Cl ratios in excess of 2:1, and although i.r. spectroscopy indicated coordinated dimethyl sulphoxide, these crystals were not investigated further. The reaction involved the reduction ruthenium(III) → ruthenium(II) and an attempt was first made to elucidate the exact nature of the reduction process.

(ii) Mechanism of the reduction process

The reaction can be summarised by the equation

$$RuCl_3.3H_2O \xrightarrow[190^{\circ}C,\ 4\ min]{Me_2SO} RuCl_2(Me_2SO)_4$$

Two significant observations made during the reaction were

(a) the production of a considerable quantity (ca. 20% of the Me_2SO used), of a white sublimate in the condenser,

(b) the evolution of a gas with a typical 'thiol-like' odour.

Me_2SO is known to decompose slightly at its boiling point over a period of 72 hours to give 3.7% of its own weight of volatile products: dimethyl sulphide, dimethyl sulphone, dimethyl disulphide, bis(methylthio)-methane, water and paraformaldehyde.[49] Elemental analysis indicated the stoichiometry $(CH_2O)_n$ for the white volatile product formed in the reaction between $RuCl_3.3H_2O$ and Me_2SO; it was confirmed as paraformaldehyde

by comparison of its i.r. spectrum with that of a genuine sample. The insolubility of the product in water indicated n > 12.

The decomposition of the dimethyl sulphoxide as indicated by the production of paraformaldehyde can be used to elucidate the mechanism of the reduction process. Initial cleavage of Me_2SO probably occurs to give formaldehyde and methane thiol:

$$(CH_3)_2SO \rightarrow CH_2O + CH_3SH \qquad 2.1$$

This certainly involves the ruthenium atom acting as a template for the reaction when the rate of decomposition in the reaction is compared with the very much slower rate of decomposition of pure Me_2SO at its boiling point. The exact nature of the cleavage reaction 2.1 was not studied. The subsequent reactions 2.2 and 2.3 would then be expected to occur rapidly

$$n\ CH_2O \rightarrow HO(CH_2O)_nH \qquad 2.2$$

$$2CH_3SH \rightarrow CH_3S\text{-}S\ CH_3 + 2H^+ + 2e \qquad 2.3$$

The conversion of thiols to disulphides is an oxidation process, somewhat idealistically described by 2.3. The formaldehyde, if formed as a reaction intermediate, must polymerise rapidly as no ruthenium carbonyl species could be isolated from the reaction mixture.

(iii) Purification

Although the yellow $RuCl_2(Me_2SO)_4$ as obtained direct from the reaction mixture was analytically pure, slight differences in solubility and i.r. spectra were noted for different samples. Recrystallisation from hot (80°C) Me_2SO yielded crystalline samples with reproducible spectra, and all spectroscopic work was carried out, except where specifically stated, on the purified material. Attempts to purify the material to give reproducible spectra by chromatography were not successful, despite using a wide variety of chromatographic materials.

(iv) Conventional i.r. spectroscopy

To enable a complete assignment of all bands to be made, the corresponding fully deuteriated complex $RuCl_2[(CD_3)_2SO]_4$ was prepared from $RuCl_3.3H_2O$ and $(CD_3)_2SO$ in an essentially similar manner to $RuCl_2[(CH_3)_2SO]_4$. All bands were assigned by utilising known data on Me_2SO complexes.[11,16,50] (Table 2.1)

After assignment of all C - H stretching, deformation and rocking modes, there are strong bands at 1120, 1090 and 915 cm^{-1} in the undeuteriated complex which do not shift significantly on deuteriation. These bands are assigned to ν (SO) of S-bonded Me_2SO (1120 and 1090 cm^{-1}) and ν (SO) of O-bonded Me_2SO (915 cm^{-1}). The shift of this last band to 928 cm^{-1} on deuteriation is somewhat surprising in its magnitude, but as the S - O stretch is strongly coupled to the C - H or C - D rocking modes, some slight shift is not unexpected.

The complex thus contains mixed sulphur and oxygen coordination sites. The assignments of Rempel et al.[48] in the region of the S - O stretch are thus incorrect; it is not possible to distinguish unequivocally between ρr CH and ν (SO) of O-bonded Me_2SO in this region without recourse to deuteriation.

(v) Far i.r. spectroscopy

The region studied was 600 - 250 cm^{-1}; below this region ligand modes such as M - O - S or M - S - O deformations occur,[51] which are in themselves uninformative. The Ru - Cl stretches were of especial interest as trans-$RuCl_2(Me_2SO)_4$ should have a single ν(Ru-Cl) whereas cis-$RuCl_2(Me_2SO)_4$ should have two. Both the recrystallised material and the product obtained from the initial reaction mixture were studied. The former had a rather broad band with two, through overlapping, peaks at 345 cm^{-1} and 330 cm^{-1}, whereas the latter had a single band at 348 cm^{-1},

$RuCl_2(Me_2SO)$		$RuCl_2(CD_3)_2SO$		ν_{CH}/ν_{CD}
Frequency	Assignment	Frequency	Assignment	
3000 m[a]	ν CH[b]	2250 m	ν CD	1.33
2908 m	ν CH	2190 m	ν CD	1.33
1430 s[a]	δ_d[b] CH	Hidden by νSO	-	-
1400 s	δ_d CH	1077 sh [a]	δ_d CD	1.33
1303 s	δ_d CH	1010 s	δ_d CD	1.29
1282 m	δ_d CH	Hidden	-	-
1120 s	νSO S-bonded	1120 s	νSO S-bonded	-
1090 s	νSO S-bonded	1095 s	νSO S-bonded	-
1024 s	ρ_r[b] CH	810 m	ρ_r CD	1.26
980 m	ρ_r CH	770 m	ρ_r CD	1.27
970 m	ρ_r CH	760 m	ρ_r CD	1.28
915 s	νSO O-bonded	928 s	νSO O-bonded	-
705 m	ν_a[b] CS	628 m	ν_a CS	1.12
670 w[a]	ν_s[b] CS	Not observed	-	-

a s, strong; m, medium; w, weak; sh, shoulder band.

b ν, stretching; ν_a, asymmetric stretching; ν_s, symmetric stretching; δ, deformation; δ_d, degenerate deformation; ρ_r, rocking.

Table 2.1 Infra-red spectra (4000 - 600 cm^{-1}) of $RuCl_2(Me_2SO)_4$ and $RuCl_2[(CD_3)_2SO]_4$. (Nujol or hexachlorobutadiene mulls; NaCl or KBr plates).

although the band was somewhat asymmetric. It seems that the complex as first precipitated is mainly the trans-isomer, whereas after recrystallisation the cis-isomer predominates. (Table 2.2)

$RuCl_2(Me_2SO)_4$		$RuCl_2[(CD_3)_2SO]_4$		ν_{CH}/ν_{CD}
Frequency	Assignment	Frequency	Assignment	
479 s	ν Ru-ligand	450 s	ν Ru-ligand	-
420 m	δ_s [a] CSO	355 m	δ_s CSO	1.18
380 m	δ_{as} [a] CSO	340 s	δ_{as} CSO	1.12
345 m	ν Ru-Cl	330 s	ν Ru-Cl	-
330 m	ν Ru-Cl	325 sh	ν Ru-Cl	-
295 w	CSC deformation?	295 w	CSC deformation?	-

a δ_s, symmetric deformation; δ_{as}, asymmetric deformation.
For other symbols, see Table 2.1.

Table 2.2 Infra-red spectra (600 - 250 cm^{-1}) of $RuCl_2(Me_2SO)_4$ and $RuCl_2[(CD_3)_2SO]_4$. (Polystyrene plates, vaseline mulls).

Since mixed coordination sites were known to be present in the complex, it was somewhat surprising that only one band attributable to a metal - ligand stretching mode could be detected at 479 cm^{-1} in the undeuteriated complex and at 450 cm^{-1} in the deuteriated complex. The frequency shift on deuteriation of this mode shows the strong coupling which exists between the metal - ligand stretch and the other

modes which are shifted on deuteriation such as δ_s(CSO) and δ_{as}(CSO). Little is known about Ru - S or Ru - O stretching frequencies, but it seems from available data that they come in the region 500 - 400 cm^{-1}.[45,52] Because this region is also where the C - S stretch, C - S - O and C - S - C deformations of the ligand occur, the metal - ligand mode is strongly associated with these other bands; it is not possible to determine whether mixed coordination occurs in Me_2SO complexes from an examination of this region, as here assignments to ν (M - S) or ν (M - O) mean little in real terms.

(vi) ^{1}H n.m.r. spectroscopy

The spectrum of the material as obtained directly from the reaction mixture was extremely complex, consisting of some 13 lines, the exact intensities of which varied from sample to sample (Fig. 2.1). In contrast, the recrystallised material gave a reproducible spectrum, consisting of six lines (Fig. 2.2). These were singlets due to six sets of chemically distinct protons at τ 6.50, 6.52, 6.57, 6.68, 7.28 and 7.40, confirmed by the identity of spectra at 60 and 100 MHz. This complex spectrum is expected if both S- and O-bonded ligands are present, for, as explained in Chapter I, the methyl protons of S-bonded Me_2SO generally resonate ca. 1 p.p.m. downfield from those of O-bonded Me_2SO, which are generally little shifted from the methyl resonance of uncomplexed Me_2SO.

The resonance at τ 7.40 can be attributed to free Me_2SO since if Me_2SO was added to the solution of the complex in chloroform this peak grew in intensity in the ^{1}H n.m.r. spectrum. The peak at τ 7.28 can be attributed to O-bonded Me_2SO as the methyl resonance was not significantly shifted from that of free Me_2SO. The group of peaks about 1 p.p.m. downfield from the free Me_2SO resonance can be attributed to

Fig. 2.1 ^1H n.m.r. spectrum of $RuCl_2(Me_2SO)_4$ before recrystallisation

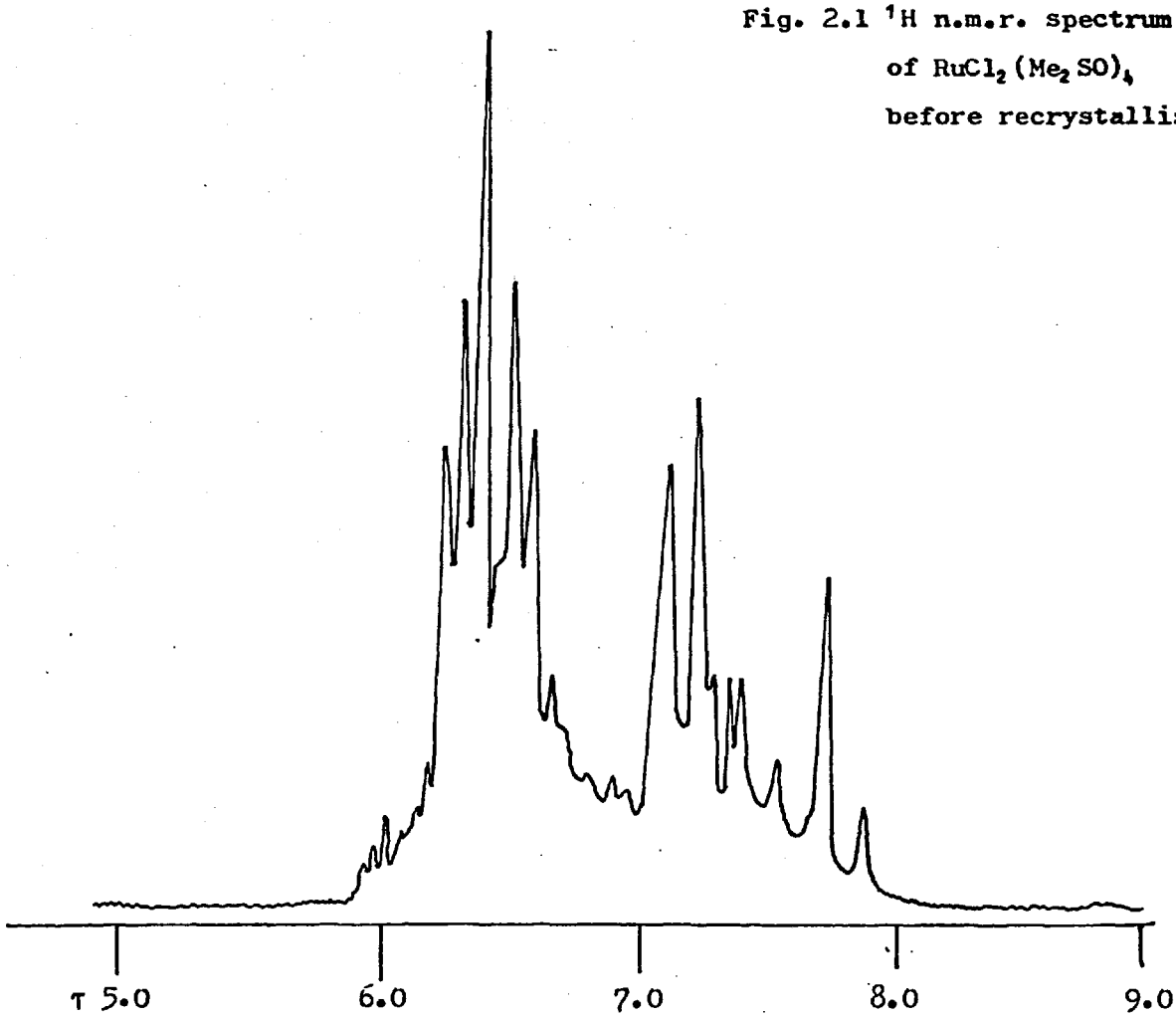
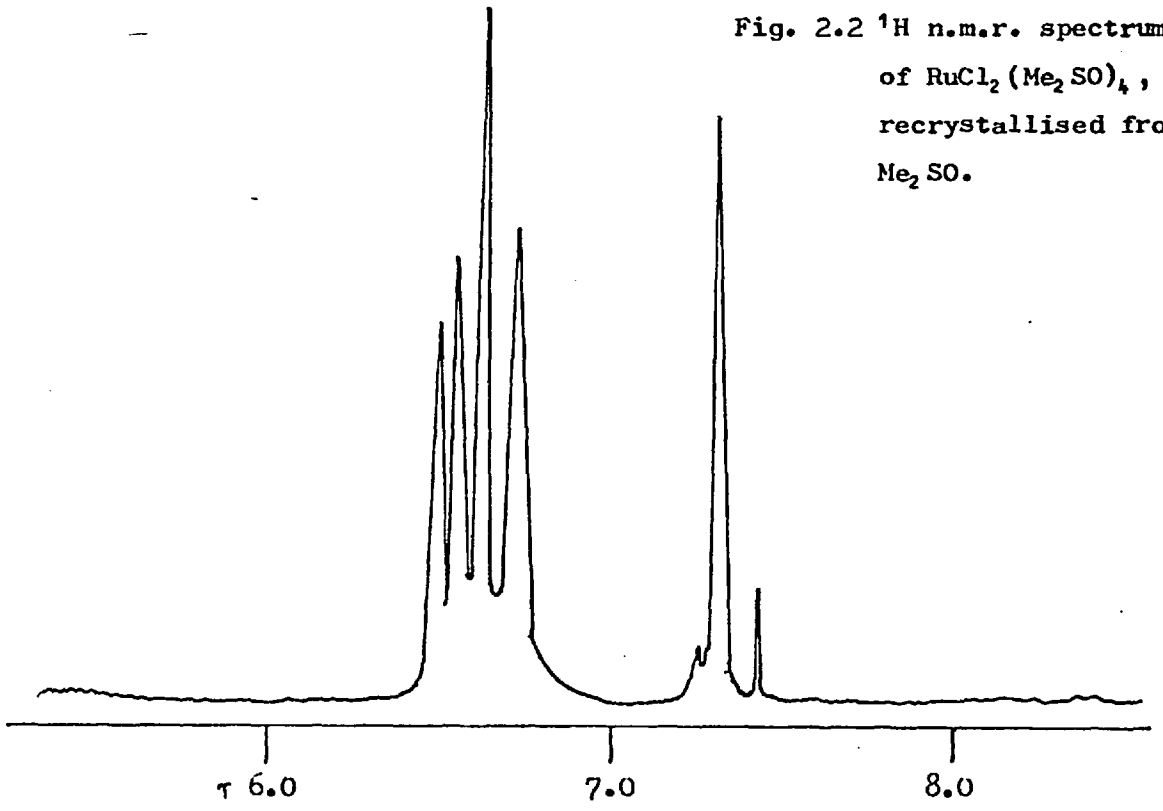


Fig. 2.2 ^1H n.m.r. spectrum of $RuCl_2(Me_2SO)_4$, recrystallised from Me_2SO.



S-bonded Me_2SO. Integration of the spectrum showed that there were three S-bonded Me_2SO molecules to every O-bonded one. The peak at τ 7.40 due to free Me_2SO results from a ca. 10% dissociation of the O-bonded Me_2SO. This was shown by the following observations:

(a) integration of the peaks due to the S-bonded ligands against the peak at τ 7.28 gave a ratio > 3:1, if the peak at τ 7.40 was included the ratio then became exactly 3:1,

(b) if excess Me_2SO was added to suppress dissociation, integration of the S-bonded Me_2SO peaks against the peak at τ 7.28 then gave a ratio of 3:1.

The signal due to free Me_2SO increased if the spectrum was run at elevated temperatures (60°C). The molecular weight, measured by osmometry in $CHCl_3$ at 25°C was normal within experimental error (± 10%), indicating no detectable dissociation of the form

$$RuCl_2(Me_2SO)_4 \rightleftharpoons RuCl_2(Me_2SO)_3 + Me_2SO \qquad 2.3$$

at that temperature. However, the ^1H n.m.r. spectrum of the complex is a more sensitive probe of whether dissociation is occurring and no attempt was made to obtain molecular weight data at other than ambient temperature.

Since there are three S-bonded Me_2SO ligands to every one which is O-bonded, there are two isomers when the chlorine atoms are *cis* and only one isomer when they are *trans* (Fig. 2.3, using S and O to represent S- and O-bonded Me_2SO ligands respectively). The ^1H n.m.r. spectrum was consistent with the far i.r. spectrum in that the *cis* form is the preferred isomer. Of the three S-bonded Me_2SO molecules in (a), two are *trans*- to chlorine and are equivalent, assuming free rotation about the C - S bond. The remaining one is *trans*- to O-bonded Me_2SO. Thus this isomer should give two resonances in the S-bonded Me_2SO region of

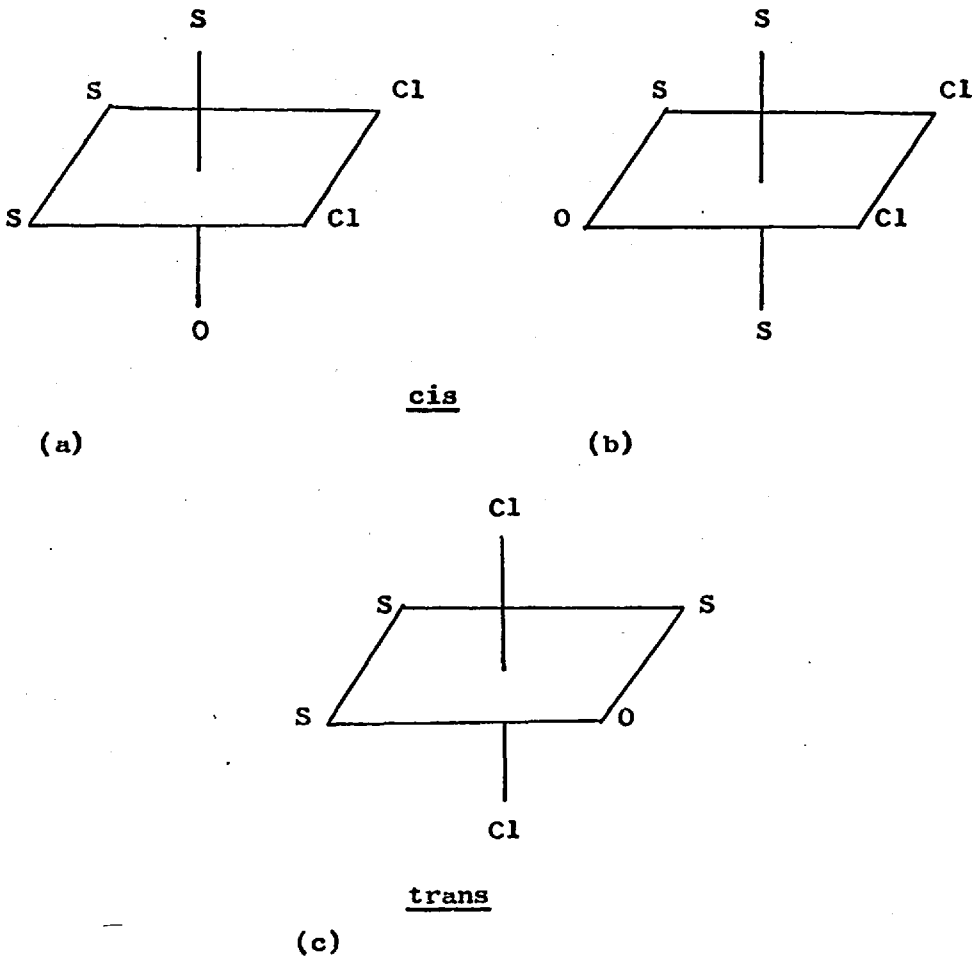


Fig. 2.3. Isomers of cis- and trans-$RuCl_2(Me_2SO)_4$.

the ^1H n.m.r. spectrum with intensity ratios 2:1. Similar arguments apply to isomer (b). If the assumption is made that these different S-bonded Me_2SO molecules have differing chemical shifts, then four peaks should be seen in the S-bonded region, their intensities depending on the relative proportions of (a) and (b) present. The spectrum is probably complicated somewhat further by the dissociation, (2.3), which yields the totally S-bonded species $RuCl_2(Me_2SO)_3(S)$, where S is a solvent molecule.

By using the ^1H n.m.r. 'shift' reagent $Eu(fod)_3$, the S-bonded region could be better resolved. The theory and utility of 'shift' reagents has been reviewed recently.[53] In this case, the free Me_2SO would be expected to coordinate most strongly and therefore be moved downfield to the greatest extent. The magnitude of the shift to lower field of the methyl protons of the complex itself depends on two factors:

(i) the distance of the protons of the methyl group from the europium atom,

(ii) the position of the equilibrium 'free' $RuCl_2(Me_2SO) \rightleftharpoons RuCl_2(Me_2SO)_4$, complexed with europium.

The equilibrium would undoubtedly be complex, as there are four oxygen atoms in the compound theoretically available for complexing. The sulphur bonded Me_2SO molecules, with the oxygen uncoordinated, would be expected to show more ability to complex than the oxygen bonded Me_2SO. In addition, assuming only one molecule of europium complex coordinates to each molecule of $RuCl_2(Me_2SO)_4$ there are three sites of S-bonded Me_2SO available to every one of O-bonded Me_2SO.

On the addition of ca. 10 mgms of $Eu(fod)_3$ to the solution in the n.m.r. tube, the S-bonded region was spread out into two sets of two peaks. One set had the peaks in intensity ratio 2:1, as would be expected for one of the isomers of <u>cis</u>-$RuCl_2(Me_2SO)_4$. The other set, however, less far downfield and about 30% of the intensity of the first set, consisted of two peaks of approximately equal intensity, rather than the 2:1 ratio expected. This observation is difficult to explain, and it may be that the explanation of the ^1H n.m.r. spectrum as offered is facile. Consistent with the argument above, however, were the magnitudes of the shifts produced: 2.83 p.p.m. for free Me_2SO, ca. 1.4 and

0.5 p.p.m. for the two sets of S-bonded peaks and 0.5 p.p.m for the O-bonded Me_2SO. Line broadening was not significant at the concentration of europium complex that was used.

On the addition of ca. 5% by volume of $(CD_3)_2SO$, the resonance attributed to O-bonded Me_2SO rapidly disappeared; the resonances attributed to S-bonded Me_2SO disappeared somewhat more slowly and at varying rates. After 4 hours the only signal observed was that due to free Me_2SO (τ 7.40) indicating that complete exchange had taken place.

These exchange studies were extended, using acetonitrile and pyridine. Addition of acetonitrile caused more rapid exchange than $(CD_3)_2SO$, and after two hours complete exchange had occurred yielding peaks due only to free Me_2SO (τ 7.40) and acetonitrile (τ 8.00). With pyridine, exchange was very rapid initially, but the peak due to O-bonded Me_2SO was less labile than the peak at τ 6.57, which had decreased significantly in intensity after 30 seconds; after two minutes, however, the peak at τ 7.28 had also decreased in intensity. After fifteen minutes, two peaks remained, apart from pyridine and free Me_2SO, at τ 6.50 and τ 6.70, possibly suggesting *in situ* formation of $RuCl_2(Me_2SO)_2(py)_2$.

Reducing the temperature caused considerable line broadening in the spectrum of $RuCl_2(Me_2SO)_4$ and this broadening continued down to -60°C, the lowest temperature at which the spectrum was recorded (Fig. 2.4). Since the slow exchange limit is evidently reached at 35°C as both free and complexed Me_2SO resonances are seen and are sharp, the broad peaks are probably envelopes concealing inequivalencies brought about by lack of free rotation of the methyl groups at these lower temperatures. In fact, the slight dissociation of the complex is probably an indication of some considerable steric hindrance.

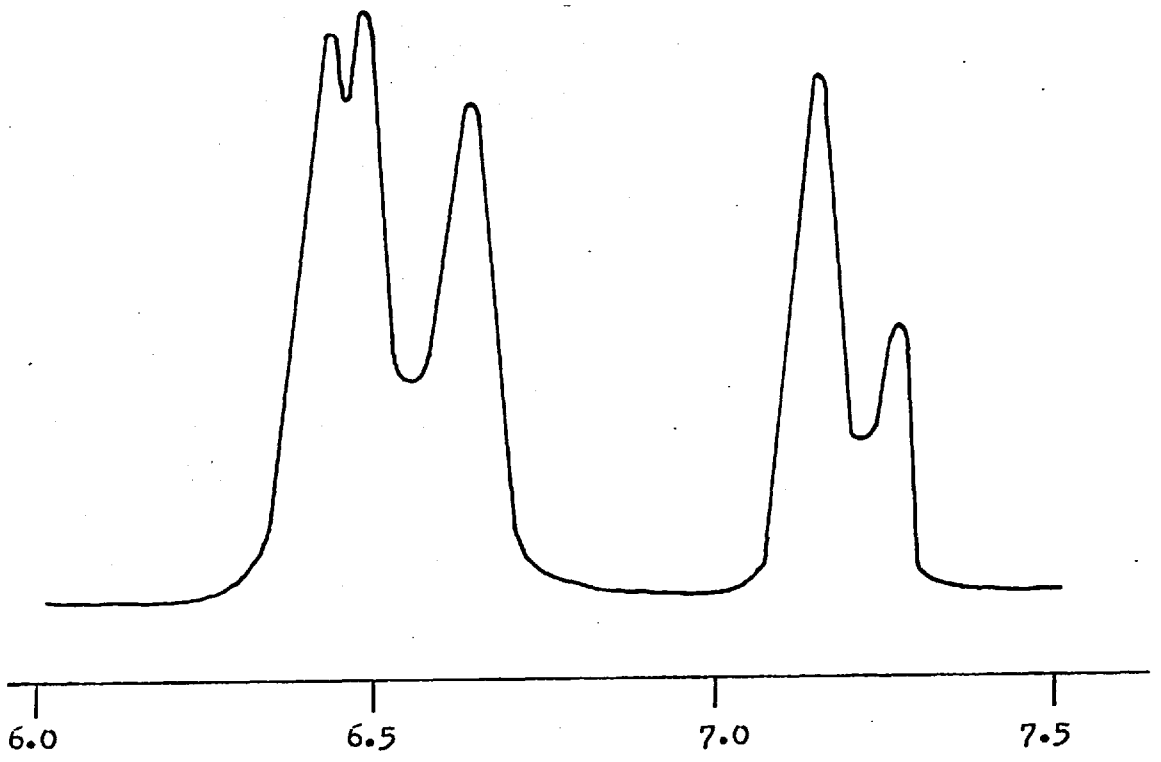


Fig. 2.4. ^1H n.m.r. spectrum of $RuCl_2(Me_2SO)_4$ at -60°C

C. Rhodium

(i) Reaction of rhodium trichloride with Me_2SO

Johnson and Walton[45] reported that the interaction of $RhCl_3 \cdot 3H_2O$ with cold Me_2SO yielded orange crystals of $RhCl_3(Me_2SO)_3$ without giving experimental details. It was found that the complex could be isolated by diluting the reaction mixture with ethanol and precipitating the compound with diethylether or light petroleum (b.p. 60 - 80°C). Refluxing Me_2SO was used in an attempt to isolate $RhCl(Me_2SO)_3$ but under the same conditions that reduced ruthenium(III) to ruthenium(II) only $RhCl_3(Me_2SO)_3$ was isolated and virtually no paraformaldehyde was noted as sublimate. This probably means that rhodium(I) was not even formed as an intermediate in the reaction. Although the chemistry of rhodium(I)

is extensive,[54] it is exclusively one involving π-acid ligands, so the failure of rhodium(III) to undergo the attempted reduction is not surprising.

The complex as isolated was analytically pure and also gave reproducible i.r. and ^{1}H n.m.r. spectra.

(ii) Conventional i.r. spectroscopy

Both $RhCl_3(Me_2SO)_3$ and $RhCl_3[CD_3)_2SO]_3$ were prepared and a full assignment of all the bands made (Table 2.3).

The i.r. spectra indicated that, as in $RuCl_2(Me_2SO)_4$, both O- and S-bonded Me_2SO molecules were present. Deuteriation showed that a previous assignment of the i.r. spectrum[46] confused a ρ_rCH mode with ν (SO) of O-bonded Me_2SO.

In $RhCl_3(Me_2SO)_3$, one of the methyl rocks occurred at 1140 cm^{-1} and so it might seem possible that the band at 900 cm^{-1} in the deuteriated complex, which is assigned to ν (SO) of O-bonded Me_2SO, could be due to a methyl rocking mode of the deuteriated complex. This would give an isotopic shift, $\frac{\nu CH}{\nu CD}$, of 1.27, which is acceptable. If this were so, however, it would necessarily imply that the band at 915 cm^{-1} in $RhCl_3(Me_2SO)_3$ was also due to a ρ_r(CH) mode. There was no corresponding band, though, in the 730 cm^{-1} region in the deuteriated complex. The assignment as given is thus consistent.

(iii) Far i.r. spectroscopy

The far i.r. spectra obtained were not sufficiently well resolved to distinguish between mer- and fac-$RhCl_3(Me_2SO)_3$. The assignments made are given in Table 2.4. The ν(Rh-Cl) region was complicated by the presence of bands due to δ_a(CSO) and methyl torsion modes. In addition, only one band which could be definitely assigned to ν(Ru-ligand) was observed, despite conventional i.r. and ^{1}H n.m.r. evidence that mixed coordination sites occur.

$RhCl_3(Me_2SO)_3$ [a]		$RhCl_3[(CD_3)_2SO]_4$ [a]		ν_{CH}/ν_{CD}
Frequency	Assignment	Frequency	Assignment	
3008 (m)	ν CH	2250 (m)	ν CD	1.34
2917 (m)	ν CH	2118 (m)	ν CD	1.38
1400 (s)	δ_d CH	1035 (s)	δ_d CD	1.35
1322 (m)	δ_d CH	1010 (s)	δ_d CD	1.31
1306 (m)	δ_d CH	Not observed	-	-
1286 (m)	δ_d CH	965 (m)	δ_d CD	1.33
1140 (m)	ρ_r CH	Hidden by ν SO	-	-
1122 (m)	ν SO S-bonded	1130 (m)	ν SO S-bonded	-
1020 (s)	ρ_r CH	818 (s)	ρ_r CD	1.25
980 (m)	ρ_r CH	762 (m)	ρ_r CD	1.29
924 (s)	ρ_r CH	716 (m)	ρ_r CD	1.29
915 (s,sh)	ν SO O-bonded	900 (m)	ν SO O-bonded	-
712 (w)	ν_a CS	620 (w)	ν_a CS	1.14
672 (vw)	ν_s CS	Not observed	-	-

[a] For symbols, see Table 2.1

Table 2.3. Infra-red spectra (4000 - 600 cm^{-1}) of $RhCl_3(Me_2SO)_3$ and $RhCl_3[(CD_3)_2SO]_3$. (nujol or hexachlorobutadiene mulls; KBr plates).

(iv) ^{1}H n.m.r. spectroscopy

Studies on the ^{1}H n.m.r. spectrum of $RhCl_3(Me_2SO)_3$ also indicated bonding of the Me_2SO through both oxygen and sulphur. There were three resonances in the S-bonded region, at τ 6.39, 6.51 and 6.57, and one resonance in the O-bonded region at τ 7.13. There was essentially no free Me_2SO present. Integration of S-bonded against O-bonded species suggested that there were two S-bonded and one O-bonded Me_2SO molecules.

$RhCl_3(Me_2SO)_3$ [a]		$RhCl_3[(CD_3)_2SO]_3$ [a]		ν_{CH}/ν_{CD}
Frequency	Assignment	Frequency	Assignment	
480 (w)	-	Not observed	-	-
430 (s)	δ_s CSO	385 (s)	δ_s CSO	1.12
418 (m)	ν Ru-ligand	410 (m)	ν Ru-ligand	-
365 (m)	δ_a CSO	Hidden by ν Rh-Cl	-	-
331 (m)	ν Rh-Cl	325 (m)	ν Rh-Cl	-
290 (w)	CSC deformation?	Not observed	-	-
255 (w)	-	Not observed	-	-

[a] For symbols, see Tables 2.1, 2.2

Table 2.4 Far infra-red spectra (600 - 250 cm^{-1}) of $RhCl_3(Me_2SO)_3$ and $RhCl_3[(CD_3)_2SO]_3$ (polystyrene plates, vaseline mulls).

The isomers possible for mer- and fac-$RhCl_3(Me_2SO)_3$ in this case are given in Fig. 2.5. For fac-$RhCl_3(Me_2SO)_3$, both S-bonded molecules are equivalent, whereas in mer-$RhCl_3(Me_2SO)_3$ there are three different

S-bonded molecules; isomer (a) has two different S-bonded molecules, one being trans to Cl and the other being trans to O-bonded Me_2SO, while isomer (b) has both Me_2SO molecules equivalent, as they are trans to one another. The ^1H n.m.r. spectrum was consistent with the mer isomer being preferred. This is not in agreement with another assignment on the basis of far i.r. measurements[45] but since the far i.r. region is complicated by ligand modes such an assignment must obviously be tentative.

Addition of $Eu(fod)_3$ again allowed improved resolution of the S-bonded region in the ^1H n.m.r. spectrum. An additional small peak was obtained further downfield than either S- or O-bonded Me_2SO. This is assigned to free Me_2SO coordinated to europium, the slight dissociation of the complex necessary to produce this being presumably assisted by the presence of the europium ion. The S-bonded region consisted of three peaks. Two peaks were close together and were of equal intensity; these are assigned to isomer (a) of Fig. 2.5. The remaining resonance, assigned to S-bonded Me_2SO, was a singlet due to the equivalent Me_2SO molecules of isomer (b) of Fig. 2.5. The protons of isomers (a), (b) were moved downfield by 1.1 and 2.5 p.p.m. respectively whereas the protons of the O-bonded Me_2SO were moved downfield by only 0.5 p.p.m. The signal assigned to free Me_2SO showed a downfield shift of 3.0 p.p.m. which is approximately the same as the shift observed for the free Me_2SO of the complex $RuCl_2(Me_2SO)_4$.

The spectrum of the pure complex did not change between 35° and -90°C, using $(CD_3)_2CO$ as solvent, probably indicating that $RhCl_3(Me_2SO)_3$ is less sterically crowded than $RuCl_2(Me_2SO)_4$, which showed broadening even at -50°C. Although there was no free Me_2SO, exchange with $(CD_3)_2SO$

was fairly rapid, the peak at τ 6.39 being most labile, but there was a significant decrease in all peaks after 10 mins. apart from that at τ 6.57 which remained for some hours.

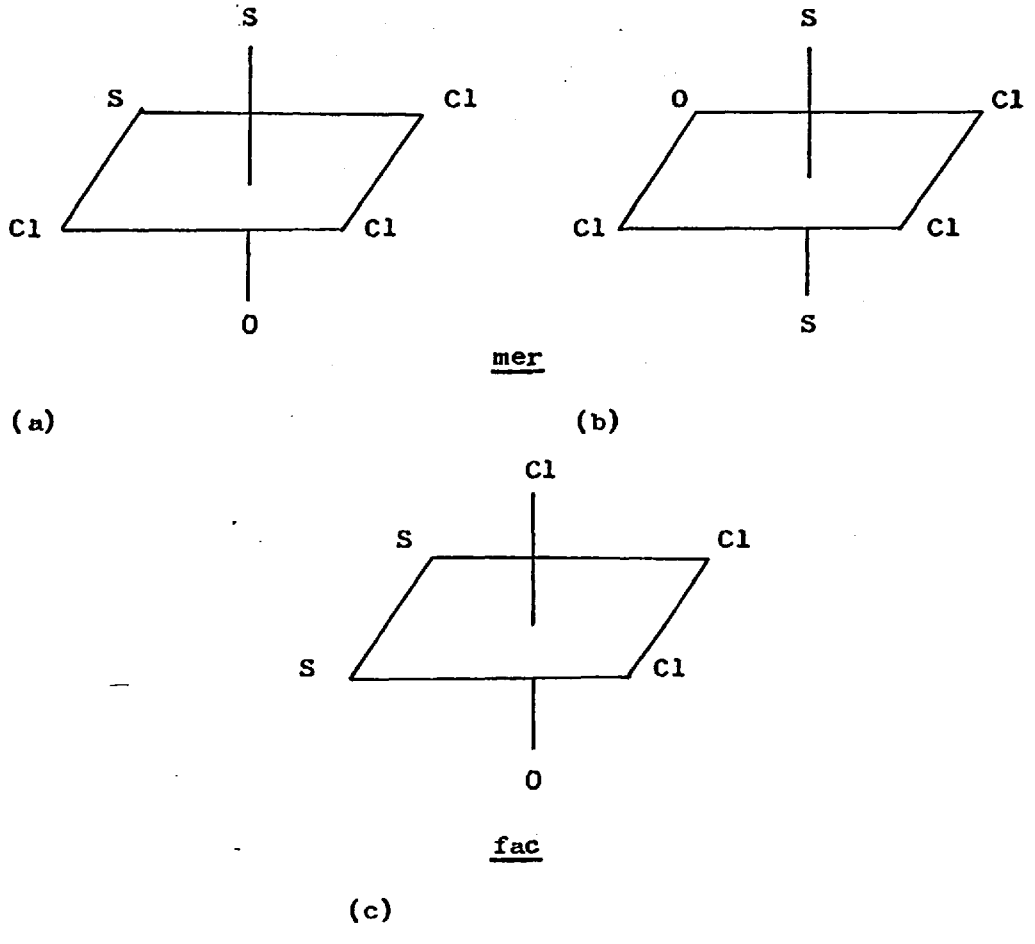


Fig. 2.5. Isomers of <u>mer</u>- and <u>fac</u>-$RhCl_3(Me_2SO)_3$

CHAPTER III

COMPLEXES OF RUTHENIUM(II) CONTAINING COORDINATED DIMETHYL SULPHOXIDE

A. Introduction

The complex $RuCl_2(Me_2SO)_4$ proved a very convenient source of new ruthenium(II) complexes containing coordinated dimethyl sulphoxide. The presence of the sulphoxide appeared to stabilise the ruthenium(II) oxidation state with respect to ruthenium(III) and no complexes of ruthenium(III) were isolated. Indeed, Rose's preparation of $RuCl_3(Me_2SO)_3$ [55] could not be repeated, as the reported preparation gave $RuCl_2(Me_2SO)_4$. Although the complexes were prepared under nitrogen they were air-stable indefinitely once isolated in the solid state.

Ruthenium is a good example of a class (b) metal and as expected complexes with sulphur and phosphorus donor ligands were readily obtained in good yield. Oxygen donor ligands were far less ready to coordinate but several complexes containing nitrogen donor ligands were obtained.

Analytical data for the complexes prepared are collected in Table 5.1 and a scheme summarising the reactions is given in Fig. 3.3.

B. Complexes with sulphur donor ligands

Sodium diethyldithiocarbamate reacted under reflux in toluene with $RuCl_2(Me_2SO)_4$ to give $Ru(Et_2NCS_2)_2(Me_2SO)_2$. The complex was isolated as green needles from acetone. The i.r. spectrum of the complex indicated bidentate $Et_2NCS_2^-$ only [56] with ν(CN) at 1488 cm^{-1} c.f. the similar complex $Ru(Me_2NCS_2)_2(PPh_3)_2$ with ν(CN) also at 1488 cm^{-1}.

The ^1H n.m.r. spectrum in $CDCl_3$ showed the methyl and methylene protons as a triplet and a quartet at τ 6.07 and τ 8.67 respectively. The quartet showed some additional splitting, possibly due to slight inequivalence of the ethyl groups because of restricted rotation about the carbon-nitrogen bond, which possesses some double bond character.[57] The triplet resonance was also slightly broadened, although no additional splitting was observed. The Me_2SO protons resonated as a singlet at τ 6.60. Both Me_2SO ligands were therefore S-bonded and this was confirmed by the i.r. spectrum which showed ν (SO) at 1075 cm^{-1}.

The far i.r. spectrum had four strong peaks at 380, 415, 425 and 438 cm^{-1}. The peaks at 380 and 415 cm^{-1} are assigned to δ_s (CSO) and δ_{as} (CSO) respectively, whereas those at 425 and 438 cm^{-1} are probably Ru-S stretching modes.

Mercaptobenzthiazole (MBTH) reacted similarly to give $RuCl_2(MBTH)_2(Me_2SO)_2$ as orange crystals from acetone. The i.r. spectrum showed coordination of the Me_2SO to be through sulphur, with ν (SO) at 1080 cm^{-1} and this was confirmed by the ^1H n.m.r. spectrum which showed the Me_2SO protons resonating as a sharp singlet at τ 6.61. A strong band at 430 cm^{-1} in the far i.r. spectrum is assigned to a Ru-S stretch.

Both the above complexes were diamagnetic as expected and had normal molecular weights in chloroform at 25°C.

Using 2-aminothiophenol no metal complex could be isolated but instead green crystals of a tetramer of the ligand were obtained. Me_2SO itself is known to convert 2-aminothiophenol into a disulphide bridged dimer[58] and the absence of any bands in the i.r. spectrum of the tetramer in the -SH stretching region, 2550 - 2650 cm^{-1},[59] suggested that the product also contained S-S linkages. The ^1H n.m.r. spectrum in $CDCl_3$ showed two sets of aromatic protons as unresolved multiplets

at τ 2.85 and τ 3.35. The $-NH_2$ protons resonated as a broad singlet at τ 5.88 and integration of aromatic against aliphatic protons showed the ratio to be 2:1 as expected. The compound was not further investigated.

C. Complexes with nitrogen donor ligands

With $RuCl_2(Me_2SO)_4$ in refluxing pyridine or 3-methylpyridine, complete substitution of the Me_2SO ligands was achieved and the known complexes $RuCl_2L_4$ (L = pyridine, 3-methyl pyridine) were obtained. Both complexes exhibited two Ru-Cl stretches in the far i.r. spectrum showing that the complexes were the cis isomers. It was not possible to replace the Me_2SO ligands systematically with pyridine or 3-methylpyridine in this way, probably because the replacement of one Me_2SO molecule tended to labilise the other ligands. In situ formation of $RuCl_2(Me_2SO)_2(py)_2$ could be shown by ^1H n.m.r. spectroscopy (see Chapter II).

The bidentate ligands, 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen), reacted in chloroform or toluene to give orange-yellow complexes of stoichiometry $RuCl_2(Me_2SO)_2(bipy)$ and $RuCl_2(Me_2SO)(phen)$.

^1H n.m.r. and i.r. spectroscopy indicated the bonding of the Me_2SO ligands to be through sulphur. The mechanism of the replacement of the Me_2SO molecules is probably initial replacement of the O-bonded Me_2SO, which is the most labile ligand, followed by displacement of the Me_2SO molecule cis to it. The other two S-bonded molecules proved inert to substitution and replacement of these was not observed even using excess of the ligand.

The same type of complexes were obtained with 2-aminopyridine ($PyNH_2$), which gave $RuCl_2(Me_2SO)_2(PyNH_2)$, and o-phenylenediamine

$C_6H_4(NH_2)_2$, which yielded $RuCl_2(Me_2SO)_2[C_6H_4(NH_2)_2]$. In these complexes the Me_2SO ligands were S-bonded as expected. In the ^1H n.m.r. spectrum of the o-phenylenediamine complex, there was a broad (ca. 30 Hz) resonance at τ 6.50. Integration showed that this peak contained both the $-NH_2$ and Me_2SO protons.

D. Complexes with phosphorus donor ligands

With triphenylphosphine in refluxing toluene, $RuCl_2(Me_2SO)_4$ gave an orange coloured solution from which a buff coloured solid was isolated. Elemental analysis indicated the stoichiometry $RuCl_2(Me_2SO)_2(PPh_3)$ and the molecular weight in chloroform at 25°C was consistent with this formulation. The ^1H n.m.r. spectrum also indicated that the complex had one triphenylphosphine molecule for every two Me_2SO molecules. This 5-coordinate complex is probably analogous to the well-known $RuCl_2(PPh_3)_3$ which is pseudo 6-coordinate with a hydrogen atom of one of the phenyl rings blocking the sixth position.[60] The alternative structure, with the metal atom bonded to the ortho carbon of one of the phenyl rings can be excluded, as this would make the metal ion ruthenium(III) and thus paramagnetic. The complex was in fact diamagnetic.

The S-O stretch in the spectrum was split, with bands at 1086 and 1115 cm^{-1}. The position of these bands confirmed sulphur as the donor atom. Attempts to determine the stereochemistry of the complex from the Ru-Cl stretches in the far i.r. spectrum were not successful, as that region of the spectrum was both complex and ill-resolved. A strong band at 420 cm^{-1} is tentatively assigned to a Ru-S stretch.

The ^1H n.m.r. spectrum was complex and provided the first known example of an upfield shift of Me_2SO protons. The spectrum is reproduced

in Fig. 3.1. It consisted of six singlets in the Me_2SO region plus a complex pattern due to the aromatic protons of the triphenylphosphine. Of the Me_2SO resonances, three, at τ 6.35, 6.82 and 6.98, were in the normal S-bonded region and one, at τ 7.28, was in the normal O-bonded region. However, two further resonances, at τ 7.57 and 7.73 showed a significant upfield shift when compared with free Me_2SO, which resonates at τ 7.40. There was no evidence in the i.r. spectrum for O-bonded Me_2SO so that the protons resonating at τ 7.28, 7.57 and 7.73 all showed anomalous chemical shifts. These shifts can be explained by assuming that one of the phenyl rings of the triphenylphosphine lies directly above one of the coordinated Me_2SO molecules. This causes shielding of the protons involved and hence the upfield shift observed. The number of isomers possible of the complex, containing Me_2SO molecules both shielded and unshielded by the triphenylphosphine, could easily give rise to the complex spectrum observed. The observations below also agree with this interpretation.

(i) The six lines observed were individual chemical shifts and not the result of coupling, as indicated by spectra measured at both 60 and 100 MHz.

(ii) The complexity was not due to additional species being present because of dissociation of Me_2SO, as addition of Me_2SO to the solution in the n.m.r. tube caused no change in the spectrum, apart from a peak at τ 7.40 due to free Me_2SO.

With triphenylphosphite, however, the white complex $RuCl_2[P(OPh)_3]_3(Me_2SO)$ was obtained with the Me_2SO bonding through the sulphur, as indicated by the ^1H n.m.r. spectrum. This had a singlet for the Me_2SO resonance at τ 6.85. The resonance was rather

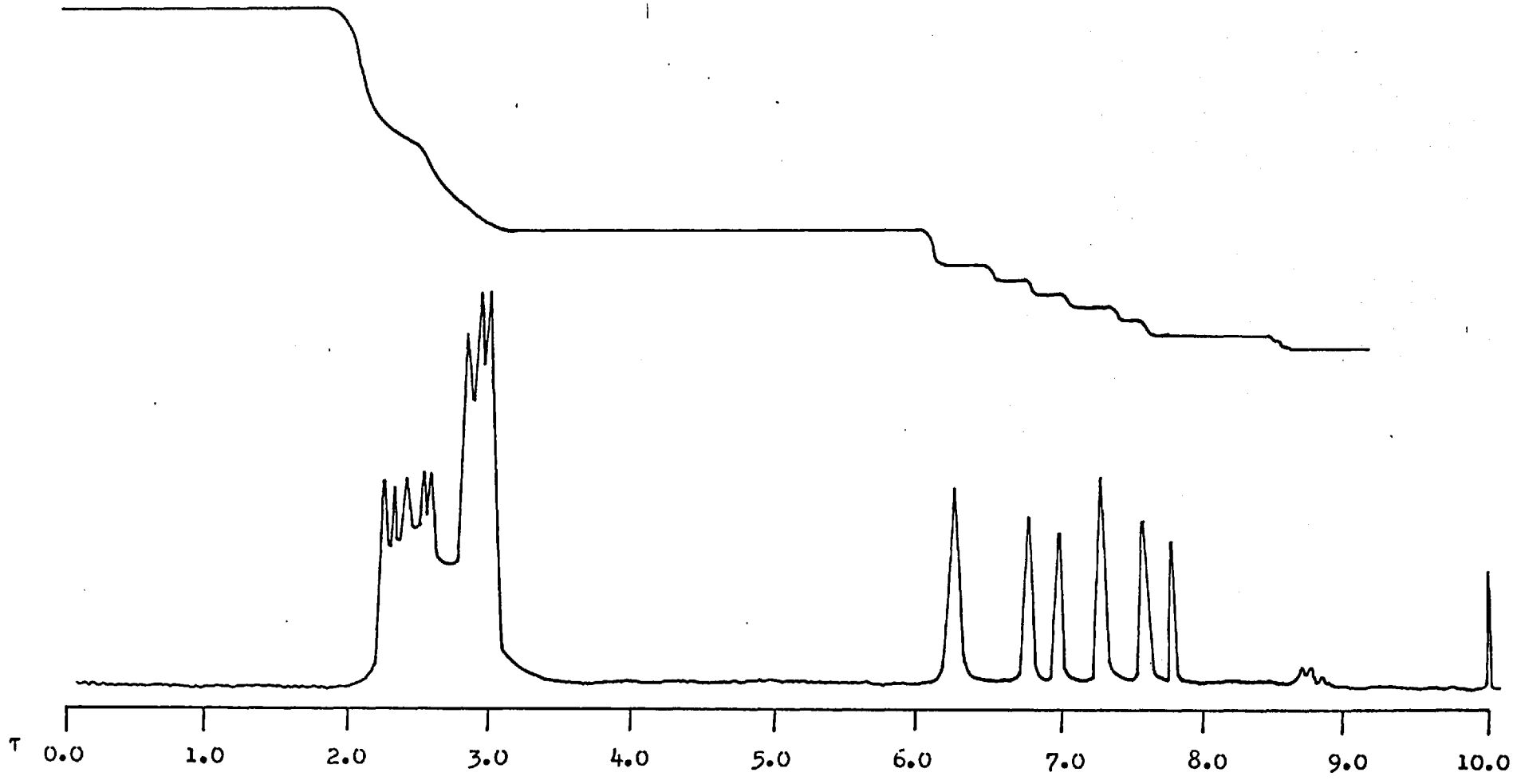


Fig. 3.1 ^{1}H n.m.r. spectrum of $RuCl_2(Me_2SO)_2(PPh_3)$

broad, suggesting that some exchange mechanism was operative, and this was further suggested by a molecular weight determination in $CHCl_3$ at 25°C, which gave a value of 581. $RuCl_2[P(OPh)_3]_3(Me_2SO)$ requires 1180. The complex was a non-conductor in acetonitrile excluding dossociation of the form

$$RuCl_2[P(OPh)_3]_3(Me_2SO) \rightleftharpoons \{RuCl[P(OPh)_3]_3\ Me_2SO\}^+ + Cl^-.$$

Dissociation of either Me_2SO or $P(OPh)_3$, if comparable with the ^1H n.m.r. time scale, would lead to broadening of the Me_2SO resonance, and it was not possible to differentiate between these two cases.

The i.r. spectrum was complex, because of the large number of bands associated with the triphenylphosphite and an assignment of ν(SO) was not possible.

The displacement of two Me_2SO molecules by one PPh_3 molecule reported earlier contrasts strongly with the displacement of three Me_2SO groups by three $P(OPh)_3$ molecules. A partial rationalisation of this can be given by noting the difference in the steric effects of the ligands as determined by their cone angles.[61] PPh_3 has a cone angle of 145 ± 2^o whereas $P(OPh)_3$ has the lesser cone angle of 121 ± 10^o. While electronic factors are also undoubtedly important, steric factors must control the degree of substitution to a large extent.

E. Complexes with oxygen donor ligands

Ruthenium(II) prefers 'soft' donor ligands,[2] and not surprisingly complexes with O-donor ligands were difficult to prepare. Salicylaldehyde and o-cresol did not react even under vigorous conditions and o-aminophenol, which has a nitrogen atom capable of coordination in addition to the oxygen, did not form a complex. $RuCl_2(Me_2SO)_4$ could

also be recovered unchanged after 24 hours refluxing in glacial acetic acid. However, using the terdentate ligand N-glycylglycine, $H_2NCH_2CONHCH_2CO_2H$, the complex N-glycylglycinato tris(dimethyl sulphoxide)ruthenium(II), $Ru(H_2NCH_2CONCH_2CO_2)(Me_2SO)_3$, could be isolated. The ligand coordinates through both nitrogen atoms and the oxygen of the carboxylato function. Coordination of the oxygen is favoured as after coordination of both nitrogens, the carboxylate oxygen is within convenient bonding distance of the metal atom. Coordination occurs in the 1,2 and 6 positions.

In the complex, the ionisation of the -CO-NH- moiety was indicated by the shift in the peptide carbonyl stretching frequency from 1665 cm^{-1} in the zwitterionic free ligand, $H_3\overset{+}{N}CH_2CONHCO_2^-$,[62] to 1613 cm^{-1} in the complex. The band was broad and somewhat asymmetric, probably because it also contained the carboxylate stretch which occurs at ca. 1598 cm^{-1}.[63]

F. Carbon monoxide; nitric oxide

With carbon monoxide, the white complex $RuCl_2(CO)_2(Me_2SO)_2$ was isolated. The best yields were obtained by refluxing the starting material in neat toluene with a stream of gas bubbling through the solution. The complex had ν (CO) at 2036 and 2082 cm^{-1} indicating *cis* carbonyl groups. Only one Ru-Cl stretch was observed, at 326 cm^{-1}; the chlorine atoms are thus *trans*. The Me_2SO ligands are therefore necessarily *cis* to one another and *trans* to the carbonyl groups (Fig. 3.2). This was confirmed by the ^1H n.m.r. spectrum which showed a singlet at τ 6.58, since the two Me_2SO molecules are equivalent. The chemical shift showed bonding to be via sulphur. In the i.r. spectrum ν (SO) was at 1126 cm^{-1}, which confirmed this.

On the addition of a little pyridine (ca. 10% by volume) to the solution in the n.m.r. tube the peak at τ 6.58 slowly decreased in intensity and a new peak appeared at τ 6.48, presumably due to the formation of $RuCl_2(CO)_2(Me_2SO)(py)$. A new peak also appeared at τ 7.45 due to free Me_2SO. After 6 hours the solution in the n.m.r. tube was essentially all $RuCl_2(CO)_2(Me_2SO)(py)$, an equal amount of free Me_2SO also having been formed. After this the signal at τ 6.48 began to decrease, due to formation of $RuCl_2(CO)_2(py)_2$; the peak at τ 7.45 continued to increase in intensity. After 24 hours the exchange was virtually complete.

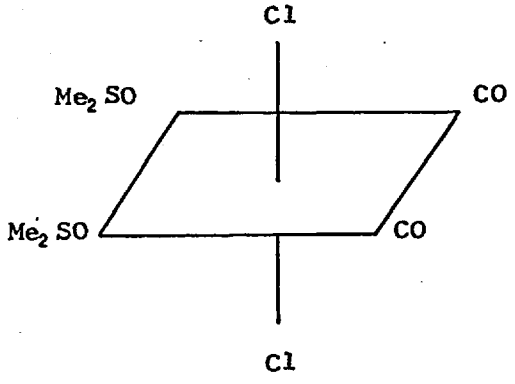


Fig. 3.2.

Using a solution of $RuCl_2(Me_2SO)_4$ in inert solvents and bubbling in NO, a low yield of the complex $RuCl_3(NO)(Me_2SO)_2$ was obtained. A virtually quantitative yield of the red complex could be achieved, however, by refluxing $RuCl_3.3H_2O$ in Me_2SO under an atmosphere of NO. The complex was insoluble in most common solvents but dissolved slightly in nitromethane and acetonitrile. It was a non-conductor in these

solvents at 10^{-3} M concentration. A ^1H n.m.r. spectrum could not be obtained because of solubility problems and in the i.r. ν(SO) could not be assigned as there were a number of strong bands in the S-O stretching region. The complex probably contains S-bonded Me_2SO by comparison with the carbonyl complex, both CO and NO being π-acid ligands.

The NO stretching frequency occurred at 1880 cm^{-1} as a strong, broad absorption. Ruthenium nitrosyls are very numerous and form an important part of ruthenium chemistry.[64] All the complexes are formally ruthenium(II) with the nitric oxide bonding as NO^+ and this Ru-NO unit, of charge 3+, is very stable and persists through many reactions. Attempts to reduce the Ru-NO grouping to a Ru $\equiv$ N terminal nitride using zinc and hydrochloric acid led to decomposition of the complex.[65]

G. Other reactions

Attempts to prepare a ruthenium hydride complex containing coordinated Me_2SO failed, as reaction of $RuCl_2(Me_2SO)_4$ with sodium borohydride or sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) both led by deposition of ruthenium metal. $RuCl_2(Me_2SO)_4$ was inert to both MeLi and MeMgI. This was not entirely unexpected as Ru-Cl bonds are known to be often inert to these reagents.[66] However the complex reacted readily with stannous chloride in hot ethanol to give the trichlorostannyl complex $Ru(SnCl_3)_2(Me_2SO)_4$.

H. Cationic species derived from $RuCl_2(Me_2SO)_4$

The simple aquo cation $Ru(H_2O)_6^{2+}$ is known, and can be prepared by electrolytic reduction of $RuCl_3 \cdot 3H_2O$ from which much Cl has been removed by $AgBF_4$; ion exchange then gives a solution containing pink $Ru(H_2O)_6^{2+}$. Interaction of $RuCl_2(Me_2SO)_4$ with silver ions in aqueous solution led to slow precipitation of AgCl; in 36 hours ca. 85% of

the chloride could be removed as silver chloride. In addition the conductivity of the complex increased over a period of 36 hours in aqueous solution to the value required for a 2:1 electrolyte (Λ = 161 mho cm^2 mol^{-1}; 10^{-3}M).

These observations prompted attempts to isolate cations of ruthenium(II) using $AgClO_4$ or $AgBF_4$ as a chloride scavenger. Using $AgClO_4$ in ethanol, complete chloride removal can be achieved in ca. 60 hours, when a solution green by reflected light and red by transmitted light can be obtained.

Refluxing the solution seemed to hasten the chloride abstraction process, but since it was difficult to monitor the faster reaction this method was not adopted. If, however, the reaction was halted immediately the $RuCl_2(Me_2SO)_4$ had dissolved and before much chloride had been removed, addition of pyridine led to the isolation of the previously unobtainable $RuCl_2(py)_2(Me_2SO)_2$ as an ethanol solvate. ν(SO) occurred at 1090 cm^{-1} indicating sulphur bonding of the Me_2SO.

Gravimetric studies showed that the amount of 'AgCl' precipitated in the reaction carried out in the cold was consistently 54% more than the theoretical. The i.r. spectrum of the 'AgCl' showed it contained coordinated Me_2SO, the ν(SO) value (1098 cm^{-1}) indicating sulphur bonding. Although gravimetric analysis indicated a stoichiometry of approximately $AgCl(Me_2SO)$, elemental analysis gave the non-stoichiometric composition of $AgCl(Me_2SO)_{0.8}$.

Silver chloride itself does not react with Me_2SO and silver chloride precipitated from aqueous solutions of silver nitrate and potassium chloride containing 20% Me_2SO showed no evidence for either lattice or coordinated Me_2SO.

Since the reaction of $RuCl_2(Me_2SO)_4$ with $AgClO_4$ in ethanolic solution yielded a precipitate approximating to $AgCl(Me_2SO)$, the cationic species in solution was presumably $Ru(Me_2SO)_5(EtOH)^{2+}_3$. Consistent with this, addition of excess Me_2SO to this solution led to the isolation of $Ru(Me_2SO)^{2+}_6(ClO^-_4)_2$. The complex was obtained as very pale green needles, which darkened in colour over a period of days. The i.r. spectrum indicated ionic (i.e. uncoordinated) perchlorate, with ν_3 of the ClO^-_4 at 1080 - 1120 cm^{-1} and only very slightly split; ν_4, which is weak in ionic perchlorates,[68] was obscured by methyl rocking modes of the coordinated Me_2SO.

The ^1H n.m.r. spectrum of the complex in $CDCl_3$ showed a singlet due to coordinated Me_2SO, S-bonded, at τ 6.62 together with a significant amount of free Me_2SO at τ 7.38. Integration showed the ratio of coordinated to free Me_2SO to be 2.7:1. In D_2O (t-BuOH reference) the resonance of the Me_2SO protons occurred at τ 6.88 and there was no significant concentration of free Me_2SO. The absence of any free Me_2SO probably implies fast exchange rather than absence of any dissociation. Using $(CD_3)_2CO$ as solvent, the spectrum was studied in the range 40°C to -90°C. At 40°C, the resonances due to coordinated and free Me_2SO were at τ 6.63 at τ 7.50 respectively and were sharp. At -60°C the resonances, at τ 6.56 and τ 7.36 had broadened, the free Me_2SO less so than the coordinated, until at -90°C the half width of the resonance due to coordinated Me_2SO was 12 Hz.

As both resonances, due to free and coordinated Me_2SO are seen and are sharp at 40°C, the slow exchange limit has been reached at this temperature in $(CD_3)_2CO$. The broadening is probably a result of steric hindrance on cooling, similar to that observed in the ^1H n.m.r. spectrum of $RuCl_2(Me_2SO)_4$ (see Chapter II).

Attempts to replace the Me_2SO in $Ru(Me_2SO)_6^{2+}(ClO_4^-)$ with water and obtain the cation $Ru(H_2O)_6^{2+}$ failed as the Me_2SO ligands were not sufficiently labile even under vigorous conditions.

The cationic species after chloride removal from $RuCl_2(Me_2SO)_4$ reacted with pyridine to give a green solution. It also reacted with 2,2'-bipyridyl and 1,10-phenanthroline to give red solutions. All these solutions gave precipitates with sodium tetraphenylborate indicating their cationic nature, but sensible analytical data could not be obtained. In addition, the preparations seemed extremely sensitive to slight changes in reaction conditions.

With sodium azide in ethanol, the cationic species gave a red precipitate of $Ru(N_3)_2(Me_2SO)_3$ virtually quantitatively. The azide asymmetric stretch occurred as a strong, broad band at 2020 cm^{-1}; ν (SO) was at 1085 cm^{-1} indicating sulphur bonding of the Me_2SO. A band at 430 cm^{-1} in the far i.r. can be assigned to either ν (Ru-N) or ν (Ru-S), probably the latter by comparison with known values of ν (Ru-S) in such complexes. The complex seemed to decompose, even under nitrogen, over a period of days; it could not be recrystallised without decomposition. Occasionally, the preparation outlined above led to a complex higher in nitrogen content than that required for $Ru(N_3)_2(Me_2SO)_3$ and this was always associated with a prominent shoulder on the band at 2020 cm^{-1}, ν_{as}(NNN). Reaction of this complex with dilute aqueous HCl gave a vigorous evolution of N_2, and the material remaining after evaporation of the solvent showed a sharp band in the i.r. at 2067 cm^{-1}. This band is in the correct region of the spectrum for coordinated N_2,[69] but the compound was not examined further as its preparation was not reproducible. The presence of coordinated dinitrogen is unlikely to stem from oxidation of the coordinated azide to dinitrogen

as this is thought to be associated with reduction of the metal ion.[69] Ruthenium(I), which would thus be formed in the reaction described above, is not a commonly occurring oxidation state of the metal.

The use of $AgBF_4$ as a chloride scavenger failed, as colloidal metal was produced in the chloride removal stage. There seems to be no straightforward explanation for the different behaviour of ClO_4^- and BF_4^- in this reaction.

I. Silver complexes containing coordinated Me_2SO

The only previously reported complex of silver(I) containing coordinated Me_2SO is $AgBF_4(Me_2SO)$ but no spectroscopic data were given for this compound. The analogous complex with $AgClO_4$ was prepared by precipitation with ether from an ethanolic solution of $AgClO_4$ containing excess Me_2SO. The complex had stoichiometry $Ag(Me_2SO)_2ClO_4$ and showed bands in the i.r. consistent with ionic perchlorate. ν_3 was only slightly split and was at 1055 - 1115 cm^{-1}; ν_4 appeared as a rather weak band at 928 cm^{-1}. In both $AgBF_4(Me_2SO)$ and $Ag(Me_2SO)_2ClO_4$ the silver is thus sp hybridised and the complexes presumably have linear structures. Attempts to obtain tris- and tetrakis Me_2SO complexes by increasing the Me_2SO concentration in the reaction still led to the linear species being isolated.

The ^1H n.m.r. spectrum of $Ag(Me_2SO)_2ClO_4$ in $CDCl_3$ showed a singlet due to the Me_2SO protons at τ 7.34. Although slightly downfield from free Me_2SO it is upfield from the normal τ values of O-bonded Me_2SO. This may imply oxygen bonding of the Me_2SO but with fast exchange with free Me_2SO. Assignment of ν (SO) in the i.r. was not possible as the ClO_4^- bands obscured the ν (SO) region.

J. Catalytic activity of $RuCl_2(Me_2SO)_4$

Me_2SO complexes of the platinum metals, notably rhodium and iridium, have been reported to catalyse the conversion of aromatic nitro compounds to isocyanates:

$$RNO_2 \xrightarrow[CO]{\text{catalyst}} RNCO.^{71}$$

No data on the catalytic activity of any ruthenium complex was given and the activity of $RuCl_2(Me_2SO)_4$ as a catalyst for the carbonylation of nitrobenzene to phenylisocyanate was investigated. $RuCl_2(Me_2SO)_4$, 3% by weight of the nitrobenzene used, was suspended in a mixture of nitrobenzene and 1,2-dichlorobenzene. The latter acted as an inert solvent for the reaction. The mixture was pressurised with 150 atmospheres of CO at room temperature, the temperature was raised to 180°C and the mixture shaken for 24 hours. The maximum pressure attained was 225 atmos. On cooling (final pressure 145 atmos.) the liquid was examined by g.l.c. for phenylisocyanate. None was detected, neither was the $RuCl_2(Me_2SO)_4$ recovered, having been reduced mostly to metal.

Presumably the inactivity of ruthenium(II) in this reaction is due to its inability to undergo oxidative addition reactions. All the platinum metals which gave significant yields of aryl isocyanate are those which are capable of undergoing oxidative addition reactions.

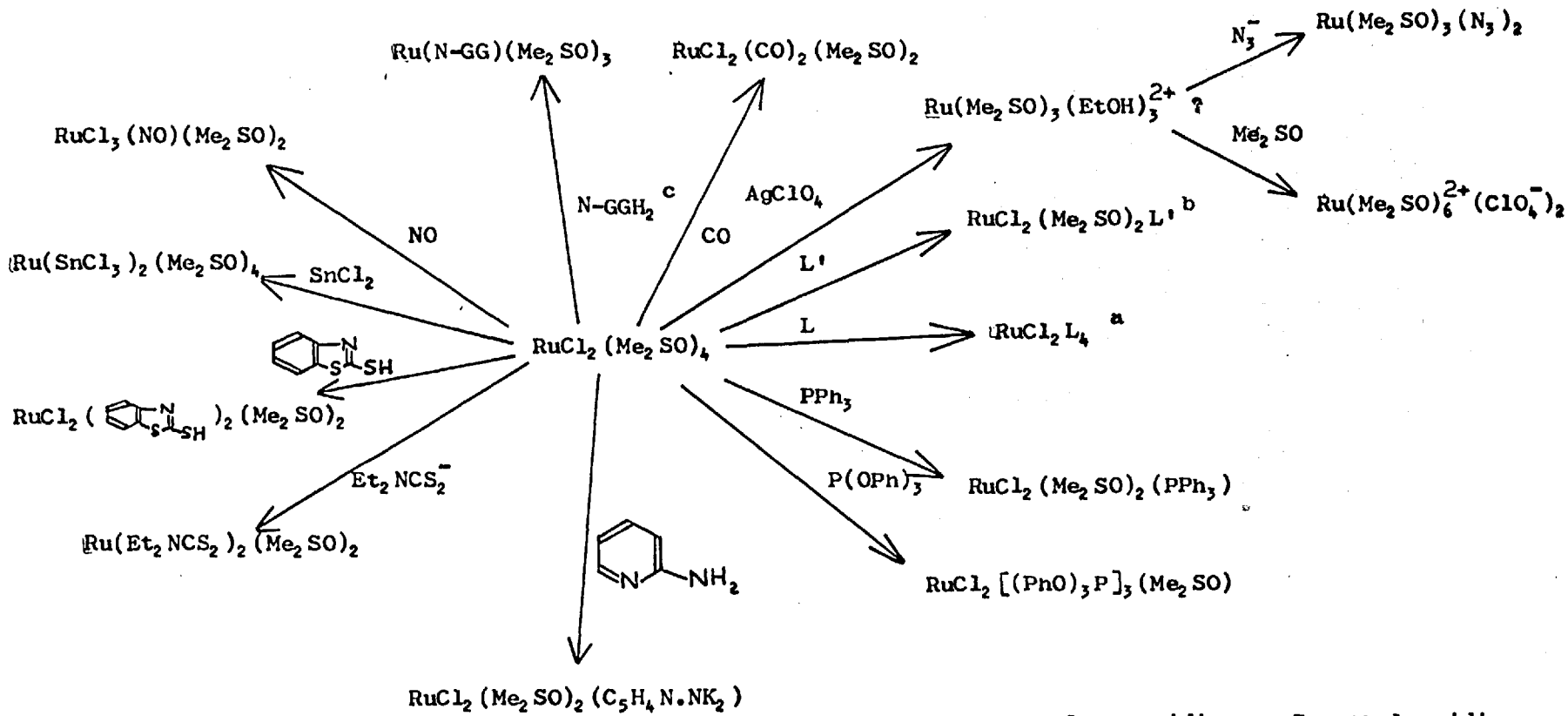


Fig. 3.3 Reactions of $RuCl_2(Me_2SO)_4$

a L = pyridine or 3-methylpyridine

b L' = 1,10-phenanthroline or 2,2'-bipyridyl

c $N\text{-}GGH_2$ = N-Glycyl glycine

CHAPTER IV

COMPLEXES OF PYRIDINE-2-THIOL WITH SOME TRANSITION METALS

A. Introduction

Although metal complexes of many ambidentate ligands have been studied (see Chapter I), little work has been done with the simple ligand pyridine-2-thiol. The first well-defined metal complex of this ligand to be prepared was $Ru(PyS)_2(PPh_3)_2$, which contained chelating pyridine-2-thiolato groups.[55] This structure was confirmed by X-ray diffraction.[72] Similar complexes of iridium, $IrH(PyS)_2(PPh_3)$,[73] and rhodium, $[Rh(PyS)_2(PPh_3)_2]^+BF_4^-$ [74] have been prepared recently.

Using this ligand, a representative number of transition metal complexes were investigated using conventional i.r., far i.r. and electronic spectroscopy, and magnetic susceptibility measurements.

As pyridine-2-thiol exists almost entirely as the tautomer[75] (Fig.4.1), it provides a simple model for the sulphur and N(1) donor atoms in thiolated nucleosides such as 6-thioguanosine (Fig. 4.2). A brief note has recently appeared,[76] where, using 6-mercaptopurine blocked at the 9- position by a benzyl substituent to simulate a riboside, a palladium complex containing coordinated 6-thioguanosine was prepared. The bonding was shown to be through the sulphur and N(7) donor atoms.

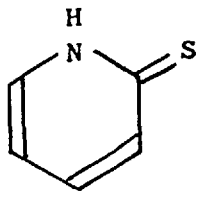


Fig. 4.1

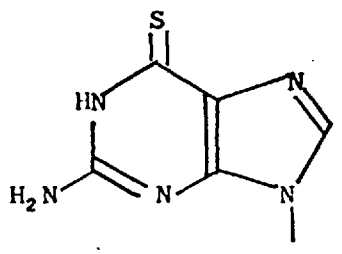


Fig. 4.2

As this work was being completed, the reactions of pyridine-2-thiol with some metal ions was described,[77] although there was only a little overlap with the studies described below. This overlap is noted in the sections on cobalt(II) and nickel(II).

The criteria by which the identity of the donor atom was determined are described in detail in the text. Data obtained from conventional i.r., far i.r. and electronic spectroscopy are collected in Tables 4.2 to 4.4 respectively. Magnetic susceptibility data are collected in Table 4.5. Analytical data for the complexes characterised are presented in Table 5.2 in the experimental chapter.

B. Iron(II)

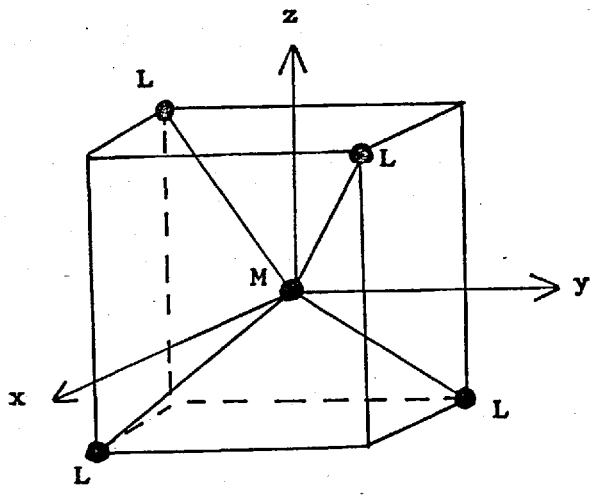
Iron(II) halides reacted readily with pyridine-2-thiol in anhydrous media (usually a 2,2-dimethoxy propane-ethanol mixture) to yield complexes of stoicniometry $FeX_2(PySH)_2$ (X = Cl, Br). The complexes were paramagnetic with values of μ_{eff} of 5.03 B.M. (X = Cl) and 4.92 B.M. (X = Br) at room temperature. These values are consistent with tetrahedral coordination although distortion in octahedral iron(II) complexes can lower the magnetic moment sufficiently to cause some doubt as to the stereochemistry if assignment is made on this basis alone.[79]

The electronic spectra exhibited broad, split bands at 4.90 and 5.62 kK (for both X = Cl and X = Br) which can be assigned to the $^5T_2 \leftarrow {}^5E$ transition of a tetrahedral iron(II) species. Octahedral iron(II) would also be expected to show a split band, corresponding to the transition $^5E_g \leftarrow {}^5T_{2g}$, but this would occur at higher energy, ca. 8 - 10 kK. A similar transition to the ones observed occurs at 4.65 and 5.78 kK in the $[Fe(NCS)_4]^=$ anion[80].

Further information as to the bonding and stereochemistry of the $FeCl_2(PySH)_2$ complex was obtained by recording the Mössbauer spectrum over a temperature range, from 4.2°K to 300°K.

At 77°K, the Mössbauer spectrum was a doublet, of isomer shift 0.87 mm sec.$^{-1}$ and quadrupole splitting 3.48 mm sec.$^{-1}$, relative to metallic iron. These values are consistent with a tetrahedral iron(II) complex containing sulphur donor ligands.[81] In addition, there was a small, somewhat broad peak, with an isomer shift of 0.29 mm sec.$^{-1}$. On raising the temperature to 300°K this split into a well-resolved doublet of isomer shift 0.39 mm sec.$^{-1}$ and quadrupole splitting 0.51 mm sec.$^{-1}$. On re-cooling to 77°K a spectrum identical with the original was obtained and this remained essentially unchanged down to 4.2°K. The spectrum recorded at 300°K was unchanged after allowing the complex to stand in air for a week, and the additional doublet is therefore more likely to be due to some phase change caused by the initial cooling to 77°K rather than the presence of some iron(III) oxidation product. In the spectrum at 77°K and 4.2°K there was a very weak magnetically split component, probably due to an impurity.

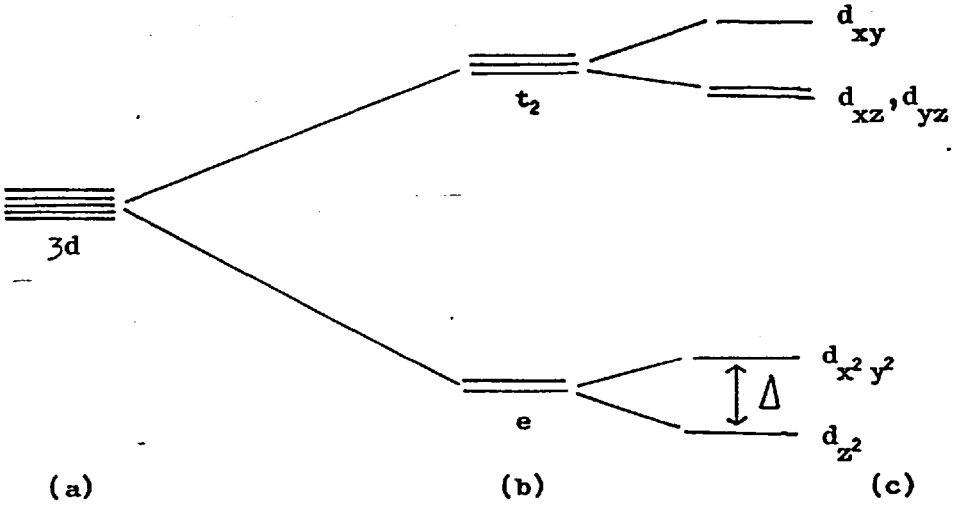
Because of the different bonding abilities and size difference of chlorine and pyridine-2-thiol, the complex is undoubtedly distorted. The raising of orbital degeneracy by a tetragonal distortion equivalent to a compression along the z axis of a tetrahedral complex is shown in Fig. 4.3. Using the temperature dependence of the quadrupole splitting, the degree of distortion, Δ, of the e levels was obtained in a manner similar to that for $FeCl_4^{2-}$.[82,83] Values for the quadrupole splitting at 300 and 77°K gave a value for Δ of 735 cm^{-1}. This large distortion is comparable with that found in thioacetamide and thiourea complexes of tetrahedral iron(II).[81]



Axes of tetrahedron

M metal ion

L ligands (not necessarily identical)



(a) Free ion, surrounded by a spherically symmetric charge of total quantity 4e

(b) Tetrahedral field

(c) Tetragonal distortion equivalent to a compression along the z axis

Fig. 4.3. Energy Level diagram for a Set of d Orbitals

The i.r. spectrum (4000 - 600 cm^{-1}) gave little information about the bonding, as the various ring modes of the ligand which have previously been used as diagnostic of the coordinating atom[37,38] proved difficult to assign with any certainty. However, the presence of an N-H stretch in both chloride and bromide suggested sulphur coordination, with the ligand in the thione form. In addition, ν (C=S) decreased slightly in both complexes when compared with the free ligand, consistent with sulphur coordination (Table 4.2). This criterion of determining the donor atom has been criticised however on the basis that the shifts observed are too small to be definitive.[36]

In the far i.r. region, ligand vibrations could be easily identified by their lack of sensitivity toward change of halogen, and the bands at 442 cm^{-1}, 358 cm^{-1} (X = Cl) and 437 cm^{-1}, 356 cm^{-1} (X = Br) are assigned to ligand modes, or modes of predominantly ligand character. Two M-X stretching bands were observed, consistent with a tetrahedral MX_2L_2 structure, and a band at 223 cm^{-1} (X = Cl) is in the region expected for an Fe-S stretching mode.[84] This stretch was obscured by ν (Fe-Br) in the bromo complex.

The compounds decomposed slowly over a period of several months even under dry, oxygen-free conditions. They were immediately solvolysed by water with concomitant precipitation of the free ligand and were insoluble in non-polar solvents such as benzene and light petroleum (b.p. 60 - 80°C). The complexes dissolved in solvents of high coordinating ability such as dimethyl sulphoxide, where there was evidence for some dissociation (Λ = ca. 50 mho $mol.^{-1}$ cm^2, 10^{-3}M).

No complexes of stoichiometry $FeX_2(PySH)_4$ could be obtained even using ligand to metal ratios > 6:1. The non-existence of the 4:1 species

when compared with the well-known $FeX_2(py)_4$ [85] is probably due to the size difference of the ligands concerned, rather than to electronic factors.

C. Cobalt(II)

The complexes CoX_2L_2 (X = Cl, Br, I) were prepared from ethanolic solutions of the ligand and the appropriate metal halide. No dehydrating agent was necessary and there were no differences in the spectral characteristics of the complexes obtained if anhydrous instead of hydrated salts were used.

The magnetic moments of the complexes were in the range 4.5 - 4.9 B.M., typical of tetrahedral cobalt(II),[86] and the electronic spectra obtained were also in agreement with this. From the electronic spectra, values of Dq, B and β were calculated by an established procedure[87] and these are presented in Table 4.1. These values are in the range expected for a CoX_2L_2 system where L is a ligand bonding through sulphur.[77,88] The low value of B (and hence of β) reflects the high covalency of the metal-ligand bond.

In the far i.r. spectrum, both Co-X stretches expected for a tetrahedral molecule were observed for X = Cl, I; when X = Br however, only one broad band was observed, probably because of overlap of the Co-S stretch with the Co-Br stretch, both of which would be expected to occur in the same region.[41,42]

The complexes were immediately solvolysed by water and were insoluble in all common solvents. These complexes have also been prepared recently by Lever and Kennedy,[77] who reached essentially the same conclusions as those set out above.

Recently, cobalt(II) complexes of the ligand 2-imino-4-oxo-1,3-thiazolidine (Fig. 4.4) have been prepared and the spectral data interpreted on the basis of nitrogen bonding.[89] It is of interest in that this work exemplifies the dangers, outlined in Chapter I, of determining the donor atom by using shifts in the i.r. spectra of the so-called 'diagnostic' ligand modes. No attempt was made to eliminate hydrogen bonding effects and the far i.r. region was not extended sufficiently (to low energy) to examine for the possibility of sulphur bonding of the ligand. Analysis of the electronic spectra obtained shows that the values of Dq in these complexes are more consistent with sulphur than with nitrogen bonding.

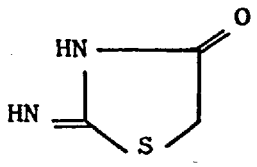


Fig. 4.4

D. Nickel(II)

Using a 2:1 ratio of ligand to metal halide the complexes $NiX_2(PySH)_2$ (X = Cl, Br, I) were isolated, whereas a 4:1 or 6:1 ratio gave the complexes $NiX_2(PySH)_4$. Intermediate ratios such as 2.5:1 or 3:1 inevitably led to mixtures of products and it is probable that the yellow and green mixtures reported by Kennedy and Lever[77] in some of their recent preparations of these complexes are due to formation of compounds intermediate in composition between $NiX_2(PySH)_2$ and $NiX_2(PySH)_4$.

The series of complexes of stoichiometry $NiX_2(PySH)_2$ were green (X = Cl, Br) or brown (X = I). The magnetic susceptibilities of the compounds were between 3.30 and 3.45 B.M. which suggested tetrahedral coordination. Tetrahedral nickel(II) complexes usually have moments in the range 3.60 - 4.0 B.M. if undistorted, but departures from regular tetrahedral symmetry or electron delocalisation can lower this somewhat, so that the effective range for tetrahedral nickel(II) complexes becomes 3.2 to 4.0 B.M.[78] By comparison with the distortion observed in $FeCl_2(PySH)_2$, it is likely that these nickel(II) complexes are also somewhat distorted.

The electronic spectra were however much more in accord with octahedral coordination of the nickel, and the three spin-allowed transitions expected could be assigned for all complexes. As these were reflectance spectra it was unfortunately not possible to obtain ϵ values. It must also be noted that oscillator strengths are not necessarily related to band intensities in reflectance spectra, especially over a wavelength range.

In the far i.r. region, terminal M-X stretches were observed for all complexes, which meant that if the complexes were octahedral, then the pyridine-2-thiol must necessarily be bridging. In such a structure the halogen atoms would be trans and thus only one M-X stretch would be expected. Two bands were observed for both X = Cl, I, consistent with a tetrahedral, monomeric structure. The single band observed for $NiBr_2(PySH)_2$ was probably broadened by the proximity of the Ni-S stretch. It is possible that the complexes were octahedral but sufficiently distorted to allow two M-X stretching modes to become i.r. active.

The electronic spectra probably gave the most unambiguous indication of the stereochemistry and in the light of this, the parameters Dq, B and β quoted in Table 4.1 are calculated on the basis of octahedral coordination.

Complex	Dq (cm^{-1})	B (cm^{-1})	β
$CoCl_2(PySH)_2$	308	770	0.80
$CoBr_2(PySH)_2$	398	651	0.67
$CoI_2(PySH)_2$	355	633	0.65
$NiCl_2(PySH)_2$	930	609	0.58
$NiBr_2(PySH)_2$	877	612	0.58
$NiI_2(PySH)_2$	794	677	0.64
$NiCl_2(PySH)_4$	833	697	0.66

Table 4.1 Ligand field parameters for cobalt and nickel complexes.

Using a 4:1 ratio of ligand to metal, complexes of stoichiometry $NiX_2(PySH)_4$ (X = Cl, Br, I) were obtained. With X = Cl, the complex was mustard-yellow and had μ_{eff} = 3.16 B.M. (299.5°K) typical of octahedral nickel(II). The electronic spectrum was consistent with this, showing the three spin-allowed bands expected at 8.33 kK ($^3T_{2g} \leftarrow {}^3A_{2g}$), 13.70 kK ($^3T_{1g} \leftarrow {}^3A_{2g}$) and 21.74 kK ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$). A band at 10.31 kK is tentatively assigned to the spin-disallowed $^1E_g \leftarrow {}^3A_{2g}$ transition which is frequently observed. Dq and B values for this complex, which is necessarily octahedral, agree well with those calculated for the $NiX_2(PySH)_2$ series of complexes, which is further evidence that these 2:1 complexes are in fact octahedral. Only a single Ni-Cl stretch was observed in the far i.r. spectrum of $NiCl_2(PySH)_4$, at 242 cm^{-1}, indicating a <u>trans</u> octahedral structure for the complex. The complexes $Ni(PySH)_4X_2$ (X = Br, I) were red-brown and black-green respectively and showed very different magnetic and spectral properties to $NiCl_2(PySH)_4$. Both complexes

were diamagnetic, indicating a spin-singlet ground term characteristic of square nickel(II). The complexes were soluble in solvents such as pyridine or dimethylsulphoxide and had conductivities in these solvents at 10^{-3}M concentration of ca. 60 - 70 mho mol.$^{-1}$ cm^{-2}, apart from X = Br in pyridine, which gave a conductivity of < 10 mho mol.$^{-1}$ cm^{-2}. For the species which gave conducting solutions the cations $[Ni(PySH)_4(py)_2]^{2+}$ and $[Ni(PySH)_4Me_2SO]^{2+}$ were presumably formed.

The electronic spectra were also consistent with square nickel(II), with the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition at 20.00 kK (X = Br) and 20.83 kK (X = I). The lower energy band commonly seen in NiS_4^{2+} systems[90] was not observed, as the band at 8.84 kK in both complexes was too low in energy to be assigned to this transition. A sharp band at 6.04 kK (X = Br) and 6.02 kK (X = I) was almost certainly vibrational in origin, probably an overtone of one of the C-H stretches of the ligand at ca. 3.0 kK.

Consistent with the above, the complexes showed no bands in the region 450 - 200 cm^{-1} in their far i.r. spectra which could be attributed to metal-halogen stretches.

Nickel was the only metal investigated which gave both 2:1 and 4:1 complexes. A rationalisation of this is possible in terms of ligand field stabilisation energies (L.F.S.E.). Nickel(II) has the highest negative ΔH for the transformation from tetrahedral to octahedral stereochemistry, if this is calculated in terms of L.F.S.E.[91] Since the other parameters which influence stereochemistry probably change uniformly from metal to metal, it is likely that L.F.S.E. plays an important role in determining the final stereochemistry attained. Consistent with this explanation was the failure to prepare any manganese(II) complexes with pyridine-2-thiol, despite using vigorous conditions. Manganese(II) possesses no L.F.S.E. and this was probably the dominant reason for its lack of reactivity.

E. Copper

Copper(I) chloride and bromide reacted readily as ethanolic suspensions with pyridine-2-thiol to give complexes of stoichiometry $CuCl(PySH)_3$ and $CuBr(PySH)_2$ respectively. CuI did not react directly with pyridine-2-thiol but $CuI(PySH)_2$ was prepared by the addition of a methanolic solution of the ligand, containing excess potassium iodide, to a solution of copper(II) sulphate in methanol, in the presence of sulphur dioxide.

As expected, the complexes (d^{10}) were diamagnetic and showed no absorptions in their electronic spectra apart from high-energy charge transfer bands. Because of these bands the complexes were all bright orange in colour.

The compounds are doubtless tetrahedral.[92] The chloro complex had ν(Cu-Cl) at 251 cm^{-1} but the bromo complex showed no absorption above 200 cm^{-1} which could be attributed to ν(Cu-Br). This implies that halogen bridges maintain the tetrahedral coordination of the copper ion in this case; for bridging bromide, ν(Cu-Br) would be expected to occur below 200 cm^{-1}. In the iodo complex, only two bands were noted in the region 200 - 20 cm^{-1}, at 93 and 56 cm^{-1}. These bands, which are of very low energy, are probably not due to simple metal-iodine modes, unless the halogen atoms are bridging more than two metal ions. Triply bridging iodide has been discovered in the complexes $Cu_4I_4L_4$ (L = Ph_3P, Ph_3As), but the metal-halogen stretch was not detected in the far i.r. region studied.[93]

Copper(II) chloride and bromide reacted with pyridine-2-thiol in ethanol to give insoluble yellow complexes which were diamagnetic and which had stoichiometry CuCl(PySH) and $CuBr_2(PySH)_2$. Pyridine-2-thiol could reduce copper(II) to copper(I) by being oxidised itself to the

disulphide and the chloride complex is probably a genuine copper(I) species. It is difficult to rationalise the bromide being diamagnetic with its formulation as a copper(II) complex and its structure is undoubtedly not as simple as its stoichiometry suggests.

A ligand similar to pyridine-2-thiol, 6-mercaptopurine (MP) has also been found to be strongly reducing, copper(II) salts being immediately reduced to copper(I).[94] The complex $Cu(MP)Cl_2$, reported by Weiss,[95] is very possibly a complex of copper(I) with the protonated ligand, $Cu^{(I)}(MPH^+)Cl_2$, as the preparation was carried out in an extremely acid medium. This exemplifies the danger of suggesting structures for such complexes merely from the stoichiometry. As the complexes prepared in this section were extremely insoluble, spectroscopic data were all that could be obtained, and thus any speculation as to the nature of these compounds has been kept to a minimum.

Copper(II) nitrate, sulphate, acetate and perchlorate also gave insoluble yellow species. The sulphate and nitrate complexes had stoichiometry $CuSO_4(PySH)_{1.5}$ and $Cu(NO_3)_2(PySH)_{1.5}$ respectively and their i.r. spectra indicated coordination of the anions. The sulphate complex was slightly paramagnetic with $\mu_{eff} = 0.45$ (296.5°K) and it possessed a rather featureless e.s.r. spectrum consistent with a polymeric structure ($g = 2.013$). Whether these observations implied a copper(II) species with considerable metal-metal interaction or simply incomplete reduction to copper(I) with protonated ligand present was not clear; the extreme insolubility of the complex rendered it somewhat intractable.

Copper(II) acetate gave a yellow complex of stoichiometry Cu(PyS) and the absence of any acetate in the complex was confirmed by the i.r. spectrum which showed bands due only to pyridine-2-thiol. No N-H stretch

was observed, consistent with ionised pyridine-2-thiolato groups being present rather than unionised pyridine-2-thiol. A similar reaction between pyridine-2-thiol and mercuric acetate to give bis(pyridine-2-thiolato)mercury(II), $Hg(PyS)_2$, has been reported recently.[77] The copper complex was insoluble in all common solvents and was presumably polymeric with sulphur bridging. Consistent with complete reduction having been achieved, the complex was diamagnetic, gave no e.s.r. spectrum, and had no bands in the electronic spectrum apart from those at high energy due to charge transfer.

Thiourea also reduces copper(II) to copper(I) but copper(II) complexes containing coordinated thiourea could be isolated by using copper(II) perchlorate stabilised by coordination to ligands such as 1,10-phenanthroline or 2,2'-bipyridyl.[95] The reactions of both $Cu(phen)_2(ClO_4)_2$ and $Cu(bipy)_2(ClO_4)_2$ with pyridine-2-thiol were investigated. The bipyridyl complex was inert to reaction with the ligand but $Cu(phen)_2(ClO_4)_2$ yielded $Cu(phen)_2(PySH)(ClO_4)_2$. The green-brown complex possessed an i.r. spectrum consistent with this formulation, showing bands due to both pyridine-2-thiol and 1,10-phenanthroline. The far i.r. region was complex and the large number of bands observed precluded any assignment of metal-ligand modes. The compound had a normal magnetic moment for copper(II) of 1.88 B.M. (293.5°K) and possessed an electronic spectrum with a single, very broad band centred at 11.43 kK.

F. Silver(I)

Using silver tetrafluoroborate in ethanol, reaction with pyridine-2-thiol gave $Ag(PySH)_4BF_4$. As expected, ν_3 of the BF_4^- anion was unsplit showing that it maintained its T_d symmetry in the solid state. The complex was diamagnetic and possessed no electronic spectrum below 20.00 kK.

In the far i.r. region, two strong bands were observed at 252 and 243 cm^{-1} and these could possibly be assigned to Ag-S stretches. However, the paucity of data on M-S stretches in general and on silver in particular makes it impossible to be definitive.

With $AgClO_4$, the complex $Ag(PySH)_2ClO_4$ was obtained. The i.r. spectrum indicated uncoordinated perchlorate with ν_3 as a broad absorption, essentially unsplit, from 1028 - 1130 cm^{-1}. The far i.r. spectrum was somewhat complex, but a strong band at 278 cm^{-1} could possibly be due to some metal-ligand mode. Attempts to prepare $Ag(PySH)_4ClO_4$, analogous to the tetrafluoroborate complex described above were unsuccessful.

G. Palladium(II) and Rhodium(II)

The interaction of $PdCl_2$ with the ligand in refluxing ethanol led to the complex $Pd(PySH)_4Cl_2.EtOH$. The orange complex dissolved in water and in methanol in which it gave a conducting solution. The conductivity (Λ = 120 mho $mol.^{-1}$ cm^{-2}; 10^{-3}M) was much lower than that expected for a 2:1 electrolyte however, the range in methanol being generally 160 - 220 mho $mol.^{-1}$ cm^{-2}.[97] Analogous behaviour has been noted in the similar complex $Pt(PySH)_4Cl_2$.[77]

The i.r. spectrum showed the usual bands associated with pyridine-2-thiol, the band containing the most ν (C=S) character being higher in energy than in the free ligand, suggesting sulphur coordination. Consistent with this, a strong band was observed at 328 cm^{-1}, which can be assigned to ν (Pd-S). No metal halogen stretches were observed, indicating that the complex contained the $Pd(PySH)_4^{2+}$ cation.

With the trimeric acetate, $[Pd(OAc)_2]_3$, in boiling benzene, pyridine-2-thiol gave the inner complex $Pd(PyS)_2.PySH$. The complex was red, due

to charge-transfer absorption and was soluble in benzene, toluene, chloroform and dichlorometnane. No acetate bands were detected in the i.r. spectrum, which showed bands typical of coordinated pyridine-2-thiol; the metal-ligand stretches can be assigned to strong bands at 333 and 362 cm^{-1} in the far i.r. spectrum, although these are probably coupled with the internal ligand vibrations which occur in the same region. The molecular weight in benzene was 258 instead of the required 437, indicating extensive dissociation, probably of the unionised pyridine-2-thiol molecule.

Although the complex was very soluble in chloroform, no ^1H n.m.r. spectrum could be obtained in this solvent at room temperature, although the uneven base line in the aromatic proton region suggested that the resonance was perhaps very broad. On cooling to -60°C, some resolution in this region was obtained, the resonance extending from τ2.50 to τ3.25. The ^1H n.m.r. behaviour of a similar complex, $Pt(S_2CNEt_2)_2(PMePh_2)$, suggested equilibrium between planar and 5-coordinate species[98] and the inability to observe the ^{119}Sn(n.m.r.) resonance in $Pt(SnCl_3)_5^{3-}$ has been attributed to a rapid exchange reaction.[99]

With the dimeric $Rh_2(OAc)_4$, no displacement of coordinated acetate was achieved and the adduct $Rh_2(OAc)_4.2PySH$ was obtained. The complex was red-brown and had an i.r. spectrum similar to that of $Rh_2(OAc)_4$ with additional bands due to the coordinated pyridine-2-thiol. Adducts of $Rh_2(OAc)_4$ with many ligands have been prepared and it has been suggested that the colour of the adduct can be used to distinguish between sulphur and oxygen donor atoms,[100] as oxygen donor ligands produced green adducts and sulphur donor ligands orange or red adducts. There is more range in the colour of adducts with nitrogen donor ligands so assignment of the donor atom in $Rh_2(OAc)_4.2PySH$ from the colour of the

adduct is not feasible. However, the presence of a strong band in the far i.r. spectrum at 375 cm^{-1}, the correct region for ν (Rh-S), strongly suggested sulphur bonding of the ligand.

Attempts to prepare a pyridine-2-thiolato complex from $Rh_2(OAc)_4$ by displacement of the bridging acetate groups were unsuccessful because the 'bite' of the ligand as an anion is insufficient to bridge two metal atoms, which it would be required to do in this case, as $Rh_2(OAc)_4$ contains a rhodium-rhodium bond.

Complex	ν (N-H)	ν (C=S)	Ring mode [a]
$FeCl_2(PySH)_2$	3162	1126	990
$FeBr_2(PySH)_2$	3150	1118	985
$CoCl_2(PySH)_2$	3150	1125	996
$CoBr_2(PySH)_2$	3145	1120	988
$CoI_2(PySH)_2$	3140	1115	987
$NiCl_2(PySH)_2$	3160	1132	995
$NiBr_2(PySH)_2$	3150	1130	996
$NiI_2(PySH)_2$	3140	1119	988
$NiCl_2(PySH)_4$	3160	1132	986
$Ni(PySH)_4Br_2$	3068 (?)	1127, 1138	990
$Ni(PySH)_4I_2$	3130	1118	985
$CuCl(PySH)_3$	3130	1130	991
$CuBr(PySH)_2$	3140	1118, 1125	990
$CuI(PySH)_2$	[b]	[b]	985
$Cu(phen)_2(PySH)(ClO_4)_2$	3175	[c]	985
$Ag(PySH)_4BF_4$	3170	1123	985
$Ag(PySH)_2ClO_4$	[b]	[c]	994
$Pd(PySH)_4Cl_2 \cdot EtOH$	3090	1125	985
$Pd(PyS)_2(PySH)$	[b]	[b]	985
$Rh_2(OAc)_4 \cdot 2PySH$	3175	1120	988

[a] Ring 'breathing' mode; Thioamide I, II, III and IV bands not assigned.[37,38]

[b] Not observed

[c] Obscured

Table 4.2 Selected i.r. data for pyridine-2-thiol complexes (Nujol mulls, KBr plates, in cm^{-1}).

Complex	ν (M-X)	ν (M-S)	Others
$FeCl_2(PySH)_2$	311, 281 (m) [a]	223 (m)	
$FeBr_2(PySH)_2$	242, 226 (m)	[b]	
$CoCl_2(PySH)_2$	303, 287 (m)	220 (m)	264 (m)
$CoBr_2(PySH)_2$	230 (br, s) [a]	[b]	255 (vw) [a]
$CoI_2(PySH)_2$ [c]	210, 191 (s)	226 (s)	156, 90 (m)
$NiCl_2(PySH)_2$	298 (vs), 260 (s)	236 (m)	
$NiBr_2(PySH)_2$	233 (vs)	[b]	205, 211, 225 (w)
$NiI_2(PySH)_2$ [c]	193 (s), 168 (m)	218 (s)	281 (m), 144 (s)
$NiCl_2(PySH)_4$	242 (m)	218 (m)	287 (w)
$Ni(PySH)_4Br_2$	Not coordinated	[d]	286 (vw), 264 (w)
$Ni(PySH)_4I_2$	Not coordinated	218 (m)	272, 242 (w)
$CuCl(PySH)_3$	251 (m)	242 (m)	211, 205 (m)
$CuBr(PySH)_2$	[d]	242 (m)	219, 211 (w)
$CuI(PySH)_2$ [c]	[d]	243 (m)	206, 93, 56 (m)
$Cu(phen)_2(PySH)(ClO_4)_2$	-	243 (m)	297, 275, 206 (m)
$Ag(PySH)_4BF_4$	-	252, 243 (s)	
$Ag(PySH)_2ClO_4$	-	278 (s)	
$Pd(PySH)_4Cl_2.EtOH$	Not coordinated	328 (s)	
$Pd(PyS)_2(PySH)$	-	362, 333 (s)	255 (w)
$Rh_2(OAc)_4.2PySH$	-	340 (s)	219 (m)

[a] s, strong; m, medium; w, weak; br, broad; v, very.

[b] Obscured

[c] Measured down to 20 cm^{-1}

[d] Not observed

Table 4.3 Far i.r. data for pyridine-2-thiol complexes (450 - 200 cm^{-1} except where stated, polythene plates, vaseline mulls).

Compound	Band	Assignment
$FeCl_2(PySH)_2$	4.90, 5.62	$^5T_2 \leftarrow {}^5E$
$FeBr_2(PySH)_2$	4.90, 5.62	$^5T_2 \leftarrow {}^5E$
$CoCl_2(PySH)_2$	4.90, 5.88	$^4T_1(F) \leftarrow {}^4A_2$
	13.89, 15.62, 16.67	$^4T_1(P) \leftarrow {}^4A_2$
$CoBr_2(PySH)_2$	5.32 (?), 7.27, 7.94	$^4T_1(F) \leftarrow {}^4A_2$
	13.90, 15.87	$^4T_1(P) \leftarrow {}^4A_2$
$CoI_2(PySH)_2$	5.13, 5.99, 7.25	$^4T_1(F) \leftarrow {}^4A_2$
	12.82, 13.89, 15.38	$^4T_1(P) \leftarrow {}^4A_2$
	20.41, 22.73	Charge-Transfer
$NiCl_2(PySH)_2$	9.30	$^3T_{2g} \leftarrow {}^3A_{2g}$
	14.30	$^3T_{1g} \leftarrow {}^3A_{2g}$
	22.73	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
	15.62	$^1E_g \leftarrow {}^3A_{2g}$ (?)
$NiBr_2(PySH)_2$	8.77	$^3T_{2g} \leftarrow {}^3A_{2g}$
	14.29	$^3T_{1g} \leftarrow {}^3A_{2g}$
	21.20	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$NiI_2(PySH)_2$	5.40	
	7.94	$^3T_{2g} \leftarrow {}^3A_{2g}$
	12.58, 13.70	$^3T_{1g} \leftarrow {}^3A_{2g}$
	20.83	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$NiCl_2(PySH)_4$	8.33	$^3T_{2g} \leftarrow {}^3A_{2g}$
	13.70	$^3T_{1g} \leftarrow {}^3A_{2g}$
	21.74	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
$Ni(PySH)_4.Br_2$	8.84	
	20.00	$^1A_{2g} \leftarrow {}^1A_{1g}$
$Ni(PySH)_4I_2$	8.84	
	20.83	$^1A_{2g} \leftarrow {}^1A_{1g}$
$Cu(phen)_2(PySH)(ClO_4)_2$	11.43	

Table 4.4 Electronic Reflectance Spectra
(4 - 25 kK)

Complex	Xg (c.g.s. x 10^6)	X'_M [a] (c.g.s. x 10^6)	μ_{eff} [b] (B.M.)	T (^oK)
$FeCl_2(PySH)$	30.47	10815	5.03	296.0
$FeBr_2(PySH)_2$	22.55	10080	4.92	299.5
$CoCl_2(PySH)_2$	24.06	8648	4.52	295.5
$CoBr_2(PySH)_2$	21.45	9655	4.81	299.5
$CoI_2(PySH)_2$	17.28	9476	4.75	297.0
$NiCl_2(PySH)_2$	13.12	4794	3.37	295.0
$NiBr_2(PySH)_2$	10.21	4699	3.36	299.5
$NiI_2(PySH)_2$	8.80	4704	3.43	297.5
$NiCl_2(PySH)_4$	6.84	4239	3.16	294.5
$Cu(phen)_2(PySH)(ClO_4)_2$	1.52	1504	1.88	293.5

[a] Pascal's constants from ref. 101

[b] Reproducible to ca. $\pm$ 1%. Values uncorrected for any T.I.P.

Table 4.5 Magnetic Susceptibility Data

CHAPTER V

EXPERIMENTAL

A. General

Microanalyses by the Microanalytical Laboratory, Imperial College.

^{1}H n.m.r. spectra were measured on a Perkin-Elmer R12B spectrometer equipped with a Variable Temperature Probe Accessory at 60 MHz and a Perkin-Elmer R14 spectrometer at 100 MHz and 35°C.

I.r. spectra were taken on a Perkin-Elmer 257 spectrophotometer (4000 - 625 cm^{-1}), a Perkin-Elmer 457 spectrophotometer (4000 - 250 cm^{-1}), a Perkin-Elmer 325 spectrophotometer (4000 - 200 cm^{-1}) and on a Beckman FS 720 Fourier spectrophotometer (200 - 20 cm^{-1}).

Magnetic moments were measured on solid samples at room temperature using an improved version[102] of the Evans' modification[103] of the Gouy-Rankine balance. The balance was calibrated with cobalt mercury thiocyanate.

Diffuse reflectance spectra were measured in the region 4kK - 25 kK on a Cary 14R spectrophotometer using a Cary Model 1411 diffuse reflectance accessory.

Mössbauer spectra were measured at room, liquid nitrogen and liquid helium temperatures by the P.C.M.U. Mössbauer section at Harwell. The data were obtained with reference to an iron foil calibrant.

E.s.r. measurements were made at X-band using a Varian E9 spectrometer.

Melting points were measured on a Köfler hot-stage microscope and are uncorrected.

B. Chapters II and III

Dried, degassed solvents of reagent grade were used in all reactions, which were carried out under nitrogen, unless otherwise stated.

Dichlorotetrakis(dimethyl sulphoxide)ruthenium(II)

Ruthenium trichloride trihydrate (1 g) was refluxed in dimethyl sulphoxide (5 ml) for 5 min. The volume was reduced to half in vacuo when addition of acetone (20 ml) gave a yellow precipitate. This was filtered off, washed with acetone and ether, and vacuum dried. On standing, the filtrate deposited more of the complex. Recrystallisation from dimethyl sulphoxide by slow evaporation of a hot, concentrated solution yielded hexagonal plates (1.33 g, 72%; m.p. 193°C decomp.).

Trichlorotris(dimethyl sulphoxide)rhodium(III)

Rhodium trichloride trihydrate (1 g) was dissolved in cold dimethyl sulphoxide (8 ml) and the solution filtered. The solution was diluted with ethanol (8 ml) and the complex precipitated by the slow addition of ether (30 ml). The orange complex was filtered off, washed with ether and vacuum dried (1.34 g, 80%).

Bis(diethyl dithiocarbamato)bis(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.4 g) was suspended in toluene (50 ml) and sodium diethyl dithiocarbamate trihydrate (0.372 g) added. The suspension was refluxed for 30 min. to give a dark coloured solution. The solution was filtered and concentrated to ca. 10 ml. Addition of light petroleum (b.p. 80 - 100°C) followed to cooling to -40°C produced pale green needles which were recrystallised from acetone-ether (0.3 g, 75%).

Dichlorobis(dimethyl sulphoxide)bis(2-mercaptobenzthiazole)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.2 g) and 2-mercaptobenzthiazole (0.138 g) were refluxed in toluene (40 ml) for 40 min. The wine-red solution was reduced in volume to ca. 15 ml and cooled to -78°C. The orange-yellow precipitate which formed was filtered off, washed with cold ethanol

(2 x 10 ml) and cold ether (2 x 10 ml), and vacuum dried over silica gel. It was recrystallised from hot acetone-ether (0.12 g, 50%).

Dichlorotetrakis(pyridine)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.3 g) was refluxed in pyridine (10 ml) for ca. 30 min. Reduction of volume to ca. 40% followed by cooling to -40°C yielded the orange complex. It was washed with ethanol and dried over silica gel in vacuo (0.27 g, 90%).

Dichlorotetrakis(3-methylpyridine)ruthenium(II)

As for dichlorotetrakis(pyridine)ruthenium(II). The red-brown solution obtained after refluxing was stripped and the residue dissolved in chloroform. Addition of ether precipitated the orange complex which was washed with ether and vacuum dried (0.24 g, 80%).

Dichlorobis(dimethyl sulphoxide)bis(pyridine)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (1 g) and silver perchlorate (0.87 g) were refluxed in ethanol (60 ml) until all the solid had dissolved. The solution was cooled, the small amount of precipitate filtered out and pyridine (5 ml) added to the filtrate. The green solution was stirred for 5 hours and then cooled to -20°C overnight. The mixture of green and yellow crystals which separated were filtered off and recrystallised from ethanol (15 ml) to which pyridine (5 ml) had been added. The yellow complex was filtered, washed with ice-cold ethanol and vacuum dried (0.55 g, 60%).

Dichloro(2,2'-bipyridyl)bis(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.5 g) and 2,2'-bipyridyl (0.161 g) were refluxed in chloroform (20 ml) for ca. 30 min. The solution was cooled and the solvent removed. The residue was dissolved in acetone when addition

of ether precipitated the yellow complex. This was filtered off, washed with ether, and vacuum dried (0.4 g, 80%).

Dichlorobis(dimethyl sulphoxide)(1,10-phenanthroline)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.5 g) and 1,10-phenanthroline (0.2 g) were dissolved in chloroform (20 ml) and the solution refluxed for 30 min. The solution was cooled and the chloroform removed. The residue was dissolved in acetone and ether added. The orange-yellow complex which separated was collected, washed with ether, and dried in vacuo over silica gel (0.38 g, 76%).

Dichloro(2-aminopyridine)bis(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.2 g) and 2-amino pyridine (0.04 g) were refluxed in toluene (30 ml) for 30 min. to yield an orange solution. The solvent was removed and the residue dissolved in the minimum of acetone. Addition of ether followed by cooling to $-40^{\circ}C$ caused the separation of the orange-yellow complex. It was filtered and dried over silica gel (0.18 g, 50%).

Dichloro(o-phenylenediamine)bis(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.3 g) and o-phenylenediamine (0.1 g) were refluxed for 30 min. in ethanol (40 ml). The volume was reduced to ca. 15 ml when the addition of ether precipitated the pink complex. It was recrystallised from ethanol-ether (0.21 g, 70%).

Dichlorobis(dimethyl sulphoxide)(triphenylphosphine)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.3 g) was suspended in toluene (40 ml) and triphenylphosphine (0.325 g) added. The suspension was refluxed for 40 min. to give an orange coloured solution. The toluene was removed, the residue dissolved in the minimum of acetone and the buff complex precipitated by

the addition of ether. The complex was washed with acetone (20 ml) and ether (20 ml), and vacuum dried. It was recrystallised from acetone-ether (0.17 g, 50%; m.p. 200°C decomp.).

Dichloro(dimethyl sulphoxide)tris(triphenylphosphite)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.2 g) and triphenylphosphite (0.26 g) were refluxed in toluene (30 ml) for 40 min. to produce an orange solution. The volume was reduced to ca. 5 ml and ether was slowly added, with vigorous stirring, to the solution. The yellow precipitate which separated was filtered off. On cooling the filtrate to -40°C more precipitate was obtained. Recrystallisation from acetone-ether yielded the white complex (0.29 g, 60%).

N-Glycylglycinato tris(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_2$ (0.36 g) and N-glycylglycine (0.196 g) were refluxed in ethanol (40 ml) for ca. 30 min. The solution was cooled to room temperature and filtered. The bulk of the solution was reduced to ca. 15 ml and cooled to -78°C. The yellow complex which separated was filtered off at -78°C and washed with acetone (3 x 10 ml) and ether (2 x 10 ml). It was dried in vacuo over silica gel (0.18 g, 52%).

Dichlorodicarbonylbis(dimethyl sulphoxide)ruthenium(II)

$RuCl_2(Me_2SO)_4$ (0.5 g) was refluxed in toluene (100 ml) with a slow stream of CO passing through the solution for 24 hrs. The volume was reduced to ca. 10 ml and the white complex precipitated by adding light petroleum (b.p. 40 - 60°). The complex was washed with ether and vacuum dried (0.14 g, 35%).

Nitrosyltrichlorobis(dimethyl sulphoxide)ruthenium(II)

Nitric oxide was passed rapidly through a refluxing solution of $RuCl_3 \cdot 3H_2O$ in Me_2SO (5 ml). The bulk of the solvent was removed to give a viscous oil. Addition of ethanol (20 ml) and cooling to -78°C produced the brick-red complex. It was filtered, washed with acetone (2 x 10 ml), ether (2 x 10 ml), and vacuum dried (0.63 g, 80%).

Bis(trichlorostannyl)tetrakis(dimethyl sulphoxide)ruthenium(II)

To a refluxing solution of $RuCl_2(Me_2SO)_4$ (0.2 g) in ethanol (20 ml) was added a hot solution of tin(II) chloride (0.16 g) in ethanol (15 ml). The precipitate which formed was filtered hot and washed with acetone (2 x 10 ml) and ether (2 x 10 ml). It was dried in vacuo. The yield of the orange complex was essentially quantitative.

Hexakis(dimethyl sulphoxide)ruthenium(II) Perchlorate

$RuCl_2(Me_2SO)_4$ (0.5 g) and silver perchlorate (0.435 g) were suspended in ethanol (60 ml). The mixture was gently shaken for 48 - 72 hrs. The precipitated $AgCl(Me_2SO)_n$ was filtered off, Me_2SO (0.5 ml) was added, and the solution reduced in volume to ca. 15 ml after standing for ca. 30 min. On cooling to -20°C very pale green microcrystals separated, which were filtered off, washed with cold ethanol (2 x 5 ml), and vacuum dried over silica gel. The crystals slowly turned dark green over a period of days (0.4 g, 50%).

Bis(azido)tris(dimethyl sulphoxide)ruthenium(II)

As for hexakis(dimethyl sulphoxide)ruthenium(II)perchlorate until after the filtration of the $AgCl(Me_2SO)_n$. Sodium azide (0.27 g) was then added and the suspension stirred for 24 hrs. The precipitated red solid was filtered, washed with ethanol, and vacuum dried over silica gel. The yield was essentially quantitative.

Compound	Found (%)					Required (%)				
	C	H	N	S	Cl	C	H	N	S	Cl
$RuCl_2(Me_2SO)_4$	19.9	4.9		25.9	14.5	19.8	4.9		26.4	14.7
$RhCl_3(Me_2SO)_3$ [a]	16.7	4.0				16.2	4.1		21.6	24.0
$Ru(Et_2NCS_2)_2(Me_2SO)_2$	30.9	6.6	5.6		< 0.3	30.4	5.8	5.1	34.7	0.0
$RuCl_2(C_7H_5NS_2)_2(Me_2SO)_2$	32.8	3.5	4.2		10.6	32.6	3.3	4.2	29.0	10.7
$RuCl_2(C_5H_5N)_4$ [a]	49.7	4.1	11.2		14.5	49.2	4.1	11.3		14.5
$RuCl_2(C_6H_7N)_4$	51.8	5.7	9.5		13.5	52.8	5.2	10.2		13.1
$RuCl_2(C_5H_5N)_2(Me_2SO)_2.EtOH$ [b]	37.1	5.3	5.8	11.6	13.6	36.1	5.3	5.3	12.6	13.3
$RuCl_2(C_{10}H_8N_2)(Me_2SO)_2$	32.5	4.1	5.2	13.5	14.4	32.5	3.9	5.0	12.4	13.8
$RuCl_2(C_{12}H_8N_2)(Me_2SO)_2$	35.9	4.2	5.1	12.6	14.1	36.7	4.0	5.5	12.3	13.9
$RuCl_2(C_5H_6N_2)(Me_2SO)_2$	25.9	4.5	6.6	15.5		25.6	4.3	6.6	15.2	16.8
$RuCl_2(C_6H_8N_2)(Me_2SO)_2$	26.7	5.4	6.1			27.5	4.6	6.4	14.7	16.3
$RuCl_2(PPh_3)(Me_2SO)_2$	44.5	4.9		8.9	12.2	44.7	4.6		10.8	12.0
$RuCl_2[P(OPh)_3]_3(Me_2SO)$ [c]	57.9	4.5		2.8	6.3	56.9	4.3		5.2	6.0
$Ru(C_4H_6N_2O_3)(Me_2SO)_3$	26.3	5.8	5.7			25.8	5.2	6.0	20.6	
$RuCl_2(CO)_2(Me_2SO)_2$	18.9	3.4		19.0	17.7	18.7	3.1		16.7	18.5

continued

Compound	Found (%)					Required (%)				
	C	H	N	S	Cl	C	H	N	S	Cl
$Ru\ NOCl_3(Me_2SO)_2$	12.9	3.2	3.6	16.1	26.9	12.2	3.1	3.6	16.3	27.1
$Ru(SnCl_3)_2(Me_2SO)_4$	11.2	3.3		14.5	d	11.3	2.8		14.8	24.7
$Ru(Me_2SO)_6(ClO_4)_2$	19.2	4.9		24.6		18.8	4.7		25.0	9.2
$Ru(Me_2SO)_3(N_3)_2$	16.6	4.4	20.4			17.2	4.3	20.0	22.9	

a Known compounds

b Ru Found 19.1%; Required 19.8%. O (by difference) Found 7.9%; Required 9.0%

c P Found 8.6%; Required 7.9%.

d Sn interferes with Cl analysis

Table 5.1 Analytical data for complexes described in Chapters II and III

C. Chapter IV

Dried solvents of reagent grade were used in all reactions, but reactions were not carried out under an inert atmosphere unless specifically stated.

Dichlorobis(pyridine-2-thiol)iron(II)

Iron(II) dichloride tetrahydrate (0.5 g) was dissolved under nitrogen in a mixture of ethanol (30 ml) and 2,2'-dimethoxypropane (10 ml) which had been degassed with nitrogen. Iron wire (ca. 2 g) was added, with concentrated hydrochloric acid (0.2 ml), to provide a reducing system. The flask was sealed and shaken periodically until the solution was colourless. This solution was then filtered under nitrogen directly into a solution of pyridine-2-thiol (0.56 g) in ethanol (15 ml). The yellow powder which immediately precipitated was filtered under nitrogen, washed with ethanol (2 x 10 ml) and diethyl ether (2 x 10 ml) and dried in vacuo over silica gel (0.82 g, 93%).

Dibromobis(pyridine-2-thiol)iron(II)

As above, except that the iron(II) bromide was prepared from excess iron wire and 40% aqueous hydrobromic acid (0.63 g, 72%).

Dichloro, dibromo and diiodo bis(pyridine-2-thiol)cobalt(II)

A solution of the halide (2 m mol) in ethanol (10 ml) was added to a solution of the ligand (4 m mol) in ethanol (15 mol). The complexes that immediately precipitated were filtered, washed with ethanol (2 x 10 ml) and ether (2 x 10 ml), and dried in vacuum over silica gel. The yields were essentially quantitative. Cobalt(II) iodide was prepared by metathesis between sodium iodide and cobalt(II) chloride in ethanol at room temperature.

Dichloro, dibromo and diiodo bis(pyridine-2-thiol)nickel(II)

These were prepared in an analogous manner to the cobalt(II) complexes. The yields were quantitative.

Dichlorotetrakis(pyridine-2-thiol)nickel(II)

A solution of nickel(II) chloride hexahydrate (2 m mol) in ethanol (10 ml) was added to the ligand (8 m mol) in ethanol (20 ml). The yellow complex which quantitatively precipitated was collected, washed with ethanol and ether, and dried under vacuum over silica gel.

Tetrakis(pyridine-2-thiol)nickel(II) dibromide and diiodide

As for the chloride above, except that the nickel(II) iodide was formed in situ by adding excess sodium iodide in ethanol to an ethanolic solution of nickel(II) chloride, cooling to -30°C and filtering off the precipitated sodium chloride. The yields of the complexes were ca. 80%.

Chlorotris(pyridine-2-thiol)copper(I)

To a suspension of copper(I) chloride (5 m mol) in ethanol (25 ml) was added a solution of pyridine-2-thiol (15 m mol) in ethanol (30 ml) and the solution vigorously stirred. The halide dissolved immediately to give an orange solution and after ca. 25 seconds the complex precipitated as a bright orange powder. It was filtered, washed with ethanol and ether, and vacuum dried. The yield was ca. 75%.

Bromobis(pyridine-2-thiol)copper(I)

As for the chloride above, except that 10 m mol of ligand was used. The yield was ca. 75%.

Iodobis(pyridine-2-thiol)copper(I)

Sulphur dioxide was bubbled through a solution of copper(II) sulphate pentahydrate (0.5 g) in methanol (35 ml) and a solution of pyridine-2-thiol (0.7 g) and sodium iodide (0.7 g) in methanol (35 ml) added. An orange precipitate formed immediately and the solution was stirred for a further 10 mins. to complete the reaction. The orange complex was filtered, washed with ethanol and ether, and vacuum dried, (0.7 g, 67%).

Tetrakis(pyridine-2-thiol)silver(I) tetrafluoroborate

Silver(I) tetrafluoroborate (0.5 g) in ethanol (10 ml) was added slowly to a solution of pyridine-2-thiol (0.28 g) in ethanol (15 ml) with stirring. An initial precipitate re-dissolved and the solution was filtered from any solid which remained. On standing, the solution deposited pale yellow needles of the compound. These were collected, washed with a little cold ethanol and vacuum dried (0.35 g, 46%).

Bis(pyridine-2-thiol)silver(I) perchlorate

Pyridine-2-thiol (0.32 g) in ethanol (20 ml) was slowly added to a solution of silver(I) perchlorate (0.3 g) in ethanol (20 ml). A pale yellow precipitate formed immediately. It was filtered, washed with ethanol (2 x 10 ml), ether (2 x 10 ml) and vacuum dried (0.3 g, 50%).

Tetrakis(pyridine-2-thiol)palladium(II) dichloride

Palladium(II) chloride (0.5 g), dissolved in the minimum of hot ethanol, was added to a hot solution (60°C) of pyridine-2-thiol (0.63 g) in ethanol (15 ml). On cooling, the orange complex precipitated. It was filtered, washed with ethanol and ether, and vacuum dried over silica gel (0.8 g, 71%).

Bis(pyridine-2-thiolato)(pyridine-2-thiol)palladium(II)

Palladous acetate (0.2 g) in hot (60°C) benzene (30 ml) was added to pyridine-2-thiol (0.48 g) in boiling benzene (50 ml). On cooling, the red complex precipitated. It was washed with a little benzene, ether, and vacuum dried (0.35 g, 90%).

Tetra-μ-acetatobis(pyridine-2-thiol)dirhodium(II)

Rhodium acetate (0.5 g) was dissolved in the minimum of boiling methanol and pyridine-2-thiol (0.25 g) in methanol (25 ml) added. The initial green solution immediately turned red on the addition of the ligand and deposited the purple-brown complex on cooling. It was filtered, washed with methanol and ether, and vacuum dried. More complex could be obtained by reducing the volume of the solution and cooling to -40°C (0.4 g, 60%).

Bis(1,10-phenanthroline)(pyridine-2-thiol)copper(II) perchlorate

Bis(1,10-phenanthroline)copper perchlorate[104] (0.4 g) was suspended in ethanol (30 ml) and pyridine-2-thiol (0.1 g) in ethanol (15 ml) added. The suspension was stirred for four hours, and the green-brown solid filtered, washed with ethanol and ether, and vacuum dried (0.2 g, 45%).

Compound	Found (%)			Required (%)		
	C	H	N	C	H	N
$FeCl_2(PySH)_2$	34.8	2.9	8.2	34.4	2.9	8.0
$FeBr_2(PySH)_2$	27.4	2.4	6.4	27.4	2.3	6.4
$CoCl_2(PySH)_2$	34.3	3.0	7.8	34.1	2.8	8.0
$CoBr_2(PySH)_2$	27.7	2.2	6.2	27.2	2.3	6.4
$CoI_2(PySH)_2$	23.2	1.9	5.5	22.4	1.9	5.2
$NiCl_2(PySH)_2$	34.2	2.6	8.1	34.1	2.8	8.0
$NiBr_2(PySH)_2$	28.0	2.5	6.5	27.2	2.3	6.3
$NiI_2(PySH)_2$	21.9	1.8	5.0	22.4	1.9	5.2
$NiCl_2(PySH)_4$	41.7	3.7	9.9	41.8	3.5	9.8
$NiBr_2(PySH)_4$	36.5	3.1	8.6	36.2	3.0	8.4
$NiI_2(PySH)_4$	32.5	3.0	7.5	31.7	2.6	7.4
$CuCl(PySH)_3$	42.0	3.6	9.5	41.7	3.5	9.5
$CuBr(PySH)_2$	32.8	3.0	7.2	32.8	2.7	7.7
$CuI(PySH)_2$ [a]	29.4	2.4	6.9	29.1	2.4	6.8
$Cu(phen)_2(PySH)(ClO_4)_2$	46.8	2.9	9.4	47.4	2.9	9.5
$Ag(PySH)_4BF_4$	37.7	3.2	8.5	37.6	3.1	8.8
$Ag(PySH)_2ClO_4$	27.1	2.3	6.2	27.9	2.3	6.5
$Pd(PySH)_4Cl_2.EtOH$	40.2	3.9	8.9	39.6	3.9	8.4
$Pd(PyS)_2(PySH)$	40.5	3.1	9.2	41.2	3.4	9.6
$Rh_2(OAc)_4.2PySH$	33.3	3.6	4.2	32.5	3.3	4.2

[a] I Found 31.6%; Required 30.8%.

Table 5.2 Analytical data for pyridine-2-thiol complexes

REFERENCES

1. S. Ahrland, J. Chatt and N.R. Davies, Quart. Rev., 1958, 12, 265.
2. R.G. Pearson, J. Amer. Chem. Soc., 1963, 85, 3533.
3. J.L. Burmeister, Coordination Chem. Rev., 1966, 1, 205; ibid, 1968, 3, 225.
4. M.M. Chamberlain and J.C. Bailar, Jr, J. Amer. Chem. Soc., 1958, 81, 6412.
5. J. Lewis, R.S. Nyholm and P.W. Smith, J. Chem. Soc., 1961, 4590.
6. D. Martin, A. Weise and H.-J. Niclas, Angew. Chem. (Internat. Edit.), 1967, 6, 318.
7. W.W. Epstein and F.W. Sweat, Chem. Rev., 1967, 67, 247.
8. F.A. Cotton and R. Francis, J. Amer. Chem. Soc., 1960, 82, 2986.
9. J. Gopalakrishnan and C.C. Patel, J. Sci. Res. India, 1968, 27, 475.
10. W.L. Reynolds, Progress Inorg. Chem., 1970, 12, 1.
11. W.D. Horrocks, Jr and F.A. Cotton, Spectrochim. Acta, 1961, 17, 134.
12. W. Moffitt, Proc. Roy. Soc., 1950, A200, 409.
13. M.J. Bennett, F.A. Cotton, D.L. Weaver, R.J. Williams and W.H. Watson, Acta Cryst., 1967, 23, 788.
14. V. Krishnan and C.C. Patel, J. Inorg. Nuclear Chem., 1964, 26, 2201.
15. V. Krishnan and C.C. Patel, Indian J. Chem., 1964, 2, 416.
16. C.V. Senoff, E. Maslowsky, Jr and R.G. Goel, Canad. J. Chem., 1971, 49, 3585.
17. F.C. March and G. Ferguson, Canad. J. Chem., 1971, 49, 3590.
18. W. Kitching and C.J. Moore, Inorg. Nuclear Chem. Letters, 1968, 4, 691.
19. S. Thomas and W.L. Reynolds, Inorg. Chem., 1969, 8, 1531.

20. W. Kitching, C.J. Moore and D. Doddrell, Inorg. Chem., 1970, 9, 541.

21. W. Kitching, C.J. Moore and D. Doddrell, Austral. J. Chem., 1969, 22, 1149.

22. V.G.K. Das and W. Kitching, J. Organometallic Chem., 1967, 10, 59.

23. B.B. Wayland and R.F. Schramm, Inorg. Chem., 1969, 8, 971.

24. J.H. Price, A.N. Williamson, R.F. Schramm and B.B. Wayland, Inorg. Chem., 1972, 11, 1280.

25. R.A. Potts, J. Inorg. Nuclear Chem., 1972, 34, 1749.

26. W.F. Currier and J.H. Weber, Inorg. Chem., 1967, 6, 1539.

27. Y.M.Y. Haddad, H.B. Henbest and T.R.B. Mitchell, Proc. Chem. Soc., 1964, 361.

28. J. Trocha-Grimshaw and H.B. Henbest, Chem. Comm., 1967, 544.

29. M. McPartlin and R. Mason, Chem. Comm., 1967, 545.

30. F. Lareze, Compt. Rend., Paris, Ser. C, 1967, 264, 2037.

31. F. Basolo, W.H. Baddley and J.L. Burmeister, Inorg. Chem., 1964, 3, 1202.

32. A. Turco and C. Pecile, Nature, 1961, 191, 66.

33. J.A. Weaver, P. Hambright, P.T. Talbert, E. Kang and A.N. Thorpe, Inorg. Chem., 1970, 9, 268.

34. B. Singh, Lakshmi and U. Agarwala, Inorg. Chem., 1969, 8, 2341.

35. S.K. Madan and C. Goldstein, J. Inorg. Nuclear Chem., 1966, 28, 1251.

36. P.P. Singh and R. Rivest, Canad. J. Chem., 1968, 46, 2361.

37. C.N.R. Rao and R. Venkataraghavan, Spectrochim. Acta, 1962, 18, 541.

38. C.N.R. Rao, R. Venkataraghavan and T.R. Kasturi, Canad. J. Chem., 1964, 42, 36.

39. D. De Filippo and C. Preti, J. Chem. Soc., (A) 1970, 1904.

40. J.R. Ferraro, B.B. Murray and N.J. Wieckowicz, J. Inorg. Nuclear Chem., 1972, 34, 231.

41. C.D. Flint and M. Goodgame, J. Chem. Soc., (A), 1966, 744.

42. C.D. Flint and M. Goodgame, J. Chem. Soc., (A), 1968, 750.

43. M. Keeton and A.B.P. Lever, Inorg. Chem., 1971, 10, 47.

44. M. Keeton, A.B.P. Lever and B.S. Ramaswamy, Canad. J. Chem., 1970, 48, 3187.

45. B.F.G. Johnson and R.A. Walton, Spectrochim. Acta, 1966, 22, 1853.

46. Yu.N. Kukushkin and N.D. Rubtsova, Russ. J. Inorg. Chem., 1969, 14, 1115.

47. J.M. Fletcher, W.E. Gardner, E.W. Hooper, K.R. Hyde, F.N. Moore and J.L. Woodhead, Nature, 1963, 199, 1089.

48. B.R. James, E. Ochiai and G.I. Rempel, Inorg. Nuclear Chem. Letters, 1971, 7, 781.

49. V.J. Traynelis and W.L. Hergenrother, J. Org. Chem., 1964, 29, 221.

50. F.A. Cotton, R. Francis and W.D. Horrocks, Jr, J. Phys. Chem., 1960, 64, 1534.

51. C.V. Berney and J.H. Weber, Inorg. Chem., 1968, 7, 283.

52. T. Tanaka, Inorg. Chim. Acta, 1967, 1, 217.

53. R. von Ammon and R.D. Fischer, Angew. Chem. (Internat. Ed.), 1972, 11, 675.

54. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd Edn, Interscience, 1972, p.1018 *et seq*.

55. J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc., (A), 1970, 2765.

56. C. O'Connor, J.D. Gilbert and G. Wilkinson, J. Chem. Soc., (A), 1969, 84.

57. B.F.G. Johnson, J.A. McCleverty and K.H. Al-Obaidi, J. Chem. Soc., (A), 1969, 1668.

58. C.N. Yiannios and J.V. Karabinos, J. Org. Chem., 1963, 28, 3246.

59. N. Sheppard, Trans. Faraday Soc., 1950, 46, 429.

60. S.J. LaPlaca and J.A. Ibers, Inorg. Chem., 1965, 4, 778.

61. C.A. Tolman, J. Amer. Chem. Soc., 1970, 92, 2956.

62. M.K. Kim and A.E. Martell, J. Amer. Chem. Soc., 1963, 85, 3080.

63. M.K. Kim and A.E. Martell, Biochem., 1964, 3, 1169.

64. B.F.G. Johnson and J.A. McCleverty, Progress Inorg. Chem., 1966, 7, 277.

65. O.E. Zvyagintsev and A. Kurbamov, J. Inorg. Chem., (U.S.S.R.) Eng. Trans., 1958, 3, 108.

66. J. Chatt and R.G. Hayter, J. Chem. Soc., 1963, 6017.

67. C. Creutz and H. Taube, Inorg. Chem., 1971, 10, 2664.

68. B.J. Hathaway and A.E. Underhill, J. Chem. Soc., 1961, 3091.

69. A.D. Allen, F. Bottomley, R.O. Harris, V.P. Reinsalu and C.V. Senoff, J. Amer. Chem. Soc., 1967, 89, 5595.

70. H. Meerwein, V. Henderich and K. Wunderlich, Arch. Pharm., 1958, 291, 541.

71. U.S. Patent, No. 3,636,029.

72. S.R. Fletcher and A.C. Skapski, J.C.S. Dalton, 1972, 635.

73. C.K. Brown, D. Georgiou and G. Wilkinson, J.C.S. Dalton, in press.

74. R.W. Mitchell, J.D. Ruddick and G. Wilkinson, J. Chem. Soc., (A), 1971, 3224.

75. R.A. Jouls and A.R. Kennedy, J. Chem. Soc., 1958, 3610.

76. H.I. Heitner, S.J. Lippard and H.R. Sunshine, J. Amer. Chem. Soc., 1972, 94, 8936.

77. B.P. Kennedy and A.B.P. Lever, Canad. J. Chem., 1972, 50, 3488.

78. B.N. Figgis and J. Lewis, Progress Inorg. Chem., 1964, 6, 37.

79. W. Hieber and J.G. Floss, Z. anorg. Chem., 1957, 291, 314.

80. D. Forster and D.M.L. Goodgame, J. Chem. Soc., 1965, 268.

81. T. Birchall and M.F. Morris, Canad. J. Chem., 1972, 50, 211.

82. T.C. Gibb and N.N. Greenwood, J. Chem. Soc., 1965, 6989.

83. P.R. Edwards, C.E. Johnson and R.J.P. Williams, J. Chem. Phys., 1967, 47, 2074.

84. C.D. Flint and M. Goodgame, J. Chem. Soc., 1968, 2178.

85. H. Grossman and F. Hünseler, Z. anorg. Chem., 1905, 46, 361.

86. F.A. Cotton, D.M.L. Goodgame and M. Goodgame, J. Amer. Chem. Soc., 1961, 83, 4690.

87. A.B.P. Lever, J. Chem. Ed., 1968, 45, 711.

88. A.B.P. Lever, 'Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.

89. M.R. Udupa, G. Krishnan and G. Aravamudan, Inorg. Nuclear Chem. Letters, 1973, 9, 491.

90. C.K. Jörgensen, J. Inorg. Nuclear Chem., 1962, 24, 1571.

91. A.B. Blake and F.A. Cotton, Inorg. Chem., 1964, 3, 9.

92. W.E. Hatfield and R. Whyman, Transition Metal Chem., 1969, 5, 47.

93. F.H. Jardine, L. Rule and A.G. Vohra, J. Chem. Soc., (A) 1970, 238.

94. S.V. Waggett, Thesis, University of London, 1972.

95. R. Weiss and H. Venner, Z. Physiol. Chem., 1966, 345, 122.

96. A. Montenero and C. Pelizzi, Inorg. Chim. Acta, 1972, 6, 644.

97. W.J. Geary, Coord. Chem. Rev., 1971, 7, 81.

98. J.P. Fackler, jr, J.A. Fetchin and W.C. Seidel, J. Amer. Chem. Soc., 1969, 91, 1217.

99. D.R. Eaton, J. Amer. Chem. Soc., 1968, 90, 4272.

100. S.A. Johnson, H.R. Hunt and H.M. Neuman, Inorg. Chem., 1963, 2, 960.

101. J. Lewis and R.G. Wilkins, 'Modern Coordination Chemistry', Interscience, 1964, p.403.

102. D.F. Evans, personal communication.

103. D.F. Evans, J. Chem. Soc., (A), 1967, 1670.

104. A.A. Schilft and R.C. Taylor, J. Inorg. Nuclear Chem., 1959, 9, 211.