SPECTRAL   AND   MAGNETIC   STUDIES

ON   SOME

METAL   COMPLEXES   OF   SULPHUR-CONTAINING   LIGANDS

A Thesis

submitted for the

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by

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Abstract

A number of thiourea complexes of divalent metals have been prepared, many of them being new compounds. The far infrared spectra ($400 - 130$ cm^{-1}) of these compounds have been measured and the results correlated with the structural information obtained from other physical studies. In all cases the coordination of the thiourea is through the sulphur atom. Fundamental vibrations having mainly metal-sulphur stretching character have been observed in the range $320 - 180$ cm^{-1} in all cases. Their position within this range has been shown to give useful structural information for the compounds. A number of metal-halide and metal-oxygen stretching modes have also been observed in these compounds.

Studies have been made of the infrared, far infrared, and electronic spectra, and the magnetic properties of a series of compounds with metal – thiourea – metal bridges and of a number of anhydrous divalent metal thiocyanates. The results are interpreted in terms of their known or probable stereochemistry and the nature of the bonding.

The electronic and molecular structures of some new thioacetamide complexes of divalent metals have been studied and the results compared with those obtained for the thiourea complexes.

The infrared, far infrared, and electronic spectra, and the magnetic properties of some complexes of cobalt(II), nickel(II), and copper(II) with chelating alkyl sulphides have been measured and the results discussed with reference to their probable electronic and molecular structures. In certain cases adducts of the compounds with molecular iodine have been prepared and the nature of the bonding of the iodine to the complexes has been investigated by the above physical techniques.

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ABBREVIATIONS

Ligands

tu	thiourea	$(H_2N)_2CS$
exan$^-$	diethylxanthate	$(C_2H_5)_2NCS_2^-$
dtp$^-$	diethyldithiophosphate	$(C_2H_5O)_2PS_2^-$
R_2S	alkyl sulphide	
py	pyridine	C_5H_5N
tam	thioacetamide	CH_3CSNH_2
DTH	2:5 dithiahexane	$(CH_3SCH_2)_2$
IPTE	1:2 bis(isopropylthio)-ethane	$((CH_3)_2CHSCH_2)_2$

The following abbreviations will be used in describing spectra

s	strong
m	medium
w	weak
v	very
sh	shoulder
sp	sharp
br	broad

The notation ν_1, ν_2, ν_3, etc. that will be used for labelling vibrational modes is that given by K. Nakamoto in "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, 1963; except for the point group D_{4h} where the notation of P. J. Hendra, Nature, (1966) <u>19</u>, 37, will be used.

The notation ν_1, ν_2, ν_3, etc. that will be used for labelling the spin-allowed transitions in electronic spectra is such that, for a weak field complex, the subscripts increase as the energy of the transition increases.

For convenience, a summary of this notation is given below.

	Co^{II} in T_d ligand field	Co^{II} in O_h ligand field	Ni^{II} in O_h ligand field
1	$^4A_2 \longrightarrow {}^4T_2$	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}$	$^3A_{2g} \longrightarrow {}^3T_{2g}$
2	$^4A_2 \longrightarrow {}^4T_1(F)$	$^4T_{1g}(F) \longrightarrow {}^4A_{2g}$	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$
3	$^4A_2 \longrightarrow {}^4T_1(P)$	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$

CHAPTER ONE

Introduction

Metal complexes of nitrogen and oxygen donating ligands have been extensively studied in recent years and considerable data is also available for arsenic and phosphorus donating ligands, but until very recently sulphur-containing ligands had received relatively little attention. The studies described in this thesis were carried out with three main aims. Firstly to identify metal - sulphur stretching frequencies in some metal complexes and investigate how these frequencies are affected by changes in the metal, the symmetry of the coordination sphere, and the nature of the other ligand atoms. Secondly, using this data and other techniques, to investigate the electronic and molecular structures of some metal complexes of sulphur-containing ligands. Thirdly, to study the magnetic interactions caused by metal - sulphur - metal bridges.

Livingstone [1] has recently reviewed the complexes formed by the various types of sulphur-containing ligand and therefore a general description of the different structures and types of coordination will not be given here. The previous work on the compounds studied in this work will be described in the relevant chapters.

At this point it will be convenient to discuss three of the general features of the chemistry of sulphur-ligand complexes which are referred to later in this thesis.

(a) <u>Ahrland - Chatt - Davies "B" Character</u>

After an extensive survey of the available data on the relative affinities of ligand atoms for metals, Ahrland, Chatt and Davies [2] divided metals into two classes: (A) those which form the most stable complexes with the first ligand atom of each group of the periodic table and (B) those which form the most stable complexes with the second or subsequent atom of the group. Thus for class A metals (such as Ca^{2+} and Al^{3+}) the order of stability for donor atoms is $O > S > Se > Te$, whilst for class B metals (Ag^{+} Pt^{2+} etc.) the order is $S >> O$ but any sequence of S, Se and Te may occur. Class B metals form a diffuse area round platinum in the periodic table; the border between A and B character is not clearly defined, metals such as copper, zinc and cadmium having neither pronounced A nor pronounced B character. The oxidation state of the metal can effect the degree of B character, this being greatest for the lower states.

The classification was based on a relatively small number of equilibrium constant determinations plus the consideration of a large number of qualitative observations.

In borderline cases the equilibrium constants can be misleading as a measure of metal – ligand bond strength due to variations in the entropy contribution. However, for typical A or B behaviour, the equilibrium constants for oxygen and sulphur donors are sufficiently different for them to be indicative of the relative bond strengths.

B character has been attributed to the presence of non-bonding **d** electrons on the metal which are capable of forming $d_\pi - d_\pi$ or $d_\pi - p_\pi$ bonds with the empty ligand orbitals. This explains the tendency of class B metals to occur at the end of the transition series. The approximate order of increasing B character of the metal ions considered in this work is Mn (II)< Fe (II)< Co (II)< Ni (II)<Zn (II) <Cu (II) Cd (II)< Cu (I)<Pd (II)< Pt (II).

(b) The Ligand Field Splitting Parameter of Sulphur – Donating Ligands.

Measurement of the ligand field strength parameter 10Dq of a large number of complexes of a given metal with the same donor atom (but chemically different ligands) and the same stereochemistry show that the range of 10Dq under these conditions is rather small.[3] Thus if a spectro-chemical series containing a very large number of ligands was drawn up it would be found that most of the oxygen donors would be found in the same part of the series and similarly for the nitrogen donors.

Sulphur donors, however, would be scattered throughout the series, maleonitriledithiolate $(NC-C-S^-)2)$ and diethyl dithiophosphate coming towards the low end of the series and sulphite at the high end.

Jørgensen[3] has explained these facts by interpreting 10Dq as the difference between the σ and π - antibonding effects of the ligands on the partly filled shell. Ligands such as ammonia which have only one lone pair on the donor atom are primarily σ-bonded, π-bonding from the metal to higher empty orbitals on the ligand atoms being neglected. However, when low energy lone pairs are present on the donor atom, bonding from filled ligand orbitals to the metal d orbitals can decrease the value of 10Dq. Assuming that the major determining the extent of this π-bonding is the number of available lone pairs, then it would be anticipated that the 10Dq value produced by a sulphur donor will be inversely related to the number of lone pairs on the sulphur atom. This conclusion is well supported by the experimental results.[3, 4, 5] (For abbreviations, see page 8)

10Dq Value $\qquad$ detp$^-$ $<$ exan$^-$ $<$ tu $<$ R_2S $<$ SO_3^{2-}

lone pair electrons ~6 $>$ ~5.5 $>$ ~5 $>$ 4 $>$ ~2

However the ligand field produced by a given type of sulphur-containing ligand would not be expected to be completely independent of the particular ligand for two reasons.

Firstly, the steric requirements of the ligand may result in an increase in the metal-ligand bond distance which would cause a decrease in 10Dq by reducing the magnitude of all interactions (assuming the π effect is small compared with the σ effect) and secondly, the nature of the other atoms attached to the sulphur atom in the ligand will cause changes in both its σ and π donor ability.

This theory accounts for the much greater observed variation in 10Dq for sulphur donors than for other ligands since complexes of ligands with such a wide variation in the number of available lone pair electrons are not well known for these donors. One example of this effect for nitrogen donors is the relatively weak field produced by the azide ion,[6, 7] which has about four donor electrons available on the terminal nitrogen atoms, compared to that by amines which have only two available electrons.

(c) **The Nephelauxetic Effect**

Jørgensen[8] has published a comprehensive review of the nephelaxetic effect so that no attempt will be made to give a detailed account of this phenomenom; instead attention will be drawn to its most important aspects as they affect complexes of sulphur donors.

Calculation of the Racah parameter B from the observed electronic (d-d) spectra of transition metal complexes from the determinants of Tanabe and Sugano [9] usually gives a value somewhat below the value for the free (gaseous) ion found from atomic spectroscopy. It is convenient to define a parameter β (the nephelauxetic ratio) such that

$$B_{complex} = \beta \, B_{free\ ion}$$

Complexes of divalent first row transition elements with halide, oxygen or nitrogen donors usually have β values in the range 0.75 - 0.95 but, as first pointed out by Schäffer [10] and later emphasized by Jørgensen, [3] some sulphur donors cause a much stronger nephalauxetic effect, the value being reduced to 0.6 or lower.

The estimation of the numerical values of β from measured spectra is subject to considerable error due to the width of the spectral bands and the effects of spin-orbit coupling. Another source of error is that caused by treating real complexes as if they have idealized T_d or O_h symmetry. Even when the distortion is too small to produce observable band splittings, the experimental band positions may deviate from the values calculated taking average values of the ligand field parameters. [11] Thirdly, the calculated B values suffer from the intrinsic errors in the Tanabe - Sugano method (e.g. the assumption that "1" = 2 and that the

same radial function can be used for both t_2 and e orbitals.

Jørgensen[8] following Koide and Pryce,[12] defines the terms $\beta_{33}, \beta_{35}, \beta_{55}$ which take account of the different expansions of the σ and π antibonding metal orbitals, β_{33}, β_{55} being calculated in appropriate cases from the spin-forbidden intrasubshell transitions and β_{35} from the spin-allowed transitions. All the nephelauxetic ratios in this thesis are β_{35}.

The explanation of the nephelauxetic effect is usually considered from two directions; firstly, that covalency will cause a reduction of the positive charge on the metal to roughly one unit and secondly, the partly filled anti-bonding molecular orbitals involving the metal electrons extend out into the ligands where they overlap with the ligand orbitals. In either case the electronic radial function of the metal is expanded with a consequent reduction in the electronic repulsion constants.

The magnitude of the nephelauxetic effect for sulphur donors is then partly due to the polarizability of the sulphur atom but more significantly to the presence of low-lying orbitals in the donor. This explanation accounts for the fact that the pronounced nephelauxetic effect is characteristic of ligands which contain the sulphur atom as part of a delocalized system. Ligands which do not have low lying π

orbitals, e.g. alkyl sulphides, in which the n-π^* transitions do not occur below 45,000 cm^{-1}, do not show this effect.

A detailed introduction to all of the techniques used in this work would be long and is unnecessary as many excellent books and review articles dealing with electronic spectroscopy,[13,14,15] magnetic measurements,[16,17] vibrational spectroscopy,[18,19,20] and Mössbauer spectroscopy[21] are available. There is, however, no general account of the use of far infrared spectroscopy in inorganic chemistry and as applications of this technique form a major part of this thesis a brief introduction to the material described in later chapters will be given.

Far Infrared Spectroscopy

Direct observation of metal-ligand stretching modes is potentially capable of giving detailed information on the bonding in, and the stereochemistry of, metal complexes; but until recently these vibrations had been observed in only a few complexes. Except when the ligand is very light (e.g. H$^-$, O^{2-}, F$^-$, CO and CN$^-$) or when the metal-ligand force constant is exceptionally high (e.g. in complexes of metals in high oxidation states or when formal multiple bonding occurs) metal - ligand stretching vibrations occur below 400 cm^{-1} and therefore beyond the range of most spectrometers.

Research in far infrared spectroscopy (for convenience in this thesis the term far infrared will be reserved for the spectral region below 400 cm^{-1} and infrared for the region 4000 - 400 cm^{-1}) has been carried out for many years using specially designed and constructed instruments. The availability of replica echelette gratings and sensitive detectors in the 1950's gave considerable impetus to this work. However, it was not until commercial instruments capable of giving high performance down to at least 200 cm^{-1} became available in the early 1960's that metal complexes were studied in any detail.

The low frequently vibrations of a number of metal complexes have been studied by Raman spectroscopy, but this technique is usually limited to concentrated solutions of lightly coloured materials. The method has the advantage that polarization studies are possible without the need to align the molecules along a particular axis and the selection rules governing the interaction of the molecular vibrations with the incident radiation are different from those governing infrared spectroscopy.[18] Raman spectroscopy can provide useful information in addition to that available from far infrared spectroscopy but its application is at present severely limited. Very recently, very high performance Raman spectrometers using lasar sources have become available.

These instruments enable good low frequency spectra to be obtained on dark solids [22] and it seems probable that in the next few years Raman spectroscopy will be used increasingly to complement far infrared data.

The instrumental difficulties in far infrared spectroscopy have now been largely solved - at least down to about 100 cm^{-1} - and the resolution and signal to noise ratio obtainable is adequate for most applications to metal complexes. There are, however, certain difficulties which arise from the nature of the sample.

(a) There are no satisfactory solvents available for far infrared studies on many metal complexes. Hexane, benzene, pyridine and methyl cyanide have large regions of transmittance but the complexes studied in this work are either not sufficiently soluble in, or are decomposed by these solvents. It was therefore necessary to examine micro-crystalline mulls, the absorption due to a thin film of nujol being negligible.

(b) Spectra taken in the solid states are likely to show vibrational frequencies corresponding to translations or rotations of discrete molecules or ions in the crystal lattice; however, for ions and molecules with a mass of a few hundred atomic units or more these modes do not, in general, occur above 100 cm^{-1}.

In order to avoid interference from lattice modes in cases where there is a relatively light molecule or ion in the lattice, these complexes have been studied as far as possible with two different light ions present, e.g. $(Ni(tu)_6)(NO_3)_2$ and $(Ni(tu)_6)Br_2$.
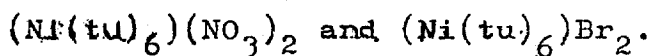
The predicted number of metal – ligand stretching modes for the various stereochemistries and symmetries and whether they are infrared active, or Raman active or both is readily obtained by the methods described in references 18 and 20. The results of these calculations for the more common symmetries are given in Table I.

It will be convenient to use the terms octahedral, tetrahedral and square planar to describe the steriochemical type which corresponds roughly to these spatial arrangements of not necessarily identical ligands. The Schoenflies symbols O_h, T_d and D_{4h} will be used to describe these precise symmetries. Frequently it will be necessary to use the terms approximately C_{3v} etc. to describe a complex which is closer to the stated symmetry than it is to any comparably high symmetry. Thus $Co(tu)_3OSO_3$ will be said to have tetrahedral stereochemistry and to have a coordination sphere of approximately C_{3v} symmetry, although the true symmetry will be very low.

TABLE I

Predicted Numbers of Metal – Ligand Stretching Modes in Various Stereochemistries

Stereochemical type	Symmetry (ideal)	IR Active Strs. M – L	M – X	Raman Active Strs. M – L	M – X
Tetrahedral ML_4	T_d	T_2	–	$A_1 + T_2$	–
" ML_3X	C_{3v}	$E + A_1$	A_1	$E + A_1$	A_1
" ML_2X_2	C_{2v}	$A_1 + B_1$	$A_1 + B_2$	$A_1 + B_1$	$A_1 + B_2$
" ML_4	D_{2d}	$B_2 + E$	–	$B_2 + E + A_1$	–
Planar " ML_4	D_{4h}	E_u	–	$A_{1g} + B_{2g}$	–
" ML_4	C_{4v}	$E + A_1$	–	$E + A_1 + B_2$	–
" ML_3X	C_{2v}	$A_1 + B_1$	A_1	$A_1 + B_1$	A_1
" cis ML_2X_2	C_{2v}	$A_1 + B_2$	$A_1 + B_1$	$A_1 + B_2$	$A_1 + B_1$
" trans ML_2X_2	D_{2h}	B_{3u}	B_{2u}	A_g	A_g
Octahedral ML_6	O_h	T_{1u}	–	$E_g + A_{1g}$	–
" ML_6	S_6	$A_u + E_u$	–	$E_g + A_g$	–
" ML_5X	C_{4v}	$E + A_1$	A_1	$E + A_1$	A_1
" cis ML_4X_2	C_{2v}	$2A_1 + B_1 + B_2$	$A_1 + B_1$	$2A_1 + B_1 + B_2$	$A_1 + B_2$
" trans ML_4X_2	D_{4h}	E_u	A_{2u}	$A_{1g} + B_{2g}$	A_{1g}
" cis ML_3X_3	C_{3v}	$E + A_1$	$E + A_1$	$E + A_1$	$E + A_1$
" trans ML_3X_3	C_{2v}	$2A_1 + B_2$	$2A_1 + B_2$	$2A_1 + B_2$	$2A_1 + B_2$

Examination of Table I shows that in many complexes there will be two or more stretching modes of the same symmetry and in certain cases the energies of these bands will be similar. Under these conditions extensive inter-action between these two vibrational modes will occur resulting in each acquiring some of the character of the other and the two vibrational modes moving apart.[18] This complication, however, apparently does not prevent meaning ful assignments of the majority of spectra; experience suggests that it is only in those cases where the inter-acting modes lie very close together that the interaction causes a marked difference between the observed spectrum and that which would have been anticipated in the absence of any such interaction. (One of the aims of the present study was to determine to what extent the far infrared spectra of complexes of low symmetry could be interpreted without performing a complete vibrational analysis.) Even for the most symmetrical molecules many of the normal vibrations involve both bond stretching and angle bending,[20] the relative amounts depending on the atomic masses and the detailed structure involved. In the case of the **thiourea** complexes which are discussed in Chapters two and three the C - S - Metal bond angle is about 120°,

the skeletal vibrations of the complex which occur in the far infrared must therefore involve appreciable amounts of both bond stretching and angle bending character. However the spectra of a large number of thiourea complexes show a band or bands which vary in the same way as metal-halide stretches on changing the metal atom or the stereochemistry. It therefore seems reasonable to call these metal-sulphur stretching modes or, more simply, metal - sulphur stretches, although they must involve some bending character. In addition, at lower energies, bands are sometimes observed which appear to have the properties of bending modes, these will be termed metal-sulphur bending modes. It may be mentioned here that the normal vibrational modes of a polyatomic species involve the relative motion of every atom in the species[18] and therefore, for example, the energy of the M - X modes in a complex species ML_2X_2 are dependent on the nature of L. Again, experience suggests that, in most cases, the energies of the M - X stretching modes are sufficiently constant for different L to enable assignments of observed spectral bands to vibration largely located in the M - X bonds. [23]

At the time this work was started only metal - halide, [24,25,26] metal - ammonia, [27,28] metal - pyridine, [29] metal - isocyanate, [30] metal - thiocyanate, [31] metal - isothiocyanate, [32] and metal - isoselenocyanate [33] modes had been studied in any detail. Nakamoto et al. had carried out vibrational analysis of some metal acetylacetonates, [34] and metal - oxalato complexes, [35] and of dithioxalatoplatinum (II) [19] and bisdithiocarbonato-platinum (II) [36] but in these compounds the metal - ligand stretching modes involve ring deformation. Since then, a number of papers dealing with far infrared spectra of metal - complexes have appeared, but few systematic studies on other types of donor have been reported. Of the latter, those dealing with metal - nitrate [37] and metal - sulphate [38] modes are the most relevant to this work.

Apart from the above mentioned studies, the only metal-sulphur stretching frequencies to have been unambiguously assigned as those associated with the thioanions such as $(AsS_4)^{3-}$ (symmetric stretch 386 cm^{-1}, asymmetric stretch 380 cm^{-1}). [39] These frequencies effectively form the upper limit for metal - sulphur stretching frequencies in complexes of metals in all but the highest valency states.

Complexes of thiourea were selected for the initial study of metal-sulphur stretching modes for three reasons. Firstly, this ligand is relatively light and is one of the few non-chelating sulphur donors that forms stable compounds with first row transition metals. Secondly, there is a considerable amount of structural information available for thiourea complexes. Thirdly, there are no fundamental vibrations of the free thiourea molecule below about 400 cm^{-1}. (35)

CHAPTER TWO

Metal-Sulphur and Metal-Halogen Stretching Frequencies in Some Complexes of Divalent Metals with Thiourea

In this chapter the magnetic properties, electronic spectra, infrared spectra and X-ray powder patterns of some thiourea complexes of divalent metals are discussed, and where possible, their structures are deduced from this data. The far infrared spectra ($400-130$ cm^{-1}) of these compounds are then interpreted in terms of their known or probable structures.

Infrared Spectra of Thiourea and its Complexes

There has been much discussion of the assignments of the infrared absorption bands of thiourea and related molecules.[41] Extensive interaction occurs between the NH_2 wagging mode, the C – N stretching modes, and the C – S stretching mode so that simple assignments of the observed bands to motion largely restricted to one bond or angle cannot be made.
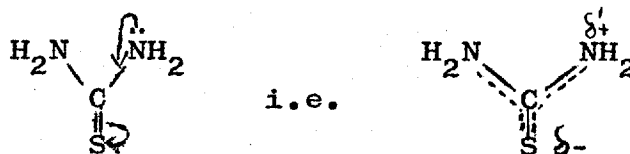
Stewart[40] has studied the infrared spectrum of thiourea over the range $4000 - 270$ cm^{-1} and has attempted a complete interpretation; all 18 fundamentals are assigned to bands above 400 cm^{-1} so that no bands should be observed in the far infrared region (except for lattice vibrations).

The far infrared spectrum of thiourea in the solid state has been measured to 135 cm^{-1} in this work and no bands were observed. Stewart's assignments are largely confirmed by the normal coordinate analysis of Yamaguchi et al.[42]

The infrared spectra of thiourea complexes have been extensively studied - mainly with a view to deciding whether coordination occurs through the sulphur or nitrogen atoms. Yamaguchi et al.[42] have studied the infrared spectra of some metal thiourea complexes to 270 cm^{-1} and have assigned the observed frequencies in terms of the fundamental vibrations of the thiourea molecule. They conclude that thiourea coordinates through the sulphur atom in the complexes they have studied.

The infrared spectra of the thiourea complexes described in this work have been measured. They are rather similar to those reported by Yamaguchi, thus indicating that thiourea is coordinated through the sulphur atom in these compounds too. This conclusion is supported by the observed strong nephelauxetic effect in the cobalt and nickel complexes.[43] In addition, all reported crystal structure determinations on thiourea complexes show that the thiourea coordinates through the sulphur atom.

The reason that thiourea usually coordinates through the sulphur atom probably lies in the capacity of the nitrogen atoms to donate electrons to the sulphur atom via the π system.

$$H_2N \diagdown \quad \diagup NH_2 \qquad \text{i.e.} \qquad H_2N \diagdown \quad \diagup \overset{\delta+}{N}H_2$$
$$\underset{S}{\overset{||}{C}} \qquad\qquad\qquad \underset{S \ \delta-}{\overset{||}{C}}$$

The nitrogen atoms then become relatively positive as the positive acceptor approaches the sulphur atom, thus strengthening the sulphur-acceptor bond. This effect is illustrated by the fact that in the salts of thiourea with strong acids the hydrogen is attached to the sulphur atom[44]. It has, however, been recently reported that the neutral acceptor boron trifluoride forms adducts with thiourea in which coordination occurs through the nitrogen atom.[45]

### X-ray Structural Data for Thiourea and its Complexes

The X-ray crystal structure determinations on the compounds considered in this chapter are summarised below.
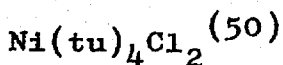
THIOUREA[46]

The molecule is accurately planar with C - S distance 1.71 A.$^{\circ}$ Single crystal nuclear magnetic resonance studies indicate that the hydrogen atoms lie in the plane.[47]

$Zn(tu)_2Cl_2$ [48]
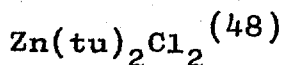
The zinc atom is tetrahedrally coordinated with $Zn - Cl = 2.32$ A$^\circ$, and $Zn - S = 2.35$ A.$^\circ$ The $C - S$ distance, 1.78 A$^\circ$ is significantly longer than in free thiourea. The $C - S - Zn$ angle is 108.6.$^\circ$ The maximum molecular symmetry is C_{2v}, but the site symmetry is only C_1.

$Cd(tu)_2Cl_2$ [49]
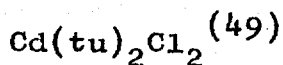
The cadmium atom is tetrahedrally coordinated with $Cd - Cl = 2.51$ A$^\circ$, and $Cd - S = 2.45$ A.$^\circ$ The $C - S$ distance, 1.64 A$^\circ$, is remarkably short. The maximum molecular symmetry is C_s.

$Ni(tu)_4Cl_2$ [50]

The nickel atom is trans-octahedrally coordinated with $Ni - Cl = 2.40$, 2.52 A$^\circ$, $Ni - S = 2.46$ A$^\circ$, $C - S - Ni$ angle $= 113.9^\circ$, $C - S = 1.73$ A$^\circ$. The $Ni - Cl$ distances are significantly different.

$Cu(tu)_3Cl$ [51]
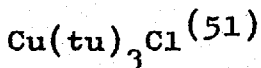
The cuprous ion is tetrahedrally coordinated by two bridging thiourea molecules and two non-bridging thiourea molecules. The chloride ion is ionic. $Cu-S$ (bridging) $= 2.42$, 2.38 A$^\circ$, $Cu - S$ (non-bridging) $= 2.35$, 2.31 A$^\circ$.

C – S = 1.81 A^O (for all thiourea molecules within experimental error) The maximum molecular symmetry about the Cu is C_{2v}.

$Pd(tu)_4Cl_2$ [52]
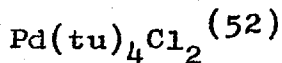
The coordination about the palladium is square planar with Pd–S = 2.33, 2.35 A^O; S – Pd – S angle = 82°, 85°, 97°; Pd – S – C angle = 107°; C – S = 1.72, 1.78 A^O

Square Planar Compounds

The compounds $Ni(tu)_4XO_4 \cdot$ MeOH (X = S, Se) are diamagnetic and their reflectance spectra (Table 2), consisting of one fairly intense, broad band in the yellow, are similar to those of the square planar nickel (II) complexes with substituted thiourea donors. [56] In the infrared spectra of the anions, the triply degenerate asymmetric stretch is only slightly split and the symmetric stretch is very weak. The anions are therefore considered to be ionic. The two compounds have similar X-ray powder patterns (Table 3) indicating that they are structurally similar. The lattice dimensions are slightly larger for the selenate. The methanol in the nickel sulphate complex could not be driven off by heating the compound at 140° in vacuo for 24 hours and the selenate complex decomposes before the methanol is removed.

Table 2

Electronic Absorption Spectra

Compound	Phase	Band Maxima (cm^{-1})
$Co(tu)_2Cl_2$	Solid	16,500;15,500;13,700; 7440; 5810; below 4500
$Co(tu)_2Br_2$	Solid	16,100sh;15,150;13,200; 6730; 5600;below 4500
$Co(tu)_2I_2$	Solid	15,600sh; 14,500;13,000; 6800; 5350;below 4500
$Co(tu)_2I_2$	Solution in acetone $(\nu_3 0.0029m)$ $(\nu_2 0.029m)$	15,100sh;14,500 (630);* 13,800 (790); 13,600sh; 12,800 (710);7300 (110); 6250 (110); 5100 (93)
$Ni(tu)_4SO_4 \cdot MeOH$	Solid	17,200
$Ni(tu)_4SeO_4 \cdot MeOH$	Solid	17,200
$Ni(tu)_6(NO_3)_2$	Solid	20,200sh;14,500; 12,700s 8650
$Ni(tu)_6Br_2$	Solid	20,000sh; 13,900; 13,000sh; 8600

* Molar extinction coefficients in parentheses

Table 3

Interplanar Spacings[*] for $Ni(tu)_4XO_4 \cdot MeOH$ (X=S,Se)

$Ni(tu)_4SO_4 \cdot MeOH$		$Ni(tu)_4SeO_4 \cdot MeOH$	
7.07 A^O	m	7.13 A^O	m
6.50	m	6.58	m
4.72	s	4.79	s
4.19	w	4.29	m
4.02	w	4.08	w
3.66	m	3.72	m
3.58	m	3.62	m
3.52	m	3.57	m
3.12	m	3.14	m
2.90	w	2.90	w
2.86	w	2.86	w

* Most prominent lines only.

Attempts to prepare a nickel sulphate-thiourea complex
from dimethyl sulphoxide gave green (octahedrally
coordinated) products from which only part of the
dimethyl sulphoxide could be removed by heating at 140°
in vacuo to give another octahedral product. These products
had analyses which indicated that they were mixtures of
compounds of several stoichiometries and they were not
characterised. The methanol in the $Ni(tu)_4XO_4 \cdot MeOH$
compounds is presumably hydrogen bonded into the crystal
lattice and its presence is responsible, at least in part,
for the stability of the square planar form of the complex.
No other nickel - thiourea complexes with square planar
coordination could be prepared in this work. These
square planar complexes do not add ligands in the axial
positions at all readily; they are insoluble in cold
pyridine and are completely decomposed on boiling in
pyridine.

The yellow complexes $M(tu)_4X_2$ (M = Pd, Pt; X = $\frac{1}{2}SO_4$:
M = Pt, X = Cl) are probably square planar, this being the
usual stereochemistry for these metals in the divalent
state. The sulphate groups are shown by their infrared
spectra to be ionic.

The far infrared spectra of all six square planar compounds (Table 4) each show a medium strength band in the region 311 - 272 cm^{-1}. This is readily assigned as due to the infrared active metal sulphur stretching vibration by comparison with the $Pd(SCN)_4^{2-}$ and $Pt(SCN)_4^{2-}$ ions [31,53] where the corresponding modes occur at 286 and 283 cm^{-1} respectively. The nickel and platinum compounds both show a strong band at about 200 cm^{-1}, the band being split in the nickel compounds and broad in the platinum complexes. This band is assigned as a metal - sulphur bending mode related to the E_u (infrared active) in - plane bending mode of a D_{4h} ML_4 species. (This mode occurs at 194 cm^{-1} in $K_2(PdCl_4)$ and and 190.5 cm^{-1} in $K_2(PtCl_4)$.[54]) The corresponding band in the palladium compounds is split into three components, the highest energy band being the weakest. In view of the large number of low frequency vibrational modes expected for a square planar $M(tu)_4^{2+}$ cation, detailed assignments of the spectra below 200 cm^{-1} cannot be given.

Table 4

Far Infrared Absorption Frequencies [*] (cm^{-1})

Compound	M–S stretches	M–X stretches	Other Bands
$Co(tu)_2Cl_2$	278sh, 249	314, 292	
$Co(tu)_2Br_2$	274, 251	235, 227sh	
$Co(tu)_2I_2$	269, 242	200, 159w	
$Zn(tu)_2Cl_2$	(266, 255–235, see text)		
$Zn(tu)_2Br_2$	259, 240	200, 185	
$Zn(tu)_2I_2$	256, 227	166, 150m	
$Cd(tu)_2Cl_2$	(225, 204, 185, see text)		
$Cd(tu)_2Br_2$	222, 212	163, 150m	
$Cd(tu)_2I_2$	231 194	140	
$Pd(tu)_4Cl_2$	275m		202w, 190, 181 150
$Pd(tu)_4SO_4$	279m		258vw, 206wsh 195br, 180br 150br
$Pt(tu)_4Cl_2$	275		250vwbr, 200 180wbr.
$Pt(tu)_4SO_4$	275		200br, 180wbr
$Ni(tu)_4SO_4 \cdot MeOH$	311m		254wm, 204, 197 156m
$Ni(tu)_4SeO_4 \cdot MeOH$	310m		256m, 207sh, 198, 156m

Table 4 (continued)

Compound	M–S stretches	M–X stretches	Other Bands
$Ni(tu)_6Br_2$	216		163
$Ni(tu)_6(NO_3)_2$	222br		172m,156
$Ni(tu)_4Cl_2$	200br ?	220sh ?	170,158sh
$Mn(tu)_4CL_2$	186, 182?	220?	158,128

* All bands are strong unless otherwise stated,

The query (?) indicates doubt in the assignment, not

the presence, of a band.

Since the overall symmetry of the complex cations will be very low, it might be expected that the $\nu_1(A_{1g})$ and $\nu_2(B_{2g})$ stretching modes, which are infrared inactive in D_{4h} symmetry, would become weakly allowed. The spectra of the nickel compounds show a weak band at about 255 cm^{-1} which may correspond to one of these modes. The corresponding frequencies for the square planar anion $PdCl_4^{2-}$ are [22,54]

ν_6 (E_u) 332 cm^{-1}, $\nu_1(A_{1g})$ 310 cm^{-1}, $\nu_2(B_{2g})$ 275 cm^{-1}

The weak, broad band at 250 - 258 cm^{-1} in the palladium complexes may have a similar explanation.

Tetrahedral Complexes $M(tu)_2X_2$

The reflectance spectra (Table 2) of $Co(tu)_2X_2$ (X = Cl, Br) indicate that they retain in the solid state the tetrahedral structure that they have in solutuion[43] The reflectance spectrum of $Co(tu)_2I_2$ is closely similar to those of the analogous chloride and bromide thus indicating a tetrahedral structure for this compound.

The high molar extinction coefficients of the solution

of the complex in acetone and the value of the magnetic

moment $\mu = 4.43$ B.M., $\theta = -4°$ after correction for

temperature independent paramagnetism of 600×10^{-6} [55]

cgs and diamagnetism of -190×10^{-6} cgs units [17] are

in agreement with this. Treatment of these results

according to the procedure used by Cotton et al. [6] and

taking $\gamma_2 = 6,000$ cm^{-1} and $\gamma_3 = 14,000$ cm^{-1} gives the para-

meters Dq$=-345$ cm^{-1}, B$=640$ cm^{-1} $\lambda = 120$ cm^{-1}. These values

are reasonable for a $Co(tu)_2I_2$ tetrahedron. (Using the

same averaging procedure to obtain γ_2 and γ_3 for the

bromide and chloride complexes as was used for the iodide

the values of Dq and B obtained are 350 cm^{-1} and 680 cm^{-1}

for the bromide; and 360 cm^{-1} and 700 cm^{-1} for the chloride.)

In a C_{2v} ML_2X_2 complex two metal-X and two metal-

sulphur stretches would be expected (Table 1.) In the

nine complexes considered here (M=Co,Zn,Cd; X= Cl, Br, I)

four bands are observed (Fig 1) except in those cases

where they would be expected to lie very close together

and partially obscure each other, and one case ($Cd(tu)_2I_2$)

where the lowest energy band would be expected to lie

below the limit of the measurements. The spectra of the

zinc and cadmium bromide and iodide complexes are

generally similar to those of the corresponding cobalt

Fig. 1

Far Infrared Spectra of Co(tu)$_2$X$_2$ Compounds
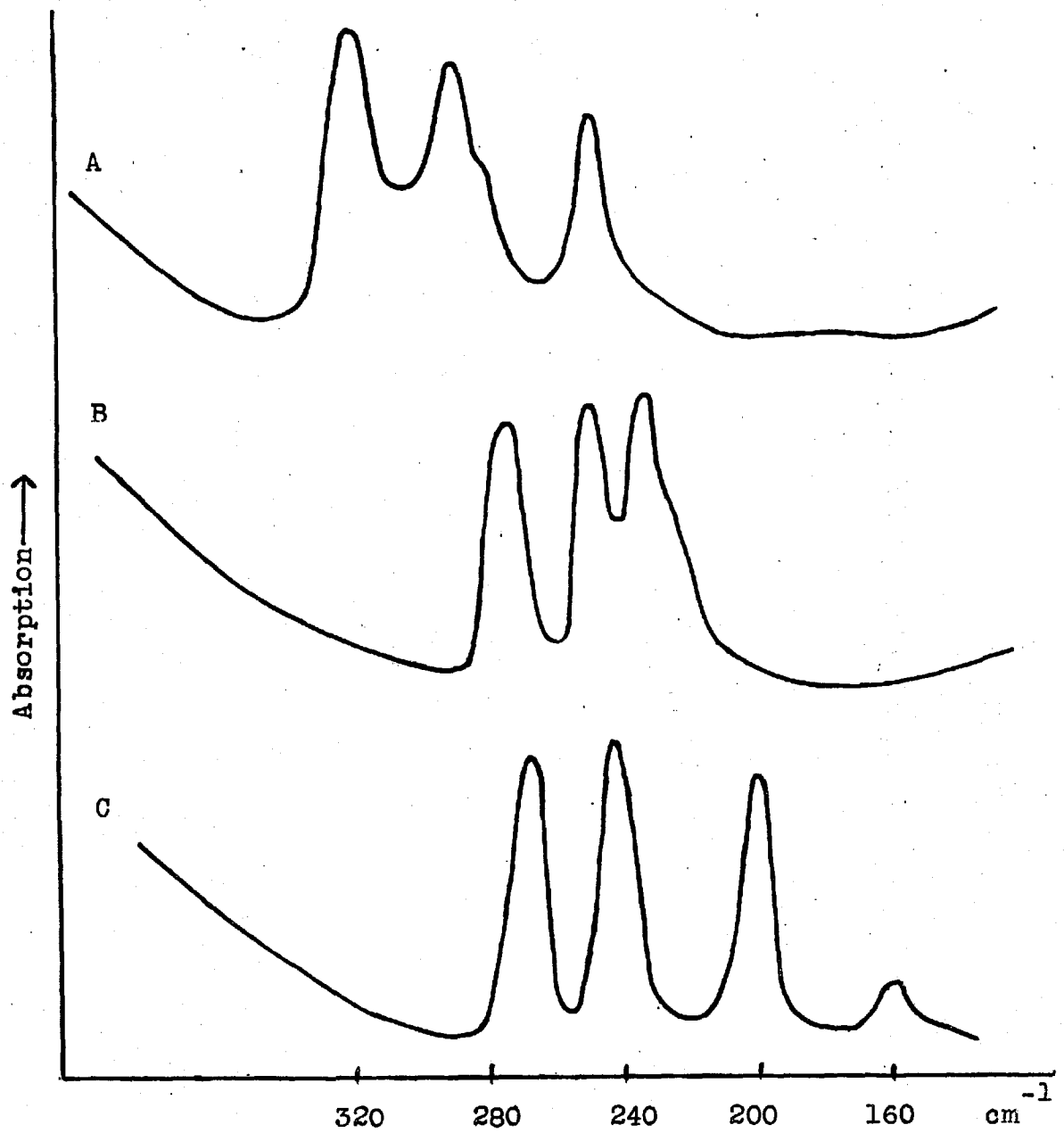
A   Co(tu)$_2$Cl$_2$

B   Co(tu)$_2$Br$_2$

C   Co(tu)$_2$I$_2$

compounds, after allowing for the usual shift to lower energy of the metal ligand stretching frequencies along the series; Co, Zn, Cd. [24-29] These compounds are therefore considered to have a tetrahedral structure.

The metal-sulphur stretches are assigned on the basis that, for a given metal in a given stereochemistry, their position would not change greatly with change of the anionic ligand. Small changes would be expected because of the motion of the other atoms in the molecule during the vibration, interaction between vibrational modes, and differences in the detailed structures. Metal-halogen stretching frequencies are assigned by comparison with the MX_4^{2-} ions [24,25,26] and the tetrahedral Mpy_2X_2 species. [29] The spectre of the iodide complexes, in which the metal-halogen stretching vibrations occur at much lower energy than the metal-sulphur stretching frequencies, permitted a clear assignment of the vibrational modes.

The spectra of $Zn(tu)_2Cl_2$ and $Cd(tu)_2Cl_2$ are not clearly resolved due to the close proximity of the metal-sulphur and the metal-chloride stretching frequencies. Consideration of the frequencies of these modes in the other compounds leads to the conclusion that all four bands will occur close to 210 cm^{-1} in the cadmium complex.

and close to 250 cm^{-1} in the zinc complex.

Under these conditions assignment of the observed absorption bands to vibrations involving a specified ligand is not justified. A similar situation probably occurs in $Co(tu)_2Br_2$ but in this case the interaction appears to be less and it seems reasonable to assign the two higher energy bands as predominantly metal-sulphur stretching vibrations and the lower one as a predominantly metal-bromine stretching mode.

The far infrared spectrum of $Cu(tu)_3Cl$ showed no band above 130 cm^{-1}. The metal-sulphur stretching frequencies for this complex probably lie below the limits of the measurements.

Octahedral Complexes

The reflectance spectra of the compounds $Ni(tu)_6(NO_3)2$ and $Ni(tu)_6Br_2$ are similar and can be interpreted in terms of octahedral stereochemistry with 10Dq=8600 cm^{-1} and B=530 cm^{-1} (β=0.49). The shoulder on the low energy side of ν_2 is probably caused by a spin-forbidden transition; using Tanabe and Sugano's determinants, the above parameters, and assuming C=4B, the $^1A_{1g}$ state is predicted to cross the $^3T_{1g}$ state at about 13,500 cm^{-1}. These two states can interact through spin orbit coupling, resulting in the singlet level acquiring some triplet

character and therefore the optical transition from the
ground state to the "singlet" level gains some intensity.
No splitting of ν_1 is observed. The difference between
the electronic reflectance spectrum of $Ni(tu)_6(NO_3)_2$ and
the solution spectrum in acetone[43] is caused by solvolysis
of the complex.[56] The magnetic moment of $Ni(tu)_6(NO_3)_2$
at room temperature is 3.09 B.M.[43]

The far infrared spectra of these two compounds are
rather similar, both consisting of broad bands at about
220 cm^{-1} and 160 cm^{-1}. The lower band is split into two
components in the nitrate. Since metal-thiourea
stretches occur in very roughly the same position as
metal-pyridine stretches in tetrahedral and planar
compounds, it is reasonable to suppose that the same will
be true of the octahedral compounds. The 220 cm^{-1} band
is then assigned as the octahedral metal-sulphur stretch
and the lower band as a bending mode. The Ni-S-C bond
angle will be less than $180°$ (probably about $110°$) and
the highest symmetry about the nickel atom is then S_6.
In this point group the T_{1u} stretch in O_h symmetry splits
into A and E stretches which are both infrared active.
It is possible that the two bands observed are these two
stretching modes but the splitting seems very large at such
low energies.

The far infrared spectrum of $Ni(tu)_4Cl_2$ is similar to that of the $Ni(tu)_6^{2+}$ ion with the addition of a strong band at 200 cm^{-1}.(Fig 2) It is therefore reasonable to assign this band to the Ni-Cl stretching frequency, this involves having a metal sulphur stretch at higher energy than a metal-chlorine stretch which is contrary to the situation in the tetrahedral compounds but the symmetries of the vibrations in the two cases are quite different. This assignment also involves a very low metal-chlorine stretch compared to that in $Nipy_4Cl_2$ (246 cm^{-1}). [29] In Chapter Five, the thioacetamide analogues of the compounds discussed in this chapter will be described; it will be shown that, in tetrahedral $M(tam)_2X_2$ compounds, the metal-sulphur stretching frequency comes lower than in the thiourea complexes whereas the metal-halogen stretches are higher. If this can be extended to the octahedral compounds, then examination of the spectra leads to the conclusion that the above assignments should be reversed and the 220 cm^{-1} band assigned as the metal-chlorine stretch. This assignment removes the previous objections and is in agreement with the trend that metal-ligand stretching frequencies are higher in cationic species than they are in neutral species, [29] but does not account for the relative weakness of the band due to the metal-chlorine stretch.

Fig. 2

Far Infrared Spectra of some Octahedral Thiourea Complexes
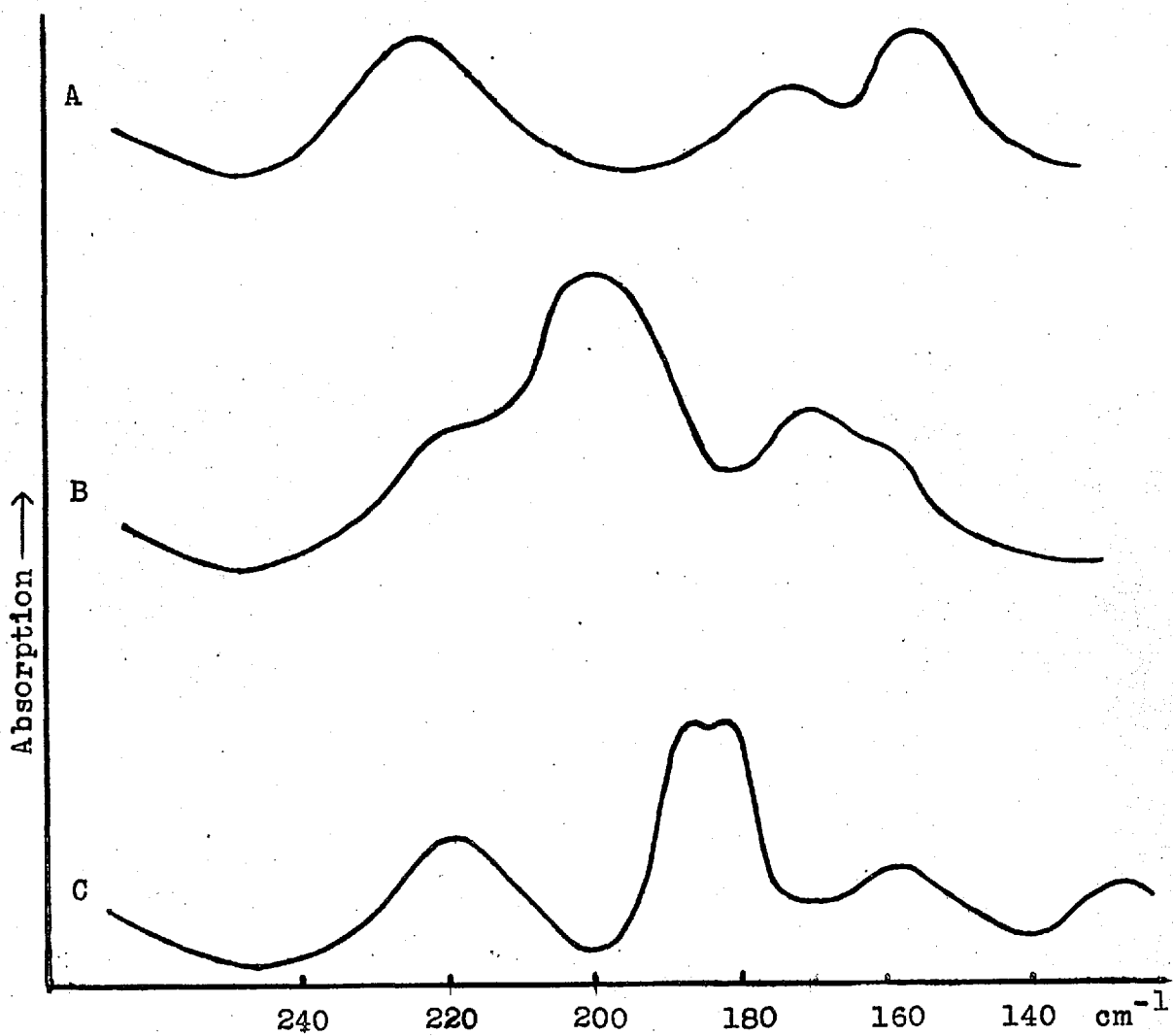
A $Ni(tu)_6(NO_3)_2$

B $Ni(tu)_4Cl_2$

C $Mn(tu)_4Cl_2$

The assignment of the far infrared spectrum of $Mn(tu)_4Cl_2$ (which is isomorphous with the nickel compound)[57] is most readily made in terms of this latter assignment, the metal-chlorine stretch coming at the same energy as in the nickel compound, but the metal-sulphur stretch is appreciably lower. These shifts are similar to those observed in the trans-octahedral $M(tu)_2(NCS)_2$ compounds (Chapter Four) and possibly reflect the greater B character of nickel relative to that of manganese.

Conclusions.

Vibrational modes involving mainly metal-sulphur stretching character have been observed for a number of thiourea complexes of divalent metals in the readily accessible spectral region $320-180cm^{-1}$. In some cases bending modes have also been observed. These complexes show the same variation in metal-ligand stretching frequency with stereochemistry that has been found for complexes with other ligands; i.e. those with tetrahedral geometry have frequencies which are higher than those of octahedral, but lower than those of planar, complexes. For the tetrahedral complexes the cobalt-sulphur stretches are $10-20$ cm^{-1} higher than zinc-sulphur stretches and $40-50$ cm^{-1} higher than the cadmium-sulphur stretching frequencies.

This decrease is somewhat less than is found for the metal-halide stretches and this may reflect the increase in B character of the metal along the series Co, Zn, Cd. The differences between the metal-sulphur stretching frequencies for the complexes of planar, tetrahedral and octahedral stereochemistry are such that their position is a useful indication of the stereochemistry of compounds for which other data is not available or is ambiguous, providing that the nature of the metal atom is taken into account.

It is of interest that the metal-halide stretching frequencies are very similar to those of the tetrahalogeno-metallate ions[23, 24, 25] and distinctly lower than those of the corresponding pyridine[29] and thioacetamide complexes. Clark and Williams[29] have suggested that the metal-ligand stretching frequencies for a given metal and ligand, and in a given stereochemistry move to higher frequencies with increasing positive charge on the species. This would suggest that the sulphur atom in the tetrahedral thiourea complexes is acting like a negatively charged species, possibly as a result of the effect mentioned on page 28 and/or the π donor effect of the sulphur lone pairs.

The ratios $\nu(\text{M-Br})/\nu(\text{M} - \text{Cl})$ and $\nu(\text{M} - \text{I})/\nu(\text{M} - \text{Cl})$ are about 0.77 and 0.65 respectively, as is found for the MX_4^{2-} ions[25] and the pyridine complexes.[29]

CHAPTER THREE

Metal-Sulphur and Metal-Oxygen Stretching Frequencies in some Thiourea Complexes of Divalent Metals.

In the previous chapter it was shown that divalent metal-thiourea stretching modes occur in a readily accessible region of the far infrared spectrum and that, from the position of these modes within this region it is possible, in principle, to distinguish between octahedral, tetrahedral, and planar compounds. In this chapter the extension of this work to some more complicated thiourea complexes containing oxyanions is described.

This study was carried out with three main aims. Firstly, in order to determine, whether the presence of metal-oxygen stretching vibrations and other modes associated with the polyatomic anions would so complicate the far infrared spectra that little chemical information could be obtained without performing a thorough vibrational analysis. Secondly, it was hoped to determine the position of some metal-oxygen stretching vibrations, there being little information available on these modes in this type of complex. Thirdly, it was hoped to obtain some information concerning the structure of the compound $Co(tu)_4(NO_3)_2$ for which previous measurements of the

magnetic susceptibility and electronic spectrum did not permit a clear distinction between tetrahedral and octahedral stereochemistries.[43]

Acetato Complexes $M(tu)_2(CH_3COO)_2$

The complexes $M(tu)_2(CH_3COO)_2$ (M=Co,Zn) are isomorphous.[58] A recent X-ray structure determination of the zinc compound shows that the zinc atom is tetrahedrally coordinated by two sulphur atoms at 2.33 and 2.26 A°, and two oxygen atoms from different acetate groups at 1.97 and 1.95 A° The two remaining oxygen atoms are at 3.00 and 2.89 A° from the zinc atom. The Zn-S-C angles are about 101° and the Zn-O-C angles about 118°. [59] The results of this crystal structure determination were not available at the time this work was carried out.[60]

The reflectance spectrum of the cobalt compound (Table 5) is readily interpreted in terms of this tetrahedral structure. Taking the $^4A_2 \rightarrow {}^4T_1$(F) ($\nu_2$) transition at 7,700 cm^{-1} and the $^4A_2 \rightarrow {}^4T_1$(P) ($\nu_3$) transition at 16,900 cm^{-1}, the ligand field parameters are calculated as 10Dq = 4,500 cm^{-1} and B=740 cm^{-1} (β = 0.76). These values are reasonable for a $Co(tu)_2O_2$ tetrahedron. The $^4A_2 \rightarrow {}^4T_2$ transition would be expected to occur as a split band at ~ 4,500 cm^{-1}; this transition accounts for the observed absorption at 4000-5000 cm^{-1}.

Table 5

Electronic Spectra of the Cobalt Complexes

Complex	Phase	Absorption Maxima (cm^{-1})		
		ν_3	ν_2	ν_1
$Co(tu)_2(CH_3COO)_2$	Solid	17,800,16,700 15,050	8700,6490	†
$Co(tu)_2(CH_3COO)_2$	MeOH sat.with tu at 30°	~17,900sh,16,130(430)* 14,750(258)	8500sh 6680(92)	
$Co(tu)_3OSO_3$	Solid	16,700,15,400	7810,6450	†
$Co(tu)_3OSeO_3$	Solid	16,600,15,700 ~13,900sh	7810,6580	†
$Co(tu)_3(S_2O_3)$	Solid	16,700,14,400 13,500	~8700sh,7400	†
$Co(tu)_3(S_2O_3)\cdot H_2O$	Solid	16,000,14,400 13,800	~8700sh,6370	†

Table 5 (cont.)

Complex	Phase	ν_3 Absorption Maxima (cm^{-1})	ν_2	ν_1
$Co(tu)_4(ClO_4)_2$	Solid	16,300, 14,700, 14,100	8000	†
$Co(tu)_4(NO_3)_2(A)$	Solid	17,000, 16,100, 14,700, 13,100	8050, 6120	†
$Co(tu)_4(NO_3)_2(B)$	Solid	16,300, 14,600, 13,300	8000, 6140	†
$Co(tu)_4(NO_3)_2(C)$	Solid	16,700sh, 14,800	8970, 6450, 5100sh	
$Co(tu)_4(NO_3)_2$	5% in $Zn(tu)_4(NO_3)_2$	16,050, 14,450, 13,650	8050, 6030	
$Co(tu)_4(NO_3)_2$	n-BuOH sat. with tu at 28°	16,000sh, 14,530(585), 13,800(535)	7520(121), 6950(129), 6700(127)	

† These compounds have more absorption in the region 5000–3700 cm^{-1} than can reasonably be assigned to ν_2 or to vibrational overtones.

* Molar extinction coefficients in parentheses

The complex is insoluble in, or solvolysed by, most organic solvents. The solution of the compound in methanol is violet, indicating considerable solvolysis. Addition of large quantities of thiourea causes the solution to become blue, but the change is incomplete when the solution is saturated with thiourea (ca.1.5 molar). The visible-near infrared spectrum of this saturated solution is similar to the reflectance spectrum of $Co(tu)_2(CH_3COO)_2$ and the extinction coefficients of the bands are similar to those found for tetrahedral cobalt(II) species.

The magnetic susceptibility of this compound obeys a Curie - Weiss law over the temperature range 350-80°K and the magnetic moment is typical of tetrahedrally coordinated cobalt (II). (Table 10) After allowing for a temperature independent paramagnetism of 465×10^{-6} [55] cgs units and a diamagnetism of -163×10^{-6} cgs units, and using the relationship given by Cotton,[55] the value of the spin-orbit coupling constant is calculated as 135 cm^{-1}. This value is similar to that obtained for the complexes of type $Co(tu)_2X_2$. (Chapter Two and ref.43)

A CoS_2O_2 tetrahedron (C_{2v} symmetry) will have two metal-sulphur stretching frequencies and two metal-oxygen stretches (Table I). The metal-thiourea stretching

modes would be expected to lie in the same spectral region as in the C_{2v} halide complexes i.e. 280-240 cm^{-1} and the metal-oxygen stretches probably at rather higher energy. The strength of the absorption bands due to metal-sulphur stretching vibrations in the cobalt halide complexes is comparable to that of the absorption due to the bending vibrations of coordinated thiourea in the region 600-400 cm^{-1}. The two bands at 299 and 270 cm^{-1} in the spectrum of $Co(tu)_2(CH_3COO)_2$ are very much stronger than this and it seems reasonable to assign them as predominately metal-acetate stretching modes. The band at 240 cm^{-1} is then assigned as a metal-thiourea stretch, the other perhaps being obscured by the stronger metal-acetate band at 270 cm^{-1}. Similarly, the two very strong bands at 287 cm^{-1} and 270 cm^{-1} in the spectrum of $Zn(tu)_2(CH_3COO)_2$ are assigned as predominately zinc-oxygen stretching modes and the band at 248 cm^{-1} as a zinc-sulphur stretch.

No definite assignments can be given for the bands below 200 cm^{-1} (Table 6) in these compounds. The spectra of the two compounds are rather similar, but different from those of tetrahedral thiourea complexes not containing acetate groups. This suggests that these bands are due to torsions or bends associated with the coordinated acetate group.

Table 6

Far Infrared Spectra 400–130 cm^{-1} [a]

Compound	M-thiourea stretches	M-anion stretches	other bands
$Co(tu)_2(CH_3COO)_2$	240	299vs, 270vs	191, 180sh, 159
$Zn(tu)_2(CH_3COO)_2$	248	287vs, 270vs	198, 159
$Cd(tu)_2(CH_3COO)_2$	(238, 228, 221sh) [b]		c
$Co(tu)_3OSO_3$	279, 260	297	179br, 135
$Zn(tu)_3OSO_3$	249	269	176br, 135
$Cd(tu)_3OSO_3$	(228, 218, 200)		130
$Co(tu)_3OSeO_3$	284, 265sh	259	169, 133
$Zn(tu)_3OSeO_3$	270, 251sh	245	169, 134
$Co(tu)_3(S_2O_3).H_2O$	(275, 259, 252)		358w, 323w, 177w, 162w, 130
$Co(tu)_3(S_2O_3)$	(276, 255, 241)		353m, 323w, 176w, 166m, 134w
$Zn(tu)_3(S_2O_3).H_2O$	(255, 233)		358w, 176w, 166w
$Zn(tu)_3(S_2O_3)$	(254, 235)		359w, 325vw, c
$Cd(tu)_3(S_2O_3)$	(236, 219)		354w, 327vw, 165, 148m

Table 6 (cont.)

Compound	M-thiourea stretches	M-anion stretches	Other bands
$Co(tu)_4(ClO_4)_2$	284, 266m	—	163wsh, 139
$Zn(tu)_4(ClO_4)_2$	250, 238m	—	157wsh, 134
$Cd(tu)_4(ClO_4)_2$	237, 209	—	148wsh, 136
$Co(tu)_4(NO_3)_2$ (A)	294, 278, 256	—	169, 149, 137, 131
$Co(tu)_4(NO_3)_2$ (B)	300, 255	—	166, 139
$Co(tu)_4(NO_3)_2$ (C)	305, 271, 253	—	223vw, 209vw, 196vw 186sh, 176, 170.
$Zn(tu)_4(NO_3)_2$	258, 238m	—	169, 130
$Cd(tu)_4(NO_3)_2$	237	—	215-195wbr, 160br 138.

a   All bands strong unless otherwise stated

b   The bands shown in brackets probably arise from modes having both metal-thiourea and metal-anion stretching character.

c   Appreciable absorption in the range 180-130 cm^{-1}, but no maxima resolved.

The infrared spectrum of $Cd(tu)_2(CH_3COO)_2$ is somewhat different from the other acetate compounds and it may have a different structure. The far infrared spectrum shows one multicomponent band in the region where cadmium-thiourea and cadmium-acetate stretching vibrations would be expected for a tetrahedral complex; but in the absence of further structural data definite conclusions are not justified.

Sulphate and Selenate Complexes

Cotton, Faut and Mague[43] have measured the electronic (reflectance) spectrum, the infrared spectrum and the magnetic susceptibility of $Co(tu)_3SO_4$ and conclude t'at the complex is tetrahedral with monodentate sulphate ions.

The complexes $M(tu)_3OXO_3$ (M = Co, Zn; X = S, Se) are isomorphous (Table 7) the lattice parameters being rather larger for the Selenates. The electronic spectrum of $Co(tu)_3OSeO_3$ is very similar to that of the sulphato-complex.

The infrared spectrum of coordinated selenate does not appear to have been previously reported. The Se-O asymmetric stretch, which occurs at 875 cm^{-1} in the Raman

Table 7

Interplanar Spacings[*] for $M(tu)_3OXO_3$ (M=Co,Zn; X = S, Se)

$Co(tu)_3OSO_3$		$Zn(tu)_3OSO_3$		$Co(tu)_3OSeO_3$		$Zn(tu)_3OSeO_3$	
7.70 A°	m	7.71 A°	m	7.89 A°	m	7.89 A°	m
6.37	w	6.38	w	6.48	w	6.48	w
5.87	s	5.89	s	5.94	s	5.93	s
5.23	w	5.23	w	5.26	w	5.26	w
4.91	m	4.92	m	4.99	m	4.99	m
4.33	s	4.35	s	4.38	s	4.39	s
4.01	m	4.01	m	4.06	m	4.06	m
3.91	vw	3.91	vw	3.93	vw	3.93	vw
3.47	w	3.47	w	3.52	w	3.52	w
3.40	w	3.40	w	3.45	w	3.45	w
3.27	w	3.27	w	3.28	w	3.28	w
3.18	w	3.19	w	3.23	w	3.23	w
3.12	m	3.14	m	3.16	m	3.16	m
3.07	w	3.07	w	3.11	w	3.10	w
2.98	s	3.00	s	3.04	s	3.04	s
2.94	m	2.94	m	2.98	m	2.98	m
2.71	w	2.71	w	2.76	w	2.76	w

[*] Most prominent lines only

spectrum of the free ion in aqueous solution[61] splits

into three components in these complexes and the

symmetric stretch (833 cm^{-1} in the Raman spectrum of

the free ion in aqueous solution, infrared inactive)

appears strongly and moves down somewhat. (Fig.3, Table 8).

In C_{3v} symmetry it is predicted that the symmetric

stretch will become allowed and the asymmetric stretch

(T_1 in T_d symmetry) will split into two components

(E and A_1). The splitting, however, closely parallels

that of the sulphato complexes and possibly reflects the

low overall symmetry of the coordinated anion as a result

of the M-O-XO$_3$ angle being less than $180.^{\circ}$ Alternatively,

the weakest of the three bands in the asymmetric stretching

region may be an overtone of a bending mode which gains

intensity by interaction with one of the fundamental

stretching modes.

The selenate complexes show a weak band or shoulder

at 345 cm^{-1} which may be assigned as the symmetric

bending mode of the coordinated ion. The corresponding

vibration of the free ion occurs at 335 cm^{-1}.

The zinc and cobalt complexes have a first coordin-
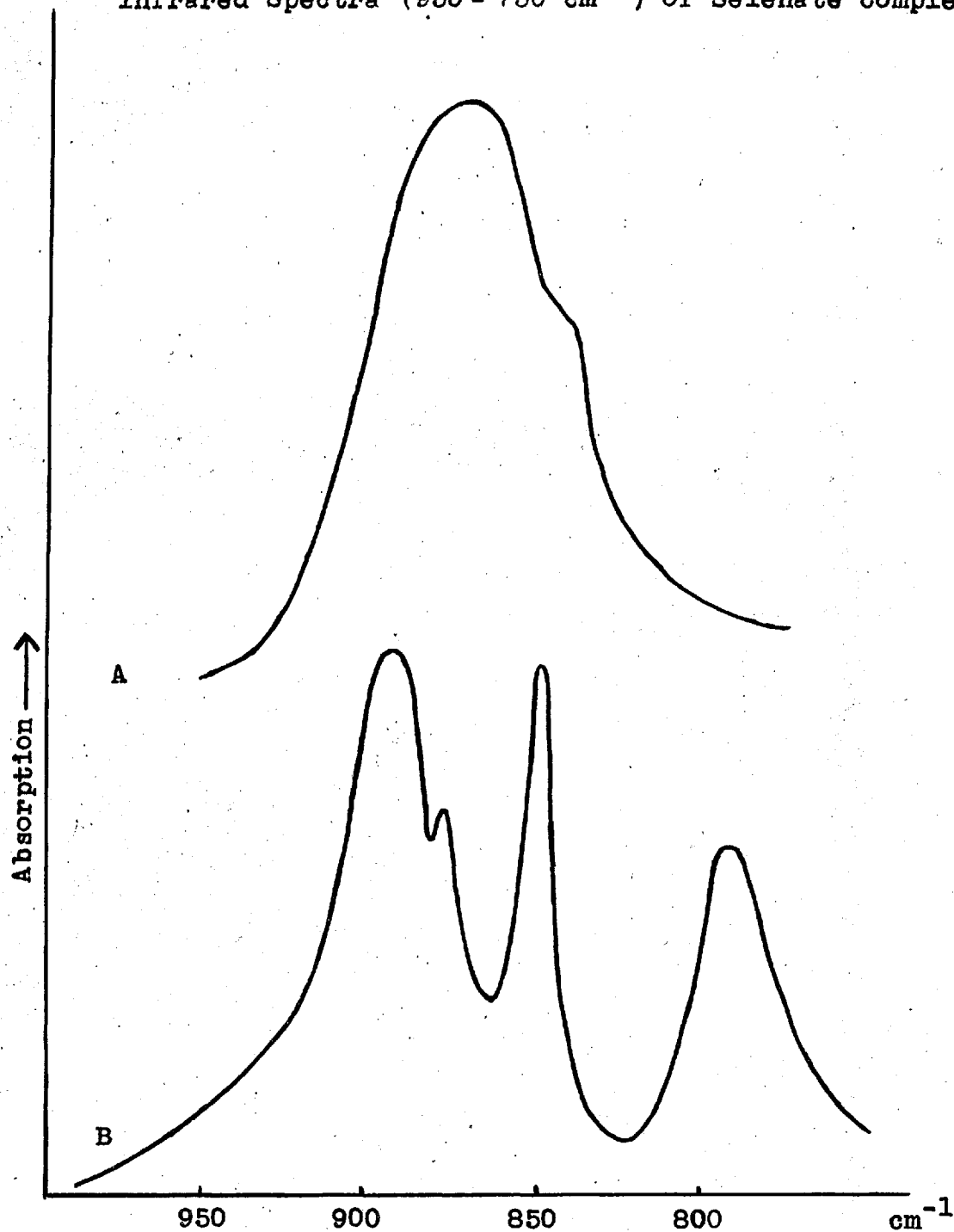
ation sphere of approximately C_{3v} symmetry and would

Fig. 3

Infrared Spectra (950 - 750 cm^{-1}) of Selenate Complexes

A $Ni(tu)_4SeO_4 . MeOH$

B $Co(tu)_3OSeO_3$

Table 8

Internal Modes of the Sulphate, Selenate and Thiosulphate Anions ,

Compound	Asymmetric Strs.	Sym Str.	Bends[*]
$Co(tu)_3OSO_3$	1151vs, 1082m, 1025vs	936vs	
$Zn(tu)_3OSO_3$	1143vs, 1088m 1034vs	959vs	
$Cd(tu)_3OSO_3$	1124vs, 1033vs	969vs	
SeO_4^{2-} ion	875	(833)	335
$Co(tu)_3OSeO_3$	893vs, 879m 849vs	792s	346vw
$Zn(tu)_3OSeO_3$	892vs, 879m 847vs	805s	
$S_2O_3^{2-}$ ion[(64)]	1125	1002	672, 339
$CH_3SSO_3^-$ [(64)]	1203–1215	1026–1032	653, 321
$Co(tu)_3(S_2O_3)H_2O$	1170s,1143s 1115sh,1070sh	1004s	644m.358w
$Co(tu)_3(S_2O_3)$	1172s,1125s 1105s,1065sh	1000s	651m,361w 323w
$Zn(tu)_3(S_2O_3)H_2O$	1171s,1143s 1120sh,1073w	1006s	646m,358w
$Zn(tu)_3(S_2O_3)$	1161s,1133s 1079w	1003s	651m,359w, 325vw
$Cd(tu)_3(S_2O_3)$	1170sh,1153s, 1127s,1110sh, 1079w	999s	645m,354w 327vw

* Bends in the range 600–400 cm^{-1} are obscured by thiourea absorption.

therefore be expected to have two metal-thiourea stretching frequencies (Table 1) in the range 280-240 cm^{-1} (for the cobalt complexes) or 260-230 cm^{-1} (for the zinc complexes), together with a metal-oxygen stretch. Cobalt-sulphate stretching frequencies have been observed in the region 280-260 cm^{-1} in some octahedral compounds with bridging sulphate groups,[62] but cobalt-monodentate sulphate stretches have not been reported. A Raman spectral study of aqueous iridium (III) sulphate solutions shows the presence of monodentately bonded sulphate groups and a band at 255 cm^{-1} which is assigned as the $(H_2O)_5Ir-OSO_3$ stretch.[63] Since octahedral iridium (III)-pyridine stretches have been observed to occur in roughly the same spectral position as tetrahedral cobalt-pyridine stretches,[29] it would be expected that tetrahedral cobalt-sulphate stretching modes would also occur at about 255 cm^{-1}. The normal vibrational modes of the $M(tu)_3OXO_3$ complexes that involve chiefly metal-ligand stretching character would therefore be expected to have both metal-sulphur and metal-oxygen stretching character. Examination of the spectra (Fig 4, Table 6) suggests that it is reasonable to assign the two bands at 279 and 260 cm^{-1} in $Co(tu)_3OSO_3$ as predominantly metal-thiourea stretching modes and the very

Fig. 4   62.

Far Infrared Spectra $(340-130\ cm^{-1})$ of some $M(tu)_3OXO_3$ Compounds
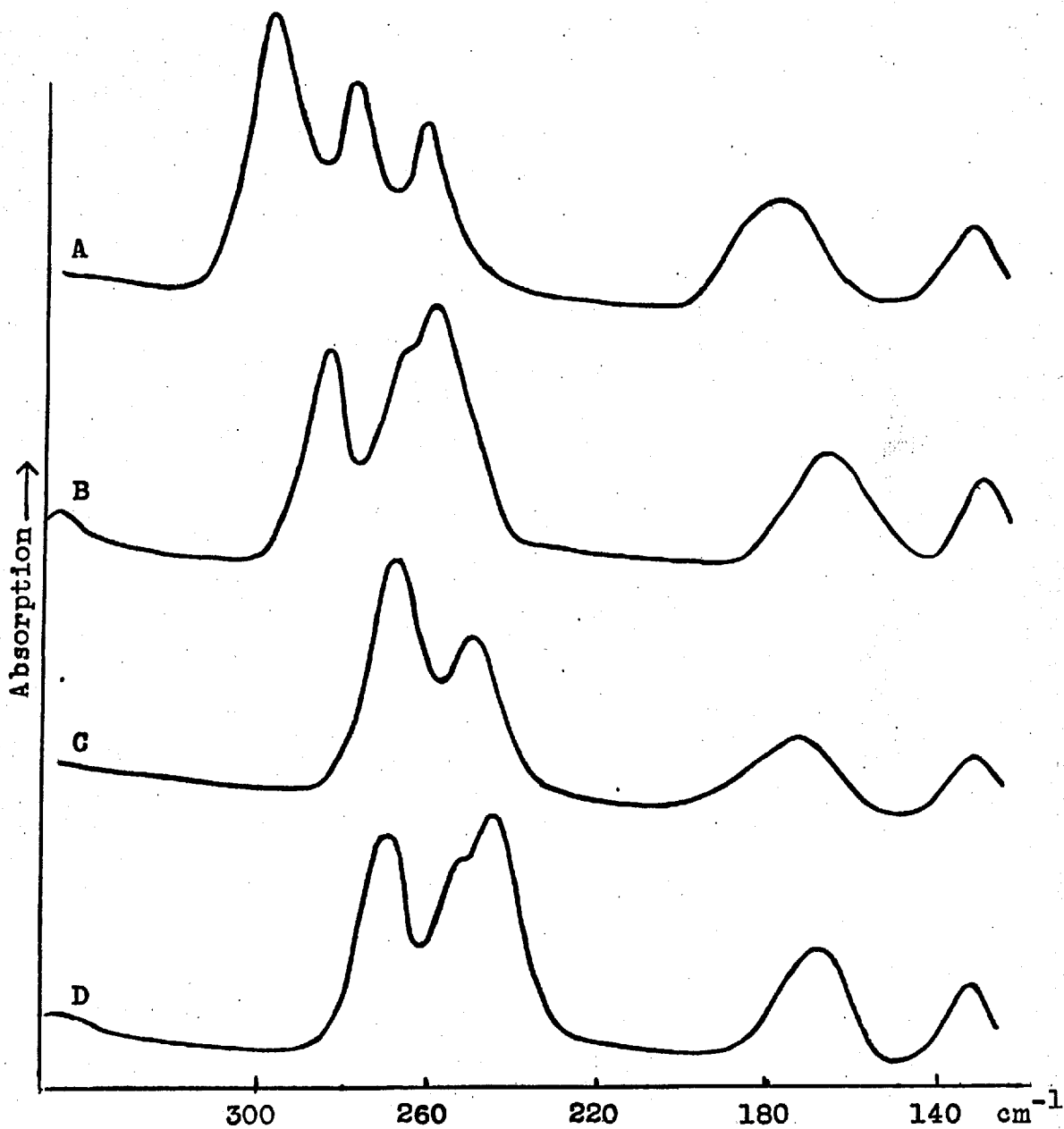
A $Co(tu)_3OSO_3$ C $Zn(tu)_3OSO_3$

B $Co(tu)_3OSeO_3$ D $Zn(tu)_3OSeO_3$

strong band at 297 cm^{-1} as the metal – oxygen stretch. In
the corresponding selenato-complex the strongest band moves
down by 38 cm^{-1} relative to the sulphate, whilst the other
two bands appear at slightly higher energies. This is in
good agreement with the suggested assignments.

The far infrared spectrum of the compound
$Zn(tu)_3OSO_3$ has only two bands between 300 and 200 cm^{-1}.
Following the assignments for the cobalt complexes, it is
reasonable to assign the stronger band as due to the zinc-
oxygen stretch and the weaker as the lower of the two
zinc—sulphur stretches. The other zinc — sulphur stretch
is probably obscured by the stronger metal — oxygen
stretching band. Again, the spectrum of the selenate
complex supports these assignments; all three bands are
seen, the strongest, at 245 cm^{-1}, being assigned as the
metal — oxygen stretch.

The position of the metal – sulphate and metal –
selenate stretching frequencies supports the assignments
of the spectra of the acetato complexes. The infrared
spectrum of $Cd(tu)_3SO_4$ is so similar to those of the cobalt
and zinc compounds as to suggest that this complex also has
a tetrahedral structure. The far infrared spectrum has a
complex absorption band with at least three components in
the region 200 – 230 cm^{-1}. It is likely that all three metal
ligand stretching vibrations occur in this region and the

position tends to confirm the tetrahedral structure.
Attempts to prepare the corresponding selenato complex
failed to give a pure product.

It is of interest that, whereas the metal-sulphate
stretch comes higher than the metal-thiourea stretches in
$Co(tu)_3OSO_3$, the three infrared active metal-ligand
stretching modes occur very close together in the corres-
ponding zinc and cadmium compounds. This may reflect the
greater B character of the d^{10} ions.

The cobalt and zinc sulphato complexes both show
a broad band at 176-177 cm^{-1} which moves down to 171 - 169 cm^{-1}
in the selenato complexes. The energy of the band and its
independence of the nature of the metal suggests that the
vibration does not have much metal-ligand stretching
character. A corresponding band is not observed in the
halide complexes, and the magnitude of the shift from
sulphate to selenate suggests that this band is a torsion
about the M - O bond or a bend associated with the
coordinated anion. There is considerable absorption below
180 cm^{-1} in the far infrared spectrum of $Cd(tu)_3OSO_3$ but
no definite band is resolved.

All the sulphate and selenate complexes show a
band at the limit of the measurements. This is probably

a bending mode associated with the metal-thiourea bond (c.f. the perchlorate compounds).

Thiosulphato Complexes

In order to clarify the band assignments in the sulphato complexes the compounds $M(tu)_3S_2O_3$ (M = Co, Zn, Cd) and $M(tu)_3S_2O_3 \cdot H_2O$ (M = Co, Zn) were studied. Comparison of the infrared spectra of the compounds with those of the halide complexes permitted a clear assignment of the bands due to the thiosulphate group (Table 8). It was not possible to observe the bands due to the thiosulphate group in the range 600 - 400 cm^{-1} because of the strong absorption due to bending modes of thiourea in this region. The infrared bands due to the thiosulphate group are rather similar in the five compounds. The S - O asymmetric stretch ν_4 moves up from the free ion value [64] and is broadened, whilst the E O-S-O bend ν_5 is lowered. These changes are similar to those observed in S - alkyl thiosulphates and suggest that the thiosulphate ion is monodentate through the sulphur in both the hydrated and the anhydrous complexes. This type of coordination occurs in most palladium, platinum and cobalt (III) complexes.[65,66] The symmetric O - S - O bending mode ν_3 (A_1 symmetry) will interact appreciably with ν_2, the S - S stretch (A_1 symmetry)

and the lowering of γ_3 probably reflects the lowering of γ_2 as a result of coordination of the sulphur. All the compounds show a weak to medium band at 353-358 cm^{-1} and the anhydrous compounds also have a weak band at about 325 cm^{-1} (This band may be too weak to be observed in the hydrated compounds; these giving somewhat poorer spectra.) These absorptions probably represent the components of γ_6 (E in C_{3v}) split by the low overall symmetry of the coordinated anion.

The electronic spectra of $Co(tu)_3S_2O_3$ and $Co(tu)_3S_2O_3.H_2O$ are virtually identical and typical of cobalt (II) in a tetrahedral environment. Analysis of the spectra by the usual method gives 10Dq = 4,000 cm^{-1}, B = 700 cm^{-1} indicating that thiosulphate lies near thiourea in the spectrochemical series as would be anticipated from the effective number of electrons available for γ— donation to the metal from the sulphur atom. However, since it only contributes about one quarter of the ligand field, the exact position of thiosulphate in this series cannot be determined.

The far infrared spectra of the two cobalt compounds are rather similar, each having three bands in the metal-sulphur stretching region. These are presumably the

three metal-ligand stretching modes predicted in C_{3v} symmetry, but assignments of individual bands to specific metal-ligand modes cannot be given. However, the similarity of the spectra confirms that the water molecule is not present in the first coordination sphere of the cobalt ion in $Co(tu)_3S_2O_3 \cdot H_2O$ and the absence of a band above 280 cm^{-1} supports the assignments of the sulphato compounds. The zinc and cadmium compounds show only two bands in this region, presumably due to the overlap of the three infrared active stretching modes. The assignments of the lower energy bands follow those of the sulphato complexes.

Perchlorate complexes $M(tu)_4(ClO_4)_2$

The compound $Co(tu)_4(ClO_4)_2$ has been shown by its magnetic susceptibility and electronic spectrum to contain an essentially tetrahedral $Co(tu)_4^{2+}$ ion. The infrared spectrum shows that the perchlorate group is ionic[43]. The magnetic moment of the sample of this compound prepared in this work was very similar to that found by Cotton,[43] but the position of γ_2 in the electronic reflectance spectrum found here is appreciably different

from that given for the mull spectrum by Cotton, and agrees more closely with the solution spectrum, although there is still some discrepency (Table 5).

For a CoS_4 grouping of T_d symmetry, only one infrared active cobalt - sulphur stretching frequency would be expected, whereas the far infrared spectrum of $Co(tu)_4(ClO_4)_2$ shows two bands in the cobalt - sulphur stretching region, one at 284 cm^{-1} and a rather weaker one at 266 cm^{-1}. This may be explained by the Co - S - C angle being less than 180° (probably about 110° as is observed in other tetrahedral thiourea complexes) and the environment of the cobalt atom when the carbon atoms are considered will therefore have a symmetry lower than T_d.

The reflectance spectrum of the compound shows much stronger absorption near to 4000 cm^{-1} than does the corresponding zinc complex although no definite maximum can be seen on account of the vibrational bands in this region. This absorption is due to the $^4A_2 \rightarrow {}^4T_2$ transition (ν_1) which is very weak in T_d symmetry but which is normally seen [67] when distortion of the tetrahedron causes one or more of its components to become electric dipole allowed.

The compounds $M(tu)_4(ClO_4)_2$ (M = Zn, Cd), although not isomorphous with the cobalt complex, have closely similar infrared and far infrared spectra, both showing two metal-thiourea stretching modes in the region expected for tetrahedral compounds. They probably also have a tetrahedral structure.

All three perchlorate complexes show a strong band at $134 - 139$ cm^{-1}. A band in this region is found for all tetrahedral complexes which have three or four molecules of thiourea coordinated to the metal ion, and it is probably due to a bending mode of the $M - S - CN_2H_4$ grouping. The corresponding mode in the $M(tu)_2X_2$ compounds presumably comes below the limit of the measurements.

The Raman spectra of concentrated (about 2 molar) aqueous solutions of $Zn(tu)_4(ClO_4)_2$ and $Cd(tu)_4(ClO_4)_2$ each show one strong, polarized band in the tetrahedral metal-thiourea stretching region. (at 242 and 228 cm^{-1} respectively). The Raman spectra of a series of aqueous solutions containing zinc perchlorate and thiourea in ratios from 1 : 0.5 to 1 ; 10 were measured using zinc concentrations of 2 molar (for the lower ratios) or 0.5 molar. In each case the spectra consisted of one

symmetrical polarized band at 242 cm^{-1}, the strength of the band increasing rapidly with increasing thiourea concentration at constant zinc concentration. The rate of increase showed no detectable tendency to decrease at the highest ratios. The spectra indicate that only one tetrahedral species is present in appreciable concentration over a thiourea concentration range of 20 : 1. Stability constant determinations[68] indicate that the predominant species present in aqueous acetone solutions of thiourea and zinc perchlorate over a wide range of thiourea concentrations is $Zn(tu)_4^{2+}$ and the apparent tendency to form higher thiourea complexes decreases with decreasing concentration of acetone. The 242 cm^{-1} band is therefore assigned as the symmetric zinc – thiourea stretching mode of the $Zn(tu)_4^{2+}$ cation. No band due to the asymmetric stretching mode could be detected, but the band due to this vibration is usually much weaker than that due to the symmetric stretch in the Raman spectra of tetrahedral species.[69] The preferential formation of the 4 : 1 species over the lower complexes may be a result of the 4 : 1 compound being tetrahedral whilst the others are octahedral. No bands due to an octahedral species were observed in the Raman spectra, but these would occur

below 200 cm^{-1} where the rising background from the
exciting line makes observation of weak bands difficult.

Nitrate Complexes M(tu)$_4$(NO$_3$)$_2$ (M = Co, Zn, Cd)

The infrared spectra of the compounds M(tu)$_4$(NO$_3$)$_2$
cannot be used to determine whether the nitrate groups are
coordinated since the regions around 1600 and 1400 cm^{-1}
are obscured by strong absorption of thiourea. ν_1 of
the nitrate groups (infrared inactive in the free ion)
occurs with weak to medium intensity at about 1050 cm^{-1}
but the band is appreciably weaker than in compounds with
coordinated nitrate ions (e.g. Cd(tam)$_4$(ONO$_2$)$_2$, Chapter five)

The complex Zn(tu)$_4$(NO$_3$)$_2$ has a far infrared spectrum
similar to that of the zinc perchlorate complex, indicating
that it has a tetrahedral structure. The greater separation
of the two zinc - sulphur stretching vibrations suggests a
greater deviation from T$_d$ symmetry. The cadmium nitrate
complex also has a far infrared spectrum that is most
readily interpreted in terms of the presence of a
tetrahedral Cd(tu)$_4^{2+}$ ion.

The Raman spectra of saturated aqueous solutions
of M(tu)$_4$(NO$_3$)$_2$ (M = Zn, Cd) are identical to those of the

perchlorate complexes, thus indicating the presence of the $M(tu)_4^{2+}$ ion in solution.

The compound of stoichiometry $Co(tu)_4(NO_3)_2$ exists in at least three different crystalline modifications which are readily distinguished by their X - ray powder patterns (Table 9.) and far infrared spectra in the range $320 - 240 \text{ cm}^{-1}$ (Fig.5) For convenience the forms are labelled A, B, and C. All three forms were obtained by the procedure described by Cotton et al.[43] although they were not recrystallized from ethyl acetate on account of their low solubility in this solvent. A small sample which was recrystallised from ethyl acetate had an X - ray powder pattern and far infrared spectrum very similar to form C. The factors influencing the form obtained could not be elucidated; variation of the ratio of thiourea to cobalt nitrate appeared not to affect this. When the preparation was carried out using acetone as solvent, a bright blue crystalline solid was initially obtained, but when filtered off the crystals rapidly crumbled to a blue-green solid identical with form A. This change was equally rapid in an open vessel, in a sealed tube and in vacuo and was not accompanied by any change in weight.
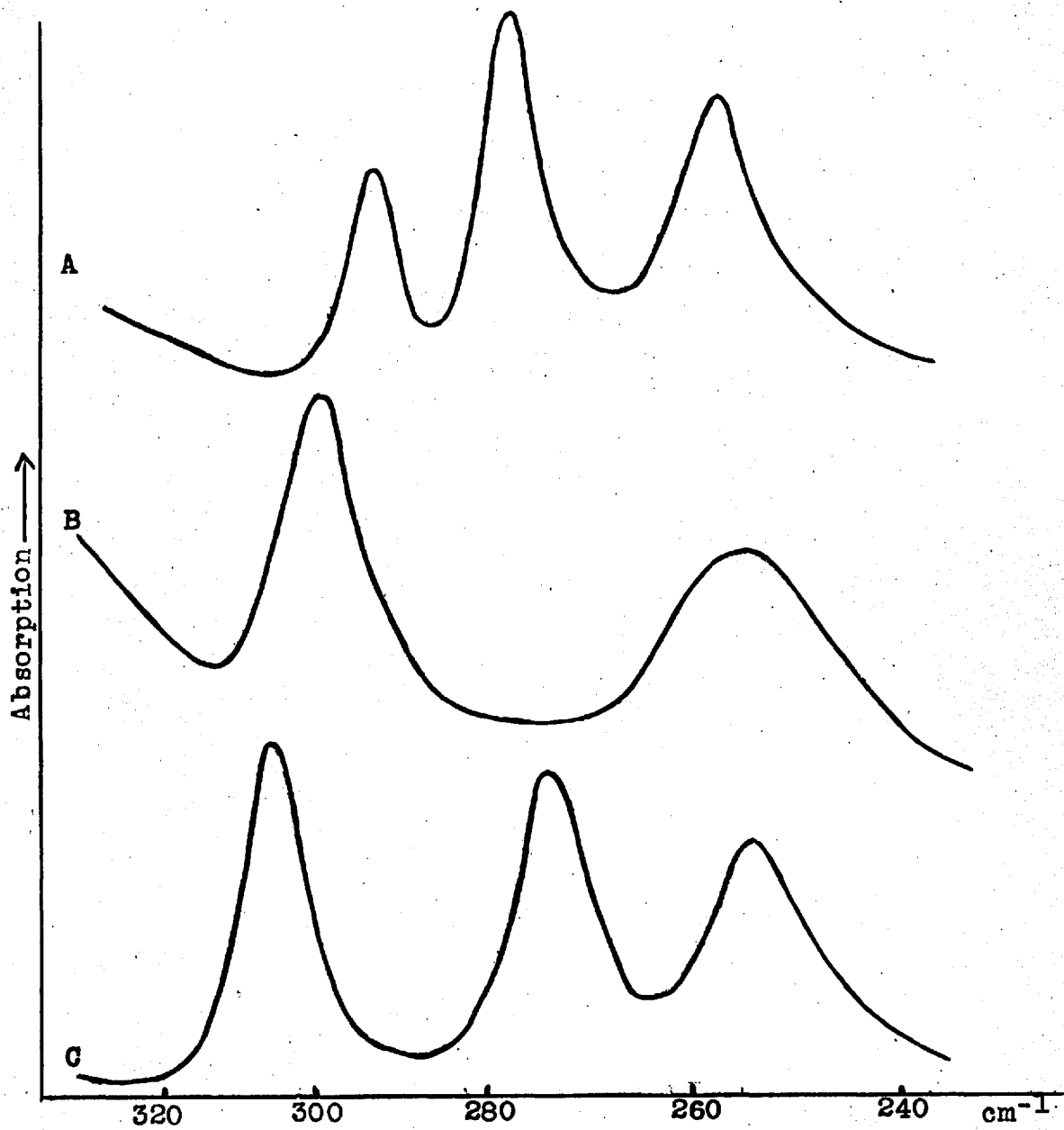
Table 9

Interplanar Spacings* for $M(tu)_4(NO_3)_2$ (M = Co, Zn)

M = Zn		M = Co (Form A)		M = Co (Form B)		M = Co (Form C)	
11.17 A°	w	11.09 A°	w	8.75 A°	w	7.23 A°	w
6.45	m	6.45	m	8.58	w	6.49	m
5.59	s	5.71	s	6.48	w	6.10	w
4.80	s	4.79	m	5.13	w	5.60	w
4.42	w	4.44	w	5.01	m	4.91	m
4.10	m	4.08	m	4.09	w	4.82	w
3.94	w	3.94	w	4.05	s	4.50	w
3.60	m	3.59	m	3.90	w	4.27	w
3.52	s	3.53	s	3.72	s	4.05	w
3.22	m	3.22	m	3.45	w	3.90	w
3.10	w	3.10	m	3.39	w	3.72	w
3.04	m	3.04	m	3.26	m	3.60	m
2.95	m	2.96	m	3.20	w	3.51	m
2.62	w	2.61	w	2.92	w	3.46	m
2.44	m	2.43	m	2.59	w	3.26	w

* Most prominent lines only.

Fig. 5

Far Infrared Spectra (320 - 240 cm^{-1}) of the Different

Forms of $Co(tu)_4(NO_3)_2$

A   Form A

B   Form B

C   Form C

Form B was also obtained by the procedure of Rosenheim.[70]

Form A gives an X - ray powder pattern very similar to that of $Zn(tu)_4(NO_3)_2$ indicating that they must be structurally very similar. The magnetic moments (Table 10), and intense reflectance spectra of forms A and B are similar to those of $Co(tu)_4(ClO_4)_2$ except that the ligand field bands are broader for the nitrates. The far infrared spectrum of form B is also similar to that of the perchlorate, having two bands in the tetrahedral cobalt-thiourea stretching region, but the energy difference between them is much greater. Form B was stable for some months when crystalline, but when finely powdered it changed in a few days to form A. Form A has three bands in the 320-240 cm^{-1} region. The spectrum is similar to that of $Co(tu)_3OSO_3$, except that the highest energy band is the weakest, and can be interpreted in terms of the structure $(Co(tu)_3ONO_2)^+$. tu. NO_3^-. Alternatively, the spectrum can be rationalized in terms of a distorted tetrahedral structure if the triply degenerate asymmetric stretch is split into two components and the symmetric stretch becomes allowed. The magnetic and electronic spectral properties of the complex $(Co(tu)_3ONO_2).$tu. NO_3^- might be very similar to those of the

Table 10

Magnetic Results for the Complexes

Compound		μ_{eff} *	θ
$Co(tu)_2(CH_3COO)_2$		4.47	-9°
$Co(tu)_4(ClO_4)_2$		4.63	-14°
$Co(tu)_4(NO_3)_2$	A	4.68	-10°
$Co(tu)_4(NO_3)_2$	B	4.66	-12°
$Co(tu)_4(NO_3)_2$	C	4.99	-11°

* Calculated from the relationship $\mu_{\text{eff}} = 2.84(\chi(T - \theta))^{\frac{1}{2}}$, where χ is corrected for diamagnetism but not for temperature independant paramagnetism. All the compounds obeyed the Curie – Weiss law over the temperature range $80 - 300^{\circ}K$.

tetrahedral $Co(tu)_4^{2+}$ ion. The former structure seems
unlikely, however, for four reasons:

a) The electronic reflectance spectrum of A – $Co(tu)_4(NO_3)_2$
in the charge transfer region is much more like that of
$Co(tu)_4(ClO_4)_2$ than that of $Co(tu)_3OSO_3$.

b) This form can be obtained in good yield from butanol
solutions containing thiourea and cobalt nitrate in the
molar ratio 2 : 1. The crystallization of a 4 : 1 complex
with included thiourea is unlikely under these conditions.

c) The strength and position of a band due to a metal–nitrate
stretching mode would be expected to be similar to that of
a metal – acetate stretching mode (i.e. much stronger,
and at higher energy than a band due to a metal – thiourea
stretching mode). All three bands in the metal – thiourea
stretching region for A – $Co(tu)_4(NO_3)_2$ are of comparable
intensity and assignment of the strongest band as a metal–
nitrate stretching mode would envolve a metal – oxygen
stretch at lower energy than a metal – thiourea stretch.
This is contrary to the situation in the acetato complexes.

d) The presence of uncoordinated thiourea in the compound
would be expected to give bands at about 1083 and 730 cm^{-1}
in the infrared spectrum.[42] These bands are not observed.

It appears therefore that the properties of both A and B forms are most readily rationalized by assuming that they contain the distorted tetrahedral $Co(tu)_4^{2+}$ grouping.

The nature of form C is more obscure. It has a distinctly higher magnetic moment than forms A and B, which would most readily be explained in terms of an octahedral structure. The reflectance spectrum, however, is similar both in band position and intensity to that of the other two forms. although the bands are somewhat broader. The electronic absorption which is present below 5000 cm^{-1} in forms A and B is not observed in form C, instead the band that would be ν_1 in an octahedral compound is broadened to lower energy. Assigning the electronic spectrum in terms of octahedral stereochemistry with $^4T_{1g} \rightarrow {}^4T_{2g}$ at 7,100 cm^{-1} and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ at 15,500 cm^{-1}, the derived spectral parameters are 10Dq = 8,000 cm^{-1}, B = 620 cm^{-1} which are reasonable values for a $Co(tu)_4(ONO_2)_2$ octahedron. However, the compound gives a much more intense absorption in the visible reflectance spectrum than is usual for octahedral cobalt compounds, the spectrum being similar in intensity to the tetrahedral cobalt compounds studied in this work. (Intensity measurements based on reflectance

spectra depend on the physical nature of the sample and
reference as well as on the oscillator strength of the
transition. However, in practice it is found that, provided
finely ground samples are used, and the conditions of
measurement are constant, then tetrahedral cobalt compounds
invariably have stronger absorption bands in the visible
than octahedral compounds of similar cobalt content. In
this work it was found that the measured maximum absorption
in the visible for all of the tetrahedral cobalt compounds
corresponded to an optical density of 1.5 - 1.7 whereas
for the octahedral cobalt compounds the maximum absorption
corresponded to an optical density of less than 0.9. An
octahedral $Co(tu)_4X_2$ compound could not be prepared in a
pure state to effect a direct comparison on intensities.
However, a sample of trans - octahedral [71] $Co(tu)_4Cl_2$
containing about 5% $Co(tu)_2Cl_2$ had a maximum absorption
in the visible corresponding to 0.8 on the optical density
scale. The strength of the absorption bands in the
octahedral nickel-thiourea complexes is similar to that
observed in other octahedral nickel compounds.)

The electronic spectrum can also be interpreted in
terms of tetrahedral stereochemistry by assigning γ_2 at
7,100 cm^{-1} and γ_3 at 15,500 cm^{-1} giving 10Dq = 4,200 cm^{-1}

and B = 670 cm^{-1}. The values are similar to those
obtained from the reflectance spectrum of $Co(tu)_4(ClO_4)_2$

Form C has three bands in the region 240 - 320 cm^{-1}
but the spread is even greater than in form A. In
octahedral stereochemistry one metal - nitrate stretching
frequency would be expected at about 255 cm^{-1} by analogy
with the other octahedral nitrato complexes[37] and the
highest metal - thiourea stretch at about 200 cm^{-1} as in
$Ni(tu)_4Cl_2$. This structure therefore does not explain
the far infrared spectrum. It is possible to explain the
far infrared spectrum by assuming that the complex is
basically tetrahedral but with a distortion similar to
that present in form A but somewhat larger in magnitude.
The average energy of the three bands (taking intensities
into consideration) being comparable to that of the two
bands in the cobalt - thiourea stretching region of
$Co(tu)_4(ClO_4)_2$. The distortion must, however, be very
large to produce such a marked effect on the magnetic moment
of the compound. There is a possibility of five coordin-
ation, but so few examples of this type are available for
comparison that no firm conclusions can be drawn. Figgis[55]
has considered the effect of a small distortion along the
C_2 axis on the magnetism of tetrahedral cobalt compounds.

He predicts that such a distortion will give rise to an appreciable negative θ value. The (negative) θ values for the nitrate complexes are smaller than that of the perchlorate complex, all four values being similar to those usually observed in complexes of approximately T_d symmetry. The treatment of Figgis is thus not applicable to the distortions present in these compounds.

All three forms are soluble in organic solvents only with extensive solvolysis; the solutions being violet in colour. Addition of excess thiourea to solutions of the compound in n - butanol gives a blue solution, but even when the solution is saturated with thiourea the extinction coefficients have not reached a limiting value. The electronic spectrum of this blue solution is similar to that of $Co(tu)_4(ClO_4)_2$ in acetone containing thiourea[43] indicating that most of the cobalt is present as the tetrahedral $Co(tu)_4^{2+}$ ion.

The existance of three forms of $Co(tu)_4(NO_3)_2$ may explain the rather wide spread in the magnetic results for this compound reported by Cotton et al.[43] Three of the pairs of μ, θ values reported are rather similar to those found here for forms A and B, but the remaining two cannot be accounted for by any of the forms, or by

mixtures of the forms, prepared in this work.

Conclusions

1)   Metal – acetate, metal – sulphate, metal – selenate and metal – thiosulphate stretching modes occur in the range 300 – 200 cm^{-1} in a number of tetrahedral complexes of cobalt, zinc, and cadmium.

2)   Although metal – oxygen stretching vibrations occur in roughly the same position as metal–thiourea stretches in a number of thiourea complexes with coordinated oxyanions, this does not preclude useful structural information being obtained from the far infrared spectra of these compounds.

3) $Co(tu)_4(NO_3)_2$ exists in at least three different forms; two of these have a distorted tetrahedral structure, but the properties of the third cannot be rationalised in terms of either octahedral or tetrahedral coordination.

CHAPTER FOUR

Compounds with Bridging Sulphur Atoms

Nardelli and his coworkers have prepared the isomorphous series of compounds $M(tu)_2(NCS)_2$ (M = Ni, Co, Fe, Mn, Cd)[72] and have carried out an X-ray crystal structure determination on the nickel compound.[73,74] The coordination polyhedron of the nickel atom approximates to D_{4h} symmetry, with infinite chains of bridging sulphur atoms from the thiourea in the plane, and nitrogen bonded thiocyanate groups in the axial positions. The nickel-thiocyanate bond distance, 1.99 A^o, is one of the shortest known[74] whereas the metal-sulphur distances (2.56, 2.53 A^o) are appreciably longer than in $Ni(tu)_4Cl_2$ (2.46 A^o).[50] In view of the unusual structure of these compounds, a study of their electronic spectra, magnetic properties, infrared and far infrared spectra was undertaken.

Assuming that the metal is octahedrally coordinated, anhydrous divalent metal thiocyanates will also have an N_2S_4 coordination sphere with bridging sulphur atoms. Previous work on these compounds is limited and of doubtful reliability. A parallel study of some of these

thiocyanates was therefore carried out. In certain cases the methanol and ethanol complexes $M(ROH)_2(NCS)_2$

were isolated as intermediates in the preparation of these anhydrous thiocyanates. Complexes with coordinated alcohols have received little attention, and therefore the properties of these compounds were studied.

Thiourea Compounds
Infrared and Far Infrared Spectra

The C-N and C-S stretching frequencies and the N-C-S bending frequencies of the thiocyanate groups (Table 11) are in the range normally found for nitrogen bonded thiocyanate[53]. The C-N stretching frequencies may have more than the usual error as the bands showed a marked Christiansen effect even when great care was taken with the mull preparation. The infrared spectrum of the cobalt compound has been briefly discussed;[80] vibrational modes of the thiourea molecule involving C - S stretching character are moved slightly to lower frequencies relative to non-bridging, coordinated thiourea.

The far infrared spectrum of $Ni(tu)_2(NCS)_2$ (Fig. 6., Table 12) has a strong band at 303 cm^{-1} which

Table 11

Internal Vibrational Modes of the Thiocyanato Groups

Compound	C – N Str.	C – S Str.	N – C – S Bend	Others
$Ni(tu)_2(NCS)_2$	2090s 2065sh	814w	481w, 470w, 461w	
$Co(tu)_2(NCS)_2$	2070s	815w	481w, 471w 461w	
$Fe(tu)_2(NCS)_2$	2055s	813w	482w, 469w, 460w	
$Mn(tu)_2(NCS)_2$	2060s	813w	482w, 470w, 461w	
$Cd(tu)_2(NCS)_2$	2060s	800w	obscured	
$Zn(tu)_2(NCS)_2$	2107s 2099s	816w	obscured	
$Ni(NCS)_2$	2165s 2117w	767w	459sh, 454s	
$Co(NCS)_2$	2100s 2085s 2031s	778w	453m	881(2 x 453)? 800vw
$Mn(NCS)_2$	2139s	778w	459s, 455s	
$Zn(NCS)_2$	2170s	787w	474s, 447s	949vw(2x474)? 895w (2x447)? 625w, 606w
$Cd(NCS)_2$	2153s 2144s	756w	447s, 441s	893w(2x447)?
$Co(NCS)_2 \cdot \frac{1}{2}H_2O$	2155s	774w	453w	

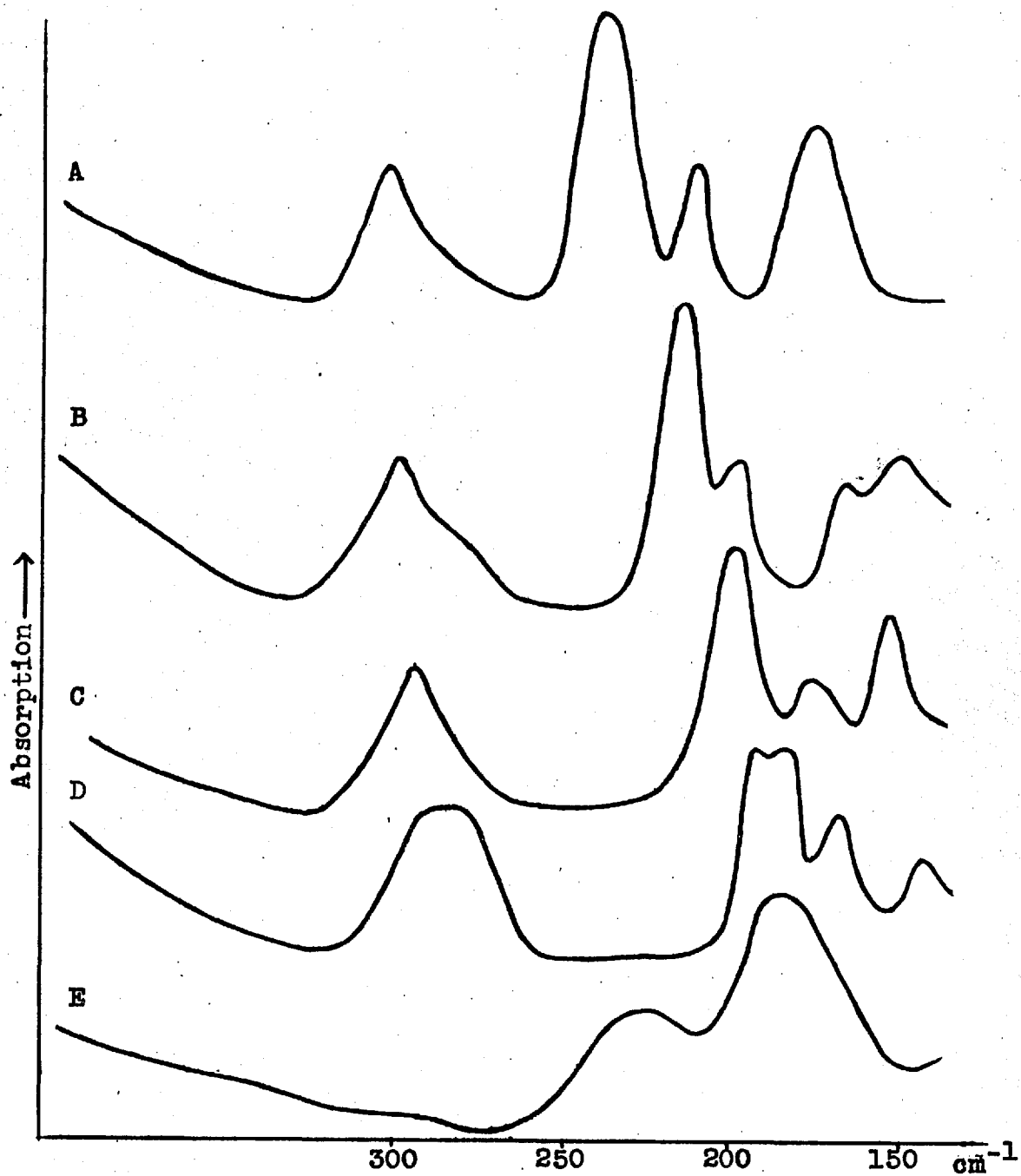# Fig. 6

Far Infrared Spectra of $M(tu)_2(NCS)_2$ Compounds

A $Ni(tu)_2(NCS)_2$ D $Mn(tu)_2(NCS)_2$

B $Co(tu)_2(NCS)_2$ E $Cd(tu)_2(NCS)_2$

C $Fe(tu)_2(NCS)_2$

Table 12

Far Infrared Spectra ($400 - 200$ cm^{-1})

Compound	M − NCS Str.	Other Bands
Ni(tu)$_2$(NCS)$_2$ *	303ms	230s, 206m, 170m
Co(tu)$_2$(NCS)$_2$ *	297ms	208s, 194m, 162m, 146m
Fe(tu)$_2$(NCS)$_2$ *	293ms	198s, 173m, 148m
Mn(tu)$_2$(NCS)$_2$ *	286brms	189s, 181s, 166m, 140m
Cd(tu)$_2$(NCS)$_2$ *	226br	181s
Zn(tu)$_2$(NCS)$_2$	(297s,269s,224s,190w − see text)	
Ni(NCS)$_2$	295s	226m
Co(NCS)$_2$	293br	$<$200
Mn(NCS)$_2$	283s	
Zn(NCS)$_2$	270br, 251s	
Cd(NCS)$_2$	200	
Co(NCS)$_2$·$\frac{1}{2}$H$_2$O	291s	
Ni(MeOH)$_2$(NCS)$_2$	282s	340brw
Ni(EtOH)$_2$(NCS)$_2$	285s	
Co(MeOH)$_2$(NCS)$_2$	284s	400brw,340brw,$<$200
Co(EtOH)$_2$(NCS)$_2$	273s	
Mn(MeOH)$_2$(NCS)$_2$	268s	400brw
Mn(EtOH)$_2$(NCS)$_2$	261s	

* The spectra of these compounds were also measured
   $200 - 130$ cm^{-1}.

is readily assigned as the nickel - thiocyanate stretching
frequency by comparison with other isothiocyanato complexes.[32]
The energy of this band is slightly higher than it is in
other monodentate nickel - isothiocyanato complexes.
This probably reflects the short Ni - NCS bond length.
The cobalt, ferrous and manganese compounds each show a
strong band in the region $297 - 286$ cm^{-1} which is
immediately assignable as the metal - thiocyanate stretch,
the corresponding band in the cadmium compound occurs at
226 cm^{-1}. The decrease in metal - thiocyanate stretching
frequency along the series Ni, Co, Fe, Mn is less than
is usually observed for these metals.

M	$(M - NCS)$ in $M(tu)_2(NCS)_2$	$(M - NCS)$ in $M(py)_4(NCS)_2$[32]
Ni	303	285
Co	297	270
Fe	293	267
Mn	286	253

The strong band at 230 cm^{-1} in the spectrum of
$Ni(tu)_2(NCS)_2$ is assigned as due to a vibrational mode
having metal - sulphur stretching character. This band
shifts 22 cm^{-1} to lower energy in the cobalt compound and
further small shifts are observed on going to the ferrous,
manganese and cadmium compounds.

The lowest frequency bands probably represent further metal – sulphur stretching and bending modes since metal – thiocyanate bending modes are not observed above 130 cm^{-1} in $Ni(py)_4(NCS)_2$[75] or $Ni(NCS)_6^{2-}$.[53] The explanation of the relative magnitudes of these shifts is as follows: The metal ligand distances in the nickel compound show that the metal is relatively weakly coordinated to four sulphur atoms in the plane and more strongly coordinated to the two axial thiocyanate groups. The strength of the in-plane bonding decreases along the series Ni, Co, Fe, Mn, partly as a result of the usual change in metal-ligand bond strength and partly as a result of the decreases in B character along this series. The decrease in in-plane bond strength is accompanied by an increase in the axial field and this largely offsets the normal decrease in the metal – thiocyanate force constant along the series. This explanation is supported by the analysis of the electronic spectra.

Electronic Spectra

The electronic energy levels of tetragonally distorted octahedral complexes have been of considerable interest in the literature. Following the methods used to describe complexes with cubic symmetry, the splitting

of the octahedral energy levels in a tetragonal field has been treated by both crystal field and molecular orbital methods. In the crystal field approximation, two parameters, Ds and Dt are required (in addition to Dq) to calculate the energy levels in the D_{4h} complex. Ds and Dt measure the splitting of the octahedral energy levels due to the second and fourth order terms of the tetragonal potential in the same way as Dq measures the splitting of the free ion terms due to an octahedral field. The perturbation of the one electron orbitals due to the tetragonal potential can then be calculated as linear combinations of Ds and Dt, and hence the splittings of the energy levels on going from O_h to D_{4h} symmetry can be calculated. Full details of the calculation are given in references 15 and 76.

In the molecular orbital method the interaction of the ligand π-orbitals with the metal t_{2g} orbitals and the ligand σ-orbitals with the metal e_g orbitals are considered. The one electron orbital displacements are evaluated in terms of the differences in the σ and π antibonding energies of the ligands, $\delta\sigma$ and $\delta\pi$. The band splittings for the various terms from each configuration are then calculated. Full details are given in reference 77.

Table 13

Splittings of the Energy Levels of Octahedral Complexes

in D_{4h} Symmetry

Ion	Energy Level in O_h Symmetry	Energy Levels in D_{4h} Symmetry	Splitting[*]
Fe(II)	^5E_g $(t_2{}^3e^3)$	$^5A_{1g} + {}^5B_{1g}$	$\frac{8}{3}\delta\sigma$ $-4Ds - 5Dt$
	$^5T_{2g}(t_2{}^4e^2)$	$^5E_g + {}^5B_{2g}$	$-2\delta\pi$ $3Ds - 5Dt$
Ni(II)	$^3T_{1g}(t_2{}^5e^3)$	$^3E_g + {}^3A_{2g}$	$2\delta\pi + 2\delta\sigma$ $\frac{5}{4}Dt - 6Ds$
	$^3T_{2g}(t_2{}^5e^3)$	$^3E_g + {}^3B_{2g}$	$2\delta\pi - 2\delta\sigma$ $35\frac{}{4}Dt$
	$^3T_{1g}(t_2{}^4e^4)$	$^3E_g + {}^3A_{2g}$	$-2\delta\pi$ $3Ds - 5Dt$
Co(II)	$^4T_{1g}(t_2{}^5e^2)$	$^4E_g + {}^4A_{1g}$	$-2\delta\pi - 2\delta\sigma$ $-\frac{5}{4}Dt \quad 6Ds$
	$^4T_{2g}(t_2{}^4e^3)$	$^4E_g + {}^4B_{2g}$	$-2\delta\pi + 2\delta\sigma$ $-35\frac{}{4}Dt$

[*] Sign Convention, Energy of non-degenerate level minus
Energy of degenerate level is positive.

These calculations do not include any allowance for
interaction between the E states arising from the split T
levels or for mixing of configurations.

The calculated splittings in terms of both sets of parameters are given in Table 13. No account has been taken of the interaction between the E states arising from the split T levels, or of the interaction between T terms coming from different configurations. Comparison of the results in Table 13 shows that the two treatments are identical and the parameters are related by:-

$$\delta\sigma = -^3/_2 Ds -^{15}/_8 Dt$$

$$\delta\pi = -^3/_2 Ds +^5/_2 Dt$$

The energy levels in this work will be discussed in terms of $\delta\sigma$ and $\delta\pi$ as these parameters are more easily related to the chemical properties of the ligands.
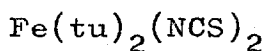
Fe(tu)$_2$(NCS)$_2$

Burbridge, Goodgame and Goodgame[78] have given expressions which relate the observed quadrupole splitting in the Mössbauer spectrum of a tetragonal iron (II) complex with the splitting of the $^5T_{2g}$ level. Fe(tu)$_2$(NCS)$_2$ gave an excellent Mössbauer spectrum with a quadrupole splitting of 2.08±0.04 mm/sec. and an isomer shift of 1.01±0.04 mm/sec. The magnetic susceptibility of Fe(tu)$_2$(NCS)$_2$ follows a Curie-Weiss law over the temperature range 80 - 360°K with μ_{eff} = 5.51 B.M., θ = -4°.

From the graph of quadrupole splitting against the splitting of the T_{2g} level in reference 78, the ground state splitting in $Fe(tu)_2(NCS)_2$ is found to be either ~ 300 cm^{-1} or ~ 4000 cm^{-1} with the B_{2g} level lowest. The measured quadrupole splitting is slightly in excess of the maximum possible value for the E_g level lowest. The magnetic moment of the compound is only slightly lower than the value (5.66 B.M.) calculated assuming no splitting of the $^5T_{2g}$ ground state, thus indicating that ground state splitting must be small (certainly much less than 4000 cm^{-1}). In addition, the magnetic moment and the quadrupole splitting fit the calculated curve of Golding, Mok, and Duncan.[79] Their calculations are based on a model in which the B_{2g} level is the ground state, and the agreement between the experimental values and the theoretical curve suggests that this must be the case in $Fe(tu)_2(NCS)_2$. The ground state splitting is therefore about 300 cm^{-1} in this compound; the exact value of this parameter is dependent on the values chosen for a number of constants in reference 78, but is almost certainly of the correct order of magnitude. $\delta\pi$ is therefore equal to approximately + 150 cm^{-1}.

The splitting of the excited state (E_g in 0_h symmetry) of $Fe(tu)_2(NCS)_2$ is given by the electronic

Table 14

Electronic Spectra

Compound	Absorption Maxima (cm^{-1})		
$Fe(tu)_2(NCS)_2$			10,800; 5420
$Fe(NCS)_2$			12,500; 7100
$Co(tu)_2(NCS)_2$	19,200sh; 18,500;	15,000;	9430: 6250
$Co(NCS)_2$	C.T.*	16,000; 15,150sh;	6670
$Co(NCS)_2 \cdot \frac{1}{2}H_2O$	C.T.	15,600;	10,000; 6370
$Ni(tu)_2(NCS)_2$	C.T.	14,800;	8400; 6200sh
$Ni(NCS)_2$	C.T.	15,400;	9600; 7000sh
$Mn(tu)_2(NCS)_2$	26,800;	22,500;	18,600
$Mn(NCS)_2$	25,800;	22,350;	21,000sh

* C.T. indicates that ν_3 is obscured by charge transfer absorption

Table 14 (cont.)

Compound	Absorption Maxima (cm^{-1})				
$Co(MeOH)_2(NCS)_2$	21,000; 19,200; 17,900;			9700; 6400	
$Co(EtOH)_2(NCS)_2$	22,000; 19,530; 18,200;			9800; 7090	
$Ni(MeOH)_2(NCS)_2$	25,000sh;		15,400; 13,000sh;	8800; 6500sh	
$Ni(EtOH)_2(NCS)_2$	24,800;		15,500; 12,700sh;	9000; 6500sh	
$Mn(MeOH)_2(NCS)_2$	26,000;		24,100;		
$Mn(EtOH)_2(NCS)_2$	25,900		23,900		

Fig. 7

Electronic Spectra of $Fe(tu)_2(NCS)_2$ and $Fe(NCS)_2$
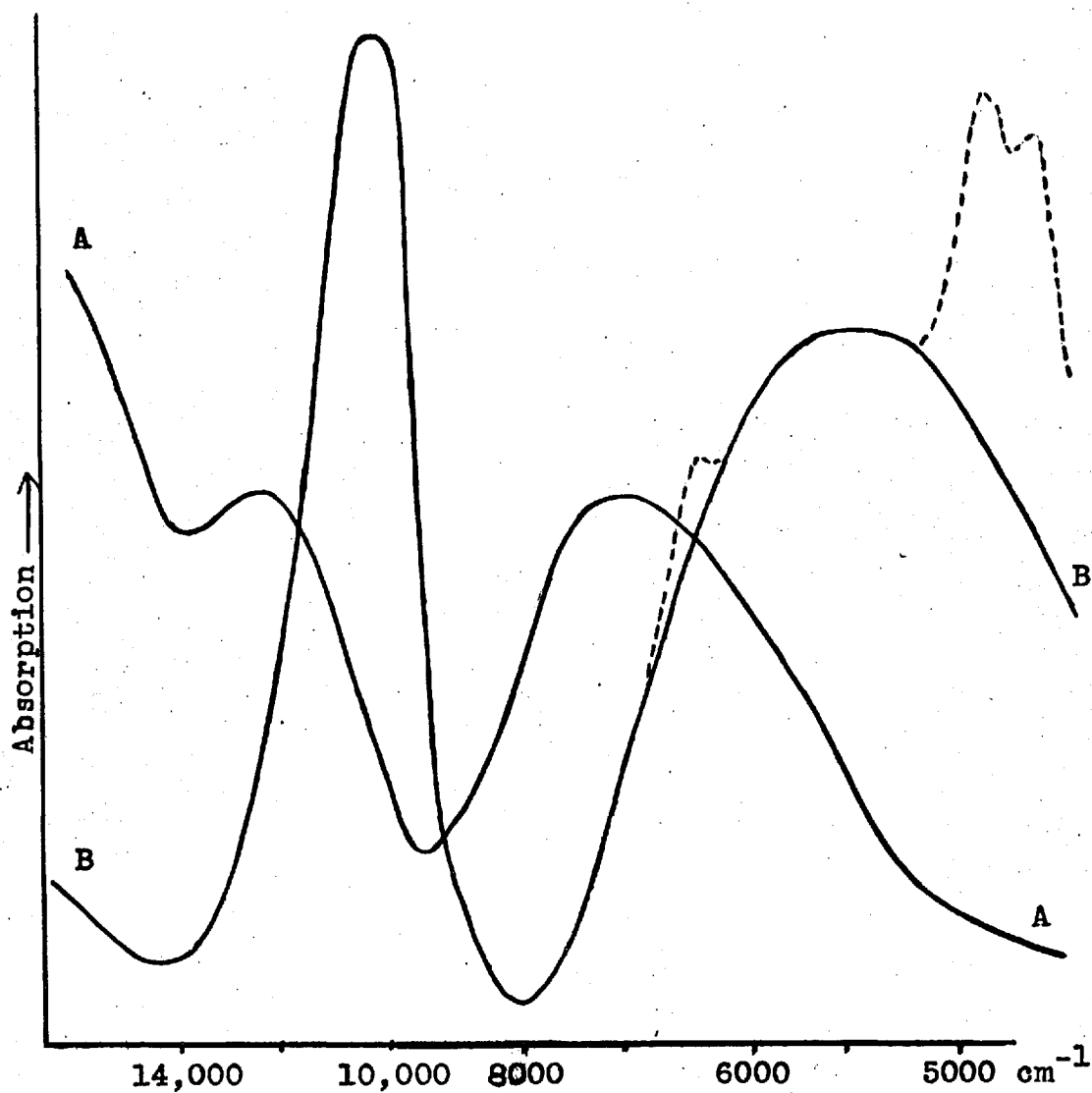
A Anhydrous $Fe(NCS)_2$

B $Fe(tu)_2(NCS)_2$

- - - - - - Vibrational bands

spectrum (Fig.7, Table 14) as 5,400 cm^{-1}, hence $\delta\pi$ = 2,000 cm^{-1}

As a result of their symmetry, the energy difference

between the $B_{2g}(d_{xy})$ and $B_{1g}(d_{x^2-y^2})$ levels will be

independent of the axial field and therefore the energy

of the $B_{2g} \rightarrow B_{1g}$ transition gives the in-plane field.

The far infrared spectrum and the positions of thiocyanate

and thiourea in the spectrochemical series indicate that

the lowest energy band in the electronic spectrum corres-

ponds to this transition. The in-plane field is

therefore equal to 5400 cm^{-1}. The axial field is then

given by the average ligand field approximation as

$3(\frac{1}{2}(5400 + 10800) - 200 - \frac{2}{3} \cdot 5400) = 12,900$ cm^{-1}.

The weak in-plane field (comparable to that of bridging

bromide[81]) and the strong axial field (a more typical

value of the ligand field produced by the isothiocyanate

group in octahedral complexes of divalent first transition

series ions is 10,000 cm^{-1}.) are in agreement with the

interpretation of the far infrared spectra

$Ni(tu)_2(NCS)_2$
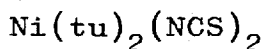
In tetragonal nickel (II) compounds, the $^3A_{2g} \rightarrow {}^3B_{2g}$

transition corresponds to an electron being transferred

from the d_{xy} orbital to the $d_{x^2-y^2}$ orbital.[81]

Table 15

Magnetic Properties of Compounds Following a Curie – Weiss Law

Compound	Temp.Range of C – W law	μB.M.	θ°
$Fe(tu)_2(NCS)_2$	80 – 360 $^{\circ}K$	5.51	–4
$Co(tu)_2(NCS)_2$	80 – 360	4.99	–7
$Ni(tu)_2(NCS)_2$ *	170 – 370	3.27	+40
$Mn(tu)_2(NCS)_2$ *	170 – 370	5.81	–1
$Co(EtOH)_2(NCS)_2$	80 – 330	4.75	–18
$Mn(EtOH)_2(NCS)_2$	80 – 320	6.00	–30
$Co(NCS)_2$ *	130 – 360	4.69	+38
$Co(NCS)_2 \cdot \frac{1}{2}H_2O$	90 – 360	5.59	–46
$Ni(NCS)_2$ *	200 – 370	3.08	+50
$Mn(NCS)_2$	80 – 360	5.78	–86

* Further data is given in Table 16

+ Further data is given in Table 19

As in the ferrous compounds, this transition has an energy equal to the strength of the in-plane field. The shoulder at $\sim$6,200 cm^{-1} in the electronic spectrum of $Ni(tu)_2(NCS)_2(NCS)_2$ (Fig.8) corresponds to this transition. The exact position of this shoulder is in some doubt ($\pm$ 200 cm^{-1}) since the first overtones of the N – H stretching vibrations of the coordinated thiourea occur in this region, but it indicates that the in-plane field is appreciably stronger than in the ferrous compound. The value of 10Dq from the position of γ_1 is 7,700 cm^{-1}, or rather similar to that of the ferrous compound. Hence the axial field (approximately 10,800 cm^{-1}) is weaker than in the ferrous compound, and is equal to, or slightly greater than, the ligand field produced by the isothiocyanate group in other octahedral nickel complexes. These differences between the nickel and ferrous compounds are in agreement with the interpretation of the far infrared spectra.

For octahedral nickel complexes it is possible, in principle, to calculate the values of $\delta\sigma$ and $\delta\pi$ from the splittings of γ_1 and γ_2. There is, however, appreciable interaction between the two $^3T_{1g}$ levels arising from the

Fig. 8

Electronic Spectra of $Ni(tu)_2(NCS)_2$ and $Ni(NCS)_2$
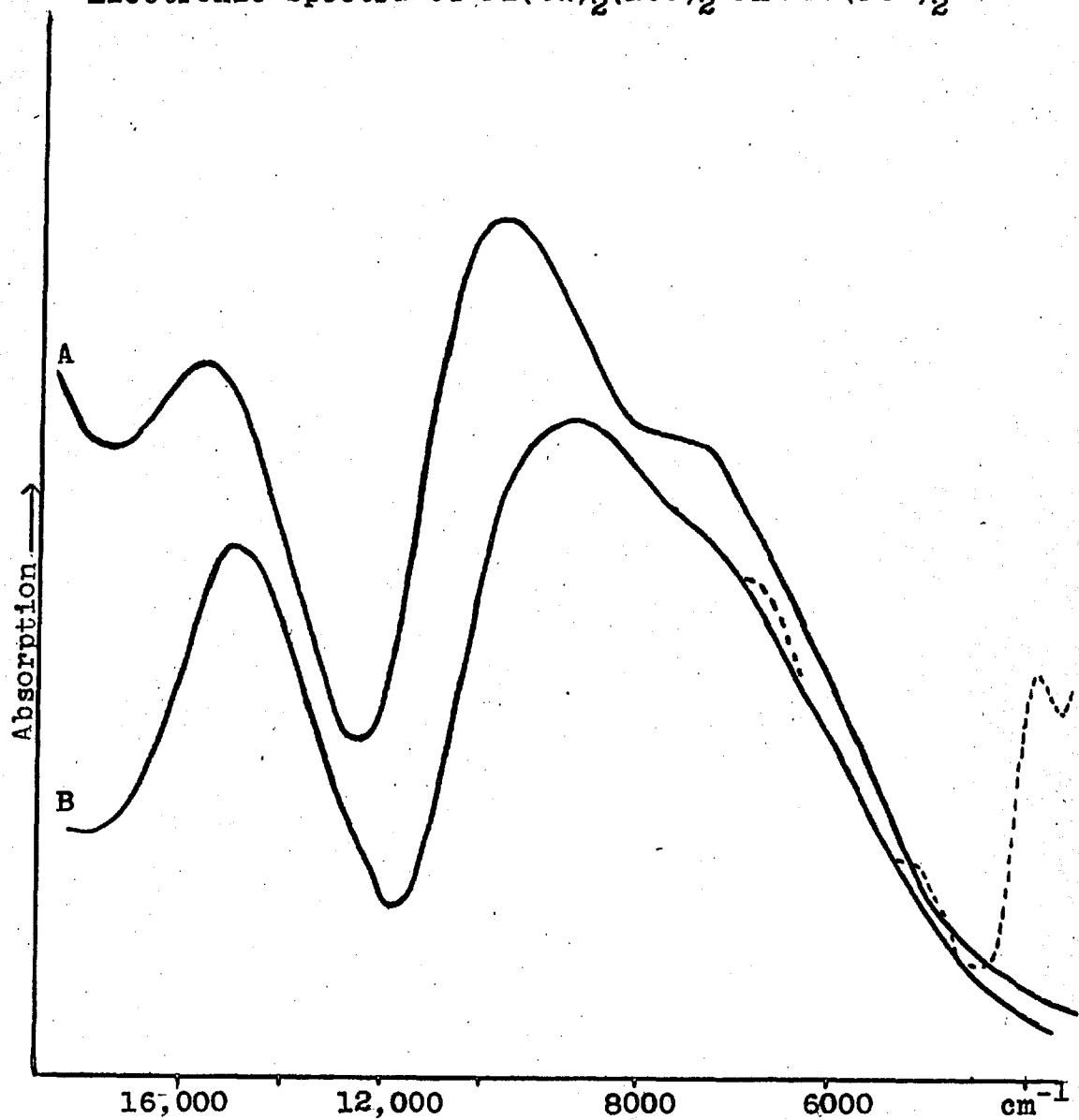

A   Anhydrous $Ni(NCS)_2$

B $Ni(tu)_2(NCS)_2$

------   Vibrational bands

configuations t^5e^3 and t^4e^4 so that the excited states
of γ_2 and γ_3 have some character from both configurations.
The splitting of ν_2 will therefore be intermediate between
those calculated for the "pure" terms $^3T_{1g}(t^5e^3)$ and
$^3T_{1g}(t^4e^4)$. The mixing coefficients for these levels
have been given by Ballhausen and Hare.[76] However, no
splitting of the ν_2 band is seen in $Ni(tu)_2(NCS)_2$,
although it is somewhat broader than in other, more
symmetrical, nickel complexes. The only information that
can be obtained from the spectrum is that the splitting
of ν_2 is between +2000 and -2000 cm^{-1} and therefore
numerical values of $\delta\sigma$ and $\delta\pi$ cannot be calculated for
this compound. The splitting of ν_1 and the position of
the lower energy component are, however, consistent with
thiourea being a stronger σ-donor and a stronger π-acceptor
relative to thiocyanate in $Ni(tu)_2(NCS)_2$ than it is in
$Fe(tu)_2(NCS)_2$.

Calculation of the Racah B parameter from the
position of ν_2' and the Tanabe - Sugano determinant, taking
10Dq as 7,700 cm^{-1} gives a value considerably greater
than the free ion value. The possible error in the
positions of ν_1 and ν_2 cannot account for this. It seems
probable that the assumptions of the Tanabe - Sugano

method (particularly the assumption of the same wave function for the t_{2g} and e_g sets) are not justified in this case.

The susceptibility of $Ni(tu)_2(NCS)_2$ follows a Curie-Weiss law over the temperature range 370 - 170° with μ_{eff} = 3.27 B.M. and Θ= +40°, thus indicating appreciable ferromagnetic interaction through the sulphur atoms. Below 170° the susceptibility is lower than that predicted by the above values. (Fig. 9 Table 16).
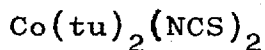
$Co(tu)_2(NCS)_2$

The electronic spectrum of $Co(tu)_2(NCS)_2$ has been interpreted as indicating the presence of a tetrahedral species in addition to the octahedral structure.[80] It was suggested that the compound consisted of short chains of octahedral units with tetrahedral end groups. Careful measurements of the reflectance spectrum of the compound in the region around 15,000 cm^{-1} did not reveal the fine structure normally associated with ν_3 of tetrahedral cobalt (II). The electronic spectra of $Co(tu)_2(NCS)_2$ and $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ are closely similar except in the charge transfer region. It seems unlikely that both of these compounds would contain comparable amounts of a tetrahedral

Fig. 9

Magnetic Susceptibility $(200 - 80^{\circ}K)$ of $Co(NCS)_2$, $Ni(tu)_2(NCS)_2$
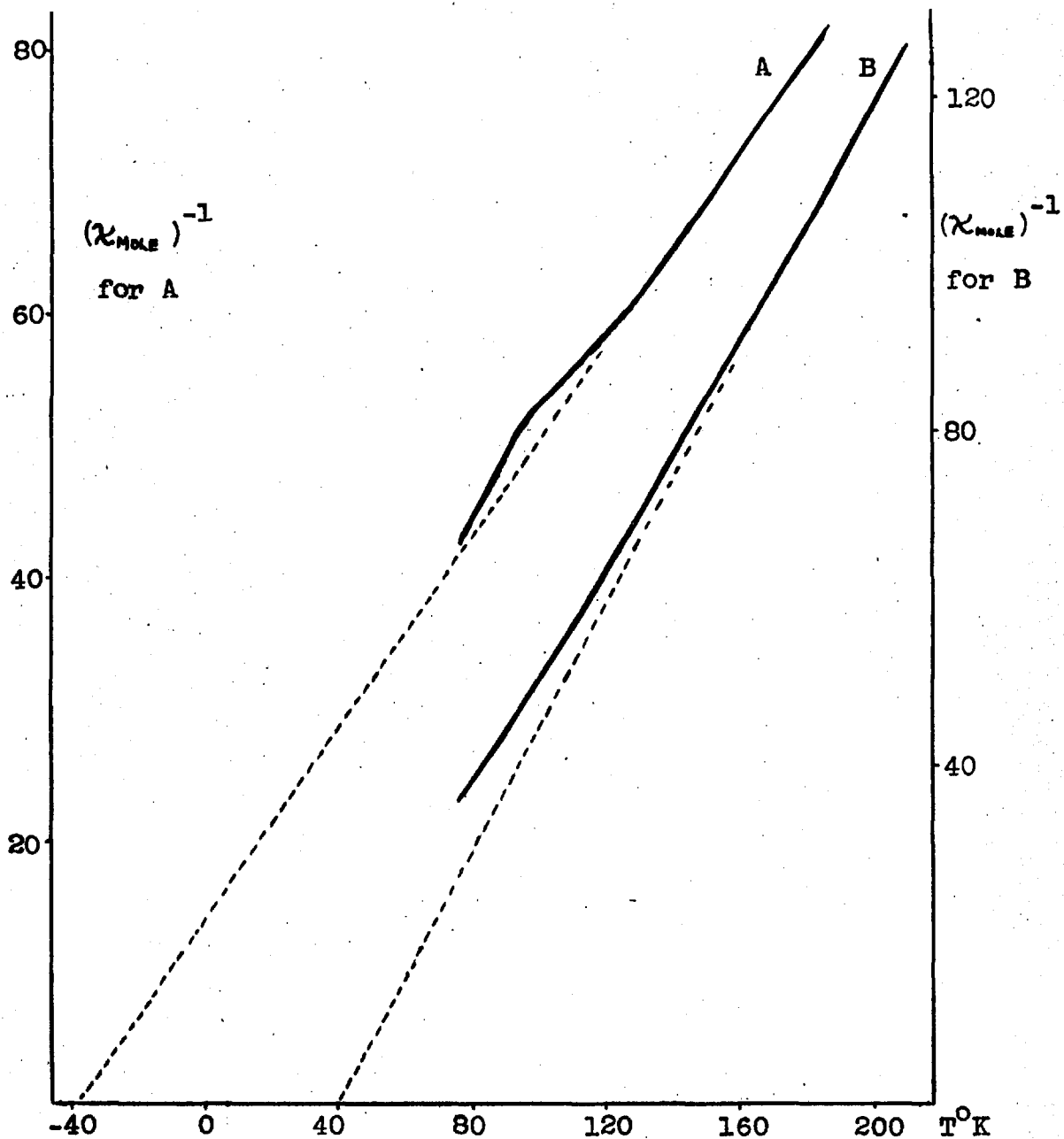
A Anhydrous $Co(NCS)_2$

B $Ni(tu)_2(NCS)_2$

χ_{mole} (c.g.s. units) corrected for diamagnetism

Table 16

Magnetic Susceptibility of $M(tu)_2(NCS)_2$ (M = Ni, Mn)

|	M = Ni			M = Mn	
Temp. °K	χ^*_{mole} x 10^{-3}	$^+\mu$ B.M.	Temp. °K	χ^*_{mole} x 10^{-3}	μ^+ B.M.
367	4.08	3.48	362	11.50	5.79
332	4.54	3.51	325	12.79	5.79
298	5.14	3.52	302	13.82	5.80
252.5	6.23	3.56	292	14.27	5.79
226	7.13	3.61	247	16.87	5.79
203.5	8.11	3.65	222	18.69	5.79
182	9.33	3.70	202	20.61	5.79
161.5	10.82	3.76	190	21.88	5.79
147.5	12.12	3.79	184	22.60	5.79
138	13.15	3.82	174	23.80	5.78
127	14.60	3.87	161	25.18	5.72
115	16.38	3.90	148.5	26.45	5.63
102	19.23	3.98	145	26.75	5.59
94	21.28	4.01	127	29.40	5.49
88	23.15	4.05	112	33.10	5.47
77	27.30	4.12	95	38.6	5.44
			83.5	42.2	5.33
			78	45.5	5.34

* Magnetic Susceptibility per mole, corrected for diamagnetism

+ Calculated from the Curie Law.

form giving absorption maxima at similar energies.
It is therefore necessary to explain all the electronic
absorption bands in terms of the energy levels of an
octahedral species.

The splitting of the lowest energy electronic
band in $Co(tu)_2(NCS)_2$ $(-2\delta\sigma-2\delta\pi)$ is clearly resolved (Fig 10)
with the weaker component, assigned as the transition to
the $^4B_{1g}$ level, highest. Taking the second band as the
two electron transition $^4T_{1g} \rightarrow {}^4A_{2g}$ (11) the position of
all three bands can be fitted for an octahedral model
by taking $10Dq = 8,200$ cm^{-1} and $B = 850$ cm^{-1} and these
are reasonable values for this complex. The agreement
is surprisingly good, since taking values of $\delta\sigma$ and $\delta\pi$
similar to those found for the iron complex, a splitting
of the ground state of some thousands of wavenumbers
would be predicted. It would appear that the splitting
of the ground state must be small, for otherwise ν_1 would
be expected to be much higher than is observed. The
splitting of ν_1 can be accounted for by taking values of
$\delta\sigma$ and $\delta\pi$ similar to those found for the ferrous compound.
However, in order to account for a ground state splitting
of less than 1000 cm^{-1} as well, $\delta\sigma$ must be $\sim$1000 cm^{-1} and
$\delta\pi \sim -600$ cm^{-1}. These values are so different from those

Fig. 10

Electronic Spectra of $Co(NCS)_2$, $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ and $Co(tu)_2(NCS)_2$
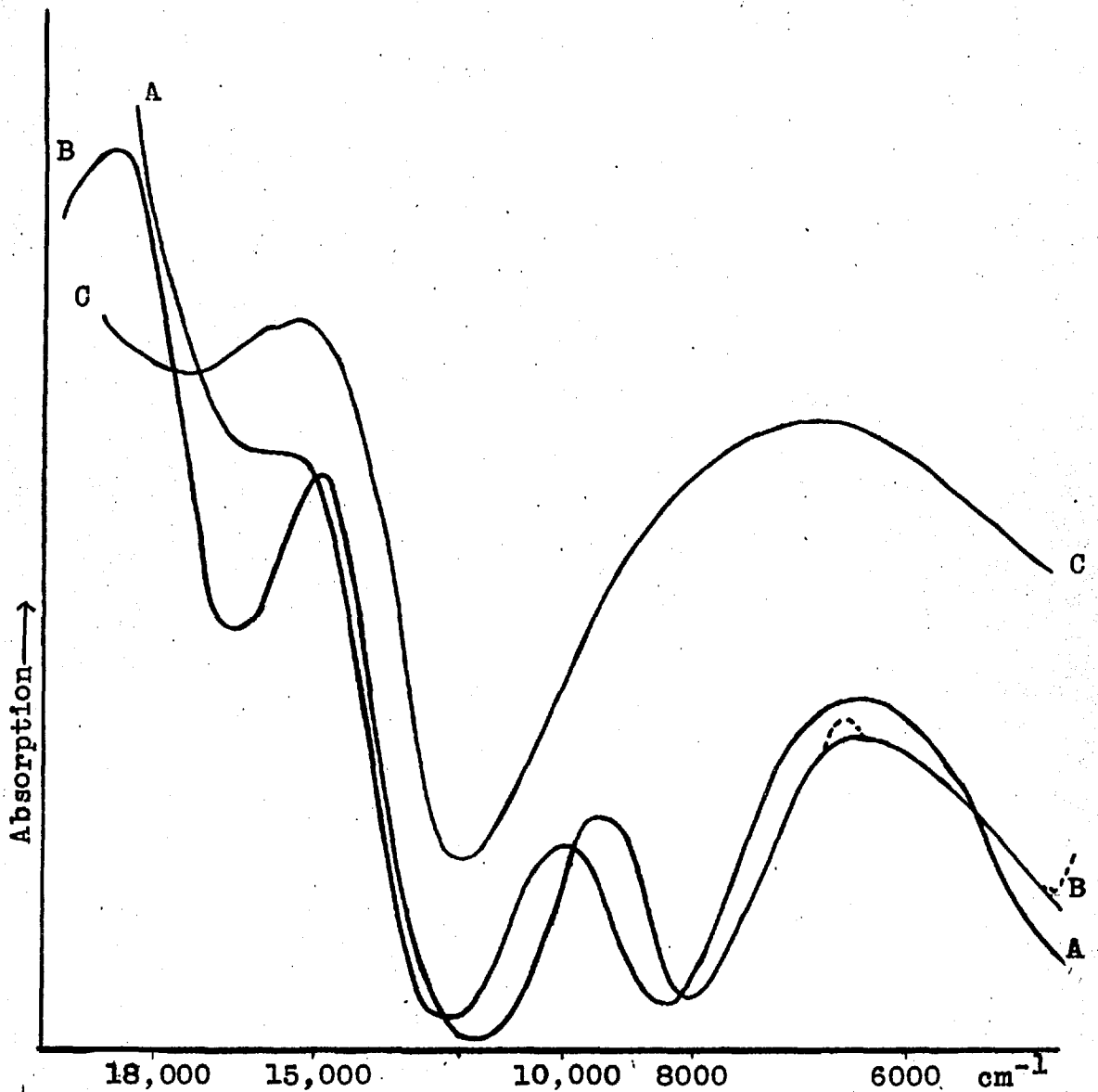
A $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ C   Anhydrous $Co(NCS)_2$

B $Co(tu)_2(NCS)_2$ ------   vibrational bands

found for the ferrous compound that considerable doubt is cast on the validity of the treatment (particularly the neglect of the interaction between the two E states from the $^4T_{1g}$ and $^4T_{2g}$ states.

The magnetic susceptibility of $Co(tu)_2(NCS)_2$ obeys a Curie-Weiss law over the temperature range 360 - 80°K with μ_{eff} = 4.99 B.M., θ = -7.° This value of μ_{eff} is somewhat higher than would be expected for an A ground state with no other level within several thousand wavelengths.

$Mn(tu)_2(NCS)_2$

The electronic spectrum of $Mn(tu)_2(NCS)_2$ is superficially similar to those of other octahedral manganese compounds,[11] three bands being detected before the onset of charge transfer absorption. No splitting of the lowest energy band is observed, although this band is split in the reflectance spectrum of $Mnpy_2Cl_2$.[83] If the three bands are identified with the transitions from the $^6A_{1g}(^6S)$ ground state to the $^4T_{1g}(^4G)$, the $^4T_{2g}(^4G)$, and the ^4E_g, $^4A_{1g}(^4G)$ excited states as is usual with octahedral manganese (II) compounds, it is not possible to account for their positions by values of 10Dq and B similar to those found for the nickel and iron complexes.

It is clear, therefore, that $Mn(tu)_2(NCS)_2$ is so
distorted that the simple assignment of the bands to
energy levels of an octahedral complex is not justified.
(The far infrared spectra indicate that this complex is
even more distorted than the ferrous compound.)

The magnetic susceptibility of $Mn(tu)_2(NCS)_2$
follows a Curie – Weiss law with μ_{eff}= 5.81 B.M., θ = -1°
over the temperature range 370 – 170.º Below 170° the
susceptibility is lower than would be predicted by these
values. (Table 16)

The most interesting feature of the magnetic
studies on this series of compounds is the difference
in behaviour for the different metals. The complexes
with T ground states obey the Curie – Weiss law over
the entire temperature range whereas the two with
A ground states, i.e. those with only filled or half-
filled sub-shells, show negative deviations (i.e. the
presence of antiferromagnetic interactions) at low
temperatures. In addition the nickel compound shows a
ferromagnetic interaction. Goodenough[84] has considered
the magnetic interaction between metal atoms with 90°
metal – ligand – metal angles in terms of the overlap
of (a) two half-filled metal orbitals, which produces

negative coupling; (b) one   half-filled and one empty

orbital, producing positive coupling and (c) one filled

and one half-filled orbital, producing positive coupling.

He concludes that ferromagnetic interaction is most

likely to occur in nickel complexes.   Detailed calculations

of the susceptibility of infinite chains of positively

coupled ions have not been made.

$Zn(tu)_2(NCS)_2$
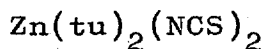
        This compound is not isomorphous with the other

compounds.[72]   The far infrared spectrum indicates that

it has a tetrahedral structure, but the normal vibrations

of the species occur so close together that assignment

of the observed bands to vibrations of a particular ligand

is not justified.

Anhydrous Divalent Metal Thiocyanates and their Ethanol and Methanol Adducts

Concentration of solutions of cobalt, manganese and nickel thiocyanates in anhydrous methanol or ethanol gave crystalline precipitates of the alcohol complexes $M(ROH)_2(NCS)_2$. The alcohol in the cobalt and manganese complexes is rather strongly held, prolonged pumping at room temperature causing no loss in weight. The alcohol, however, is rapidly removed by heating the complexes at 100° in vacuo over phosphorus pentoxide. The cobalt complexes are rapidly decomposed by moist air to give the hemihydrate $Co(NCS)_2 \cdot \frac{1}{2}H_2O$, under the same conditions the manganese compounds deliquesce. The nickel compounds are much less stable than the cobalt compounds. The alcohol is readily removed by pumping at room temperature or by heating to about 40°.

Relatively few complexes of first transition series metals with coordinated simple alcohols have been reported and no complete infrared spectra of these complexes have been published. The measured infrared absorption bands for the six compounds are therefore given in Tables 17 and 18. The infrared spectra of the three methanol complexes are virtually identical,

Table 17

Infrared Spectra of $M(MeOH)_2(NCS)_2$ Compounds

Assignment[85]	Free MeOH[85]	M = Co	M = Mn	M = Ni
O – H stretch	3683	3335s 3208sh	3354s	3354s
C – H stretch	2978	2992m 2950m 2924m 2905sh	2989m 2953m 2924m 2900sh	2988m 2946m 2914m
C – H stretch	2845	2844m	2848m	2844m
		2310m 2268m	2290m	
C – N stretch		2133vs 2088sh	2115vs	2142s
C – H bend	1477	1465m	1468m 1461sh	1467m
C – H bend	1455	1451m	1450m 1443m	1452m 1442sh
	1340	1366m	1367m	1360m
		1321w 1272w		
O – H bend	(1034)	1120m	1113m	1116m
C – O stretch	1034	1008s	1004s	1009s
(2 x 476etc.)?		947w	944w	951w
(2 x 458etc.)?		919w	922w	920w
C – S stretch		777msp	781msp	791msp
N – C – S bend		476m 471w 458m	475m 469m 459w	478m 458m 452m

Table 18

Infrared Spectra of $M(EtOH)_2(NCS)_2$ Compounds

M = Co	M = Mn	M = Ni
3320sbr	3320sbr	3345sbr
2973s	2990s	2984sh
2946m	2980s	2976s
2927mw	2952mw	2944m
2917mw	2935mw	2927m
2890m		2920m
		2890m
2133vsbr*	2119vsbr*	2130vsbr*
1466m	1466m	1462m
1460sh	1445m	1441w
1437w	1438w	1434w
1400m	1397sh	1394s
1388sh	1389s	1385sh
1376s	1376s	1373s
1350m	1350s	1345m
1260m	1261m	1264m
1086s	1083s	1069m
1037s	1038	1037s
940w*	933w*	940wbr*
906w*	909w*	900wbr*
880s	876s	874s
799m*	799m*	809m*
776m*	779m	
		765s
526sbr	503svbr	
		500vbr
471s*	467s*	
463s	455s	455br
447s	438s	
418d	417	417wbr

* Bands due to the thiocyanate group

suggesting that they have closely similar structures. The bands due to the thiocyanate group occur at 2130, 785, and 480 - 450 cm^{-1} suggesting that the thiocyanate is acting as a bridging grup in these compounds. Monodentate(N) thiocyanate usually has the C - N stretch below 2100 cm^{-1} and the C - S stretch above 800 cm^{-1}. The strong, broad band at $\sim$3350 cm^{-1} in the infrared spectra of the methanol complexes is readily assigned as the O - H stretching frequency of the coordinated methanol, the lowering of the band from its position in the free (gaseous) methanol molecule[85] being due to the ordination of the oxygen atom (compare ammino complexes), or to hydrogen bonding, or both. The group of four or five bands in the range 2850 - 3000 cm^{-1} correspond to the C - H stretching frequencies of the methanol. The number of bands in this region suggests that either two or more different types of methanol are present or, more probably, that some of the bands are overtones of the C - H bending modes gaining intensity from C - H stretching modes by Fermi resonance. The very strong band at $\sim$1000 cm^{-1} in the complexes is assigned to the C - O stretching mode, this band shifting 25 - 30 cm^{-1} to lower energy on coordination. The only bands above 200 cm^{-1} which can reasonably be assigned to the metal - oxygen stretching vibrations are the very weak, broad bands at 410 - 330 cm^{-1}.

Assignments of the remaining bands are given in Table 17.

The infrared spectra of the cobalt and manganese ethanol complexes are very similar, but that of the nickel complex is appreciably different from these. The bands due to the thiocyanate group occur at 2120, 776 - 809 and 438 - 471 cm^{-1} and are indicative of bridging thiocyanate in all three compounds. The O - H stretching frequency moves down considerably from its position in the free molecule (3660 cm^{-1}) [86] as occurs in the methanol complexes. Assignment of the C - O stretching frequency is complicated by the interaction of this vibration with the C - C stretch and other modes, [86] but the two bands at about 1080 and 1037 cm^{-1} are related to the two bands in free ethanol at 1104 and 1070 cm^{-1} and probably involve this mode. The C - C - O bend in ethanol (at 453 cm^{-1}) moves down slightly on coordination. The assignments of the other low frequency vibrations in the ethanol molecule are obscure.

The electronic spectra of the ethanol and methanol complexes (Table 14) for a given metal are virtually identical, ethanol producing a marginally stronger field. The electronic spectra of the manganese complexes are more like those of tetrahedral complexes than octahedral complexes in that they show no appreciable absorption

below 20,000 cm^{-1}, but the infrared spectra definitely indicate that the compounds are structurally similar to the octahedral cobalt complexes. No interpretation of the electronic spectra of the manganese compounds can be given. The positions and splittings of the $\mathcal{V}_1$ bands in the cobalt and nickel compounds are similar to those observed in the thiourea compounds suggesting that these complexes also have an essentially D_{4h} ligand field with the axial field (presumably due to two nitrogens of the thiocyanate group) much stronger than the in- plane field (oxygen donors and -SCN are both fairly low in the spectrochemical series). More detailed analysis of the spectra of the cobalt compounds is not possible due to the complexity of the absorption spectra and energy level diagram in the region above 17,000 cm^{-1}. The electronic spectra of the nickel complexes can be accounted for only rather approximately by the energy levels calculated from the Tanabe - Sugano determinants. The best fit is given by 10Dq = 8,500 and B = 1000 cm^{-1}. The shoulder on the low energy side of $\mathcal{V}_2$ is probably due to the spin forbidden transition $^3A_2 \rightarrow {}^1E_g(D)$ gaining intensity from $\mathcal{V}_2$, since if the splitting were due to the low symmetry field the ^3E_g level from $^3T_{1g}$ would be expected to lie at lower energy than the $^3A_{2g}$ level.

The magnetic measurements on the cobalt and manganese compounds gave values of μ_{eff} similar to those found in other octahedral compounds, the negative θ values indicating some antiferromagnetic coupling through the thiocyanate bridges.

Removal of the alcohol from these adducts by heating at 110° in vacuo gives the anhydrous thiocyanates. Anhydrous cobalt thiocyanate (green) very readily picks up water (to give the hemihydrate) and it is necessary to remove the alcohol over phosphorus pentoxide in a thoroughly baked out, all glass apparatus to obtain a pure product. The hemihydrate was conveniently prepared by exposing the anhydrous compound to the laboratory air for a few minutes and then heating the brown solid at 110° in vacuo over phosphorus pentoxide. The hemihydrate is somewhat hygroscopic, but no stoichiometric higher hydrate could be obtained by exposing it to moist air and the additional water thus picked up could be readily removed. Cobalt thiocyanate hemihydrate could not be dehydrated by heating at 150° in vacuo over phosphorus pentoxide for 24 hours.

Zinc and ferrous thiocyanates were prepared by evaporating their ethanolic solutions to dryness in vacuo and heating the resultant solid at 110° in vacuo over

phosphorus pentoxide. No evidence for the formation of an ethanol adduct was obtained in either case. The ferrous compound could not be obtained completely free from ferric iron due to atmospheric oxidation. Cadmium thiocyanate crystallised directly as the anhydrous compound from concentrated aqueous solutions. No evidence for the existence of hemihydrates other than of the cobalt compound was obtained, although the manganese and nickel thiocyanates are hygroscopic.

The C - N stretch of all the anhydrous thiocyanates except $Co(NCS)_2$ occurs in the range 2140 - 2170 cm^{-1}, i.e. rather higher than this vibration in bridging (N,S) thiocyanate compounds. This can be attributed to the further stabilization of the canonical form (II) of the thiocyanate ion by the proximity of a second positive metal ion to the sulphur atom.

$$^-N = C = S \qquad N \equiv C - S^-$$
$$\text{(I)} \qquad\qquad \text{(II)}$$
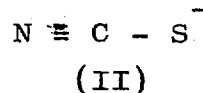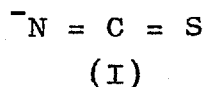
$Co(NCS)_2 \cdot \frac{1}{2}H_2O$ also has the C - N stretch in this range. The C - S stretching vibration and the N - C - S bend of the anhydrous thiocyanates occur in the range normally found for bridging thiocyanate.[87] The metal - nitrogen stretching vibration occurs at about 290 cm^{-1} in the cobalt and nickel compounds and at 283 cm^{-1} in the

manganese compound but below 200 cm^{-1} in the cadmium
compound.(Table 12) These shifts are similar to those
observed in the thiourea thiocyanate complexes and probably
have a similar explanation. The far infrared spectrum
of $Zn(NCS)_2$ has two bands in the zinc - thiocyanate
stretching region. These two bands probably correspond
to the two N - C - S bends (Table 11) and suggest that
there are two distinct types of thiocyanate group in
the compound.

The similarity of the electronic spectra of the
anhydrous ferrous and nickel thiocyanates to those of
the corresponding $M(tu)_2(NCS)_2$ compounds suggests that
they have a similar N_2S_4 trans-octahedral structure.

The Mössbauer spectrum of the sample of ferrous
thiocyanate had four bands. The outer pair had an
isomer shift of 1.08 mm/sec and a quadrupole splitting of
3.27 mm/sec; and the inner, weaker, pair had an isomer
shift of 0.35 mm/sec and a quadrupole splitting of
0.61 mm/sec. The values for the inner pair of bands are
similar to those observed in ferric compounds and they
are therefore assigned to an oxidation product of ferrous
thiocyanate. In order to confirm this, a sample of ferrous
thiocyanate was exposed to the air for a week and the
Mössbauer spectrum redetermined.

The outer pair of bands were not present in this spectrum, but the inner pair was observed in the same position as in the original spectrum. The quadrupole splitting of 3.29 mm/sec in a D_{4h} compound corresponds to a splitting of the T_{2g} levels of 600 cm^{-1} [78] with the d_{xy} orbital lowest. The spectral parameters for $Fe(NCS)_2$, calculated as for $Fe(tu)_2(NCS)_2$, are; 10Dq = 9,100 cm^{-1}, in-plane field = 7,100 cm^{-1}, axial field = 14,000 cm^{-1}, $\delta\sigma$ = 2,000 cm^{-1}, $\delta\pi$ = 300 cm^{-1}. The axial and in-plane fields are both stronger than in the thiourea compound but the difference between them is rather similar. The relatively greater ligand field strength produced by the nitrogen of bridging thiocyanate compared to monodentate (N) thiocyanate has been observed in other groups of compounds[75].

The position and splitting of γ_1 for $Ni(NCS)_2$ gives 10Dq = 8730 cm^{-1}, in-plane field = 7,000 cm^{-1}, axial field = 12,000 cm^{-1}. No splitting of γ_2 is observed, but due to rising charge transfer absorption in this region, a weak component on the high energy side would not be observed. Values of $\delta\sigma$ and $\delta\pi$ cannot therefore be calculated.

The magnetic properties of $Ni(NCS)_2$ (Table 19) are rather similar to those of $Ni(tu)_2(NCS)_2$. A Curie – Weiss law is followed over the temperature range 370 – 200° K with μ_{eff} = 3.08 B.M., θ =+50°. At lower temperatures the susceptibility is rather less than is given by this law.

In contrast to the case·with the nickel and ferrous compounds, the electronic reflectance spectrum of anhydrous cobalt thiocyanate is not similar to that of $Co(tu)_2(NCS)_2$.(Fig 10) No splitting of ν_1 is observed although the band is asymmetric. The spectrum indicates that the cobalt is octahedrally coordinated, but, due to the presence of strong charge transfer absorption above 18,000 cm^{-1}, a detailed interpretation of the spectrum cannot be given. The electronic spectrum of $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ is quite different from that of the anhydrous compound, but closely resembles that of $Co(tu)_2(NCS)_2$ (Fig.8,Table 14) The magnetic susceptibilities of the anhydrous salt and the hemihydrate are quite different. $Co(NCS)_2$ follows a Curie – Weiss law over the range 360 – 130°K with μ_{eff}=5.59 B.M., θ = ·–46°. The difference between the susceptibilities of these compounds is such that a very small amount of water in the extremely hygroscopic anhydrous compound causes a significant increase in the measured susceptibility.

Table 19

Magnetic Susceptibility of Anhydrous Thiocyanates

Temp. $^\circ$K	$Ni(NCS)_2$ $\chi_{mole}^* \times 10^{-3}$	μ^+ B.M.	Temp. $^\circ$K	$Co(NCS)_2$ $\chi_{mole}^* \times 10^{-3}$	μ^+ B.M.
368	3.69	3.31	343	7.18	4.45
353.5	3.87	3.32	296	8.15	4.42
341	4.03	3.33	238	9.80	4.34
327	4.25	3.35	207	11.12	4.31
310.5	4.51	3.36	182.5	12.33	4.25
294	4.79	3.37	165	13.45	4.23
285	4.97	3.38	146	14.70	4.16
263.5	5.46	3.41	126.5	16.60	4.12
241	5.80	3.41	113.5	17.65	4.02
217	6.84	3.46	107	18.33	3.98
201	7.42	3.47	102	18.80	3.93
187	8.25	3.53	96.5	19.55	3.90
167.5	9.48	3.58	88	20.90	3.86
149.5	10.82	3.61	77.5	23.35	3.82
137	11.98	3.64			
118.5	14.41	3.71			
103	17.04	3.77			
92	19.80	3.83			
78	24.9	3.96			

* Magnetic susceptibility per mole, corrected for diamagnetism

+ Calculated from the Curie Law

The results given in Table   correspond to the lowest
magnetic moment observed out of a total of four separate
preparations and magnetic "runs". The four measured
values of the room temperature (295 - 300°K) Curie law
susceptibility were 4.72, 4.61, 4.55 and 4.42 B.M.

The relationship between the structures of
$Co(NCS)_2$ and $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ is not clear. The infrared
spectrum of $Co(NCS)_2$ can be interpreted as indicating
that the sulphur atom of the thiocyanate group does not
interact strongly with the cobalt atom, and the position
of the metal - nitrogen stretch indicates a fairly strong
metal - nitrogen bond. On the other hand the electronic
spectrum (in particular the absence of any marked
splitting of $\mathcal{V}_1$) is most easily interpreted in terms of
a fairly weak, approximately octahedral, ligand field.
The properties of $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ are, however, readily
rationalized in terms of a   trans-octahedral N_2S_4
coordination sphere similar to that present in $Co(tu)_2(NCS)_2$.
There is no evidence that the water molecules are
coordinated to the metal. It can be concluded that a
trans-octahedral structure such as that adopted by
$Ni(NCS)_2$ is unstable in the case of the cobalt salt
and a different structure is adopted, but that the

presence of half a molecule of water in the lattice
stabilizes the trans-octahedral structure.

As is the case with the other manganese compounds
described in this chapter, no detailed interpretation of
the electronic spectrum of $Mn(NCS)_2$ can be given. The
spectrum is not well resolved and, like the $Mn(ROH)_2(NCS)_2$
compounds, shows no definite absorption below 20,000 cm^{-1}.
The magnetic susceptibility obeys a Curie - Weiss law
over the temperature range 360 - 80°K with μ_{eff} = 5.78 B.M.
θ =-86°. The antiferromagnetic interaction is clearly
much stronger than in $Mn(tu)_2(NCS)_2$.

Conclusions

a) The electronic spectra of the octahedral compounds
$M(tu)_2(NCS)_2$ (M = Fe, Co, Ni, Mn) indicate the presence
of a tetragonal field with the axial field much stronger
than the in-plane field. The far infrared spectra of
these complexes also indicates strong axial bonding.
The difference between the strength of the axial bonding
and the in-plane bonding increases along the series
Cd, Ni, Co, Fe, Mn. The explanation of these changes in
terms of the σ and π-effects of the ligands is complicated
by difficulties in the interpretation of the electronic
spectra.

b)   The complexes $M(ROH)_2(NCS)_2$ (M = Ni, Co, Mn: R = methyl, ethyl) have an octahedral coordination sphere with briding thiocyanate groups and coordinated alcohols. There is a weak antiferromagnetic interaction between the metal atoms.

c)   The compounds $Fe(NCS)_2$, $Ni(NCS)_2$ and $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ have a trans-octahedral structure similar to that of the thiourea-thiocyanate complexes and they have similar electronic spectra. $Co(NCS)_2$ probably has a different structure.

d)   The magnetic properties of $Co(tu)_2(NCS)_2$ and $Fe(tu)_2(NCS)_2$ are normal, but there is an antiferromagnetic interaction in $Mn(tu)_2(NCS)_2$, $Mn(NCS)_2$, $Co(NCS)_2 \cdot \frac{1}{2}H_2O$ and $Co(NCS)_2$ and a ferromagnetic interaction in $Ni(NCS)_2$ and $Ni(tu)_2(NCS)_2$.

CHAPTER FIVE

Some Metal Complexes of Thioacetamide

In Chapters Two, Three, and Four, the infrared, far infrared and electronic spectra, and the magnetic properties of some complexes of thiourea with divalent metals were discussed. As an extension of this work, some complexes of the isoelectronic ligand thioacetamide with divalent metals have been studied. Previous work on these compounds has been limited to the preparation and crystallographic properties of some complexes of metal chlorides[88] and thiocyanates.[89] In this chapter, the infrared, far infrared and electronic spectra of these compounds are described and the differences between these compounds and the corresponding thiourea compounds are discussed.

Infrared Spectra of Thioacetamide Complexes

Suzuki[90] has carried out detailed analyses of the infrared spectra ($4000 - 300$ cm^{-1}) of free thioacetamide and N,N dideuterothioacetamide and assigns all the observed bands to normal vibrations of the essentially planar[91] molecule. The results indicate that, in common with other molecules containing the CSNH$_2$ grouping,[41,92] it is not possible to assign some of the observed bands to vibrational modes largely located

in two or three atoms. In particular, the analysis shows
that the bands at 1306, 975 and 718 cm^{-1} (Table 20) each
involve C - S stretching character, this motion contrib-
uting about 60% of the total energy associated with the
vibration responsible for the band at 718 cm^{-1}.

The far infrared spectrum of thioacetamide shows
no bands between 370 and 160 cm^{-1}. There is, however,
a medium or strong band at 149 cm^{-1}. In view of the
analysis of Suzuki this cannot be a fundamental vibration
of the free thioacetamide molecule. It is, presumably, a
translational lattice mode.

Analysis of the infrared spectrum of thioacetamide
hexachlorostannate indicates that protonation of the
thioacetamide occurs at the sulphur atom.[93] It seems
probable, therefore, that thioacetamide will coordinate
through the sulphur atom. An X - ray crystal structure
determination of the compound Cu(tam)$_4$Cl[94] shows that
the copper atom is tetrahedrally coordinated by four
sulphur-bonded thioacetamide molecules. The infrared
spectra of all the compounds prepared in this work are
rather similar to that of Cu(tam)$_4$Cl[93] (Table 20)
indicating that coordination occurs through the sulphur
atom in these compounds too. The infrared spectra of

Table 20

Infrared Spectra ($2000 - 350$ cm^{-1}) of Thioacetamide Complexes

Assignment[a]	Solid tam	Cu(tam)$_4$Cl[b]	Co(tam)$_2$Cl$_2$	Ni(tam)$_4$Br$_2$	Ni(tam)$_4$Cl$_2$
δ(NH$_2$)	1648	1669	1657	1630	1623
			1638	1612	1614
δa(CH$_3$)	1478	1515	1475	1480	1446
γ(C-N)	1393	1409	1401	1410	1406
δs(CH$_3$)	1364	1376	1362	1366	1369
Skeletal + r(NH$_2$)	1306	1318	1292	1294	1292
r(NH$_2$) + r(CH$_3$)	1030	1305	1026	1025	1030
γ(C-C) + r(CH$_3$) γ(C-S)	975	971	960	965	970
γ(C-S) + γ(C-C)	718	690	691	664	660
w(NH$_2$) and t(NH$_2$)	709	769	732	709	707
		735			611
γ(C-C)	517	506	514	512	518
δ(N-C-S)	471, 460	481	448	455	452
δ(C-C)	375	–	395	418	420, 415

a; abbreviations r = rock, w = wag, t = torsion.   b; reference 95

representative tetrahedral, planar and octahedral

thioacetamide complexes are given in Table 20. As

expected those vibrations involving C - S stretching

character move down slightly on coordination, whilst

the C - N stretch is slightly raised.

The crystal structure determination on $Cu(tam)_4Cl$

shows that the C - S bond retains most of its double

bond character in the complexes. There is therefore a

possibility of an unusual type of isomerism in

thioacetamide complexes which is dependent on which of

the non- identical lone pairs on the sulphur atom is

used for coordination. Truter interprets her results[93]

as indicating that the coordination is of type (ii) in

$Cu(tam)_4Cl$.
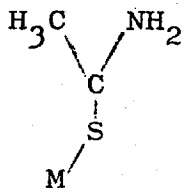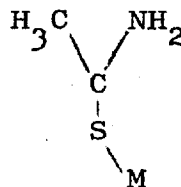
(i)   (ii)

In no case has definite evidence been obtained for the

existence of isomers of the complexes prepared in this

work.

Tetrahedral Complexes

The electronic reflectance spectra (Table 21) of the 2;1 cobalt halide complexes are very similar to those of the corresponding thiourea complexes, suggesting that they have a similar structure. The compounds are partially solvolysed in common organic solvents, but when the complex is dissolved in a 0.1 molar solution of thioacetamide in acetone, electronic spectra are obtained which are unchanged on addition of further quantities of thioacetamide. These spectra are similar to the reflectance spectra and they are therefore taken to be the solution spectra of the $Co(tam)_2X_2$ species. The molar extinction coefficients of the absorption bands are in agreement with this tetrahedral structure. Analysis of the solution spectra according to the usual method [6] gave values of the ligand field parameters 10Dq and B very similar to those of the corresponding thiourea compounds. (Chapter Two)

Table 22

Compound	ν_2 cm^{-1}	ν_3 cm^{-1}	10Dq	B
$Co(tam)_2Cl_2$	6,400	15,200	3,700	700
$Co(tam)_2Br_2$	6,300	14,600	3,650	665
$Co(tam)_2I_2$	6,100	13,800	3,500	625
$Co(tam)_2(NCS)_2$	7,200	15,200	4,200	715

Electronic Spectra of the Cobalt Complexes

Complex	Phase	ν_3 Absorption Maxima (cm^{-1}) ν_2		ν_1
$Co(tam)_2Cl_2$	Solid	16,700, 15,600 13,650	7100, 5780	<4000
$Co(tam)_2Cl_2$	Acetone soln. 0.1M with tam.	16,500(515)*,15,100(585) 13,800(465)	8000 (53), 6500sh 5500(105)	
$Co(tam)_2Br_2$	Solid	15,400, 14,900 13,300	7040, 5680	<4000
$Co(tam)_2Br_2$	Acetone soln. 0.1M with tam.	15,600(540),14,600(645) 13,700(655)	7650(64),6400(84) 5250(94)	
$Co(tam)_2I_2$	Solid	14,700, 13,800 12,700	7000, 5400	<4000
$Co(tam)_2I_2$	Acetone soln. 0.1M with tam.	14,700(600),13,800(755) 13,100(880)	7550 (100),6500(110) 5000+	
$Co(tam)_2(NCS)_2$	Solid	16,800, 16,100 13840	7700, 6940	<4000
$Co(tam)_2(NCS)_2$	Acetone soln. 0.1M with tam.	17,000(580),15,600(820) 14,250(905)	8400(72) 6800(93) 6150(100).	

* Molar extinction coefficients in parenthesis

+ Exact position of this band is in some doubt due to solvent absorption in this region.

Table 21b

Electronic Spectra of Nickel and Ferrous Compounds

Complex	Phase	Absorption Maxima (cm^{-1})		
$Ni(tam)_4Cl_2$	Solid	22,500,	14,020,	8500
$Ni(tam)_2(NCS)_2$	Solid	C.T*	14,950	9470
$Ni(tam)_4Br_2$	Solid		16,850	
$Ni(tam)_4(NO_3)_2$	Solid		17,200	
$Ni(tam)_4(ClO_4)_2$	Solid		17,500	
$Ni(tam)_4SO_4$	Solid		17,100	
$Fe(tam)_2Cl_2$	Solid	5800sh,	5400,	5050sh
$Fe(tam)_2Br_2$	Solid	5800sh,	5400,	4900sh

$^*\nu_3$ is obscured by charge transfer absorption.

The far infrared spectra of these compounds (Table 23) show three or four bands in the metal-ligand stretching region. Following the assignments of the spectra of the thiourea complex and other tetrahedral CoL_2Cl_2 compounds, the strong bands at 319 and 294 cm^{-1} in the far infrared spectrum of $Co(tam)_2Cl_2$ are assigned as the two cobalt-chlorine stretching vibrations and the band at 242 cm^{-1} as a metal — thioacetamide stretch. The other metal – sulphur stretch is presumably either coincident with 242 cm^{-1} band or is too weak to be observed. The band at 122 cm^{-1} can be assigned either as a Cl – Co – Cl bending mode or as a lattice mode. Similarly, it is reasonable to assign the bands at 255 and 238 cm^{-1} in $Co(tam)_2I_2$ as cobalt-sulphur stretches and the two lower energy bands as cobalt-iodine stretches. The lowest energy band consists of an incompletely resolved doublet. Since no splitting or broadening of the higher energy bands is observed, this broadening is probably caused by interaction with a lattice mode or combination band. In the bromide complex, the four vibrational modes involving metal—ligand stretching occur close together; the assignment of particular bands to metal — bromide or metal-sulphur stretching modes under these conditions is unjustified.

Table 23

Far Infrared Spectra of the Thioacetamide Complexes [a]

Compound	tam.bends		M – S stretches	M – X stretches[c]	other bands
tam[b]	471,460	375			149s
Co(tam)$_2$Cl$_2$[d]	448	400sh, 395	242ms	320s, 294s	136sh,122s 90br
Co(tam)$_2$Br$_2$[d]	449	400sh, 395	(266m, 247s,239s, 193w)		152w, 132w 95br, 78sp
Co(tam)$_2$I$_2$[b]	447	392	255m, 238s	212s, 160sh, 150m	
Fe(tam)$_2$Cl$_2$	447	389	230ms	324s, 302s	
Fe(tam)$_2$Br$_2$	451	388	(259s, 248s, 231s, 226sh, 192w)		
Zn(tam)$_2$Cl$_2$	450	406sh, 398	237sh,224ms	298s, 275s	
Zn(tam)$_2$I$_2$	451	404sh, 397	(243m, 224sh, 212s, 193m)		
Zn(tam)$_2$I$_2$	451	396	235m, 218m	182s	
Cd(tam)$_2$Cl$_2$	460	397	(204s,177s,170s)		
Cd(tam)$_2$Br$_2$	453	398	205m, 198m	169m	
Cd.tam)$_2$I$_2$[b]	450	392	198s, 189sh	154s,135m	
Co(tam)$_2$(NCS)$_2$[b]	453	395	252ms	330br,290br	150brw

Table 23 (cont.)

Compound	tam.bends		M – S stretches	M – X stretches	other bands
$Ni(tam)_4Cl_2$	452	420sh,415	196s	229m	
$Ni(tam)_2(NCS)_2$	458,446	393	220s, 201s	269s	179s
$Ni(tam)_4Br_2$ [b]	455	418	290vw		184s, 148s
$Ni(tam)_4(NO_3)_2$	456	418	291vw		240vw
$Ni(tam)_4(ClO_4)_2$	459	419	292vw		237vw, 186s,182s
$Ni(tam)_4SO_4$ [b]	459	417	294vw		193s 148br
$Pd(tam)_4Cl_2$ [b]	471	421,413	269w,256w		207s,194s 169s,143s
$Pt(tam)_4Cl_2$ [b]	476	424,419	257w,245w		206s,199sh 181m,141s
$Cd(tam)_4(ONO_2)_2$	477	398	173s,163s	235m,221s	

a   Spectra were measured to 160 cm^{-1} except where stated.

b   These spectra were measured to 130 cm^{-1}.

c   X is halide, thiocyanate or nitrate according to compound

d   These spectra were measured to 65 cm^{-1}

The electronic reflectance spectrum of $Co(tam)_2(NCS)_2$ is closely similar to those of the halide complexes, although the ligand field is rather stronger. This is compound is therefore also assigned a tetrahedral structure. The molar extinction coefficients of the solution of the compound in acetone containing thioacetamide confirm this view.

The far infrared spectrum of $Co(tam)_2(NCS)_2$ can be readily interpreted in terms of this structure, the doublet at 320 cm^{-1} is assigned as the cobalt - thiocyanate (N) stretches and the band at 250 cm^{-1} as one or both of the cobalt - thioacetamide stretches.

The compounds $Co(tam)_2Cl_2$, $Zn(tam)_2Cl_2$ and $Fe(tam)_2Cl_2$ are isomorphous [88] and the far infrared spectra of all three zinc halide complexes and of $Fe(tam)_2Cl_2$ and $Fe(tam)_2Br_2$ are similar to those of their cobalt analogues, allowance being made for the usual decrease in the frequency of metal - ligand vibrations on passing from cobalt to zinc. It seems likely, therefore, that all of these compounds have tetrahedral structures.

The electronic reflectance spectra of the ferrous compounds are in agreement with this; both show an intense band at about 5000 cm^{-1} which is typical of ferrous iron in an essentially tetrahedral environment. The bands show partial resolution into the three components expected for C_{2v} symmetry.

Although $Cd(tam)_2Cl_2$ is not isomorphous with its cobalt analogue,[88] it appears from the far infrared spectra that the complexes of the three cadmium halides also have tetrahedral structures. In the chloride, there are three bands rather close together which appear to represent metal - ligand stretching modes, although detailed assignments cannot be given. For all three compounds the spectra are rather similar to those of the $Cd(tu)_2X_2$ complexes.

Planar Compounds

The blue - purple complexes $Ni(tam)_4X_2$ (X = Br, ClO_4, NO_3, $\frac{1}{2}SO_4$) are diamagnetic, and have reflectance spectra consisting of one broad, rather intense band at about 17,000 cm^{-1}. These compounds are therefore considered to have square planar coordination about the nickel atom. (compare $Ni(tu)_4SO_4 \cdot MeOH$). In agreement with this, the infrared spectra of the nitrate

and sulphate ions indicate that they are not coordinated. The infrared spectrum of $Ni(tam)_4(ClO_4)_2$ has a medium to strong band at 1160 cm^{-1} in addition to the bands at 1060 cm^{-1} and 616 cm^{-1} which are apparently due to ionic perchlorate groups. All the other thioacetamide compounds have only a very weak band in this position. This band could be interpreted as indicating a perturbation of the perchlorate group, but the absence of an additional strong band in the range 900 - 1000 cm^{-1} (where γ_1 of the perturbed perchlorate ion would be expected to occur) seems to preclude this possibility. The origin of this band remains obscure.

The far infrared spectra of these compounds each show a weak band at about 290 cm^{-1} together with a strong band at about 185 cm^{-1};. In addition, a very weak band at about 240 cm^{-1} is sometimes detected. The general appearance of the spectra is very similar to those of the square planar nickel - thiourea compounds, the bands being shifted 10 - 20 cm^{-1} to lower energy. Following the assignments for the square planar thiourea compounds (Chapter Two), the band at about 290 cm^{-1} is assigned as the asymmetric stretching mode and the band at about 240 cm^{-1} as either the $A_{1g}(\gamma_1)$ or the $B_{2g}(\gamma_2)$ stretching modes of the square planar cation.

The strong band at about 185 cm^{-1} is then assigned as an in-plane bending mode.

The compounds $Pd(tam)_4Cl_2$ and $Pt(tam)_4Cl_2$ have far infrared spectra which are readily interpretable in terms of the anticipated square planar structure. In both cases the C - C out of plane bend, the asymmetric metal - sulphur stretch, and the in-plane metal - ligand bending mode (at 194 - 207 cm^{-1}) are split into two components. This presumably reflects the departure of the cation from D_{4h} symmetry. The mean energy of the in-plane bend in the platinum compound is appreciably higher than that of the palladium compound which is itself higher than that of the nickel compound. This situation is different from that in the corresponding thiourea complexes.

The two lowest internal bending modes of the coordinated thioacetamide in the square planar compounds occur at 455 - 476 cm^{-1} and 414 - 424 cm^{-1}. The corresponding bands in the tetrahedral compounds are at 447 - 460 cm^{-1} and 388 - 406 cm^{-1}. The position of the lowest energy ligand band thus enables a clear distinction between tetrahedral and planar structures to be made (see Table 23.)

Octahedral Compounds

The compound $Ni(tam)_4Cl_2$ has a reflectance spectrum which is very similar to the trans-octahedral compound $Ni(tu)_4Cl_2$,[76] and it probably has a similar structure. The ligand field in the thioacetamide complex is rather stronger, the derived spectral parameters being $10Dq = 8,500 \ cm^{-1}$, $B = 730 \ cm^{-1}$.

The far infrared spectrum of this compound shows two bands in the metal – ligand stretching region. As discussed for $Ni(tu)_4Cl_2$ (Chapter Two), it is not clear which of these bands corresponds to the predominately metal – sulphur stretching mode and which to the predominately metal – chlorine stretching mode. However, if it is assumed that the difference between the thiourea and the thioacetamide compounds that is observed for the tetrahedral complexes, i.e. that in the thioacetamide compounds, the metal – sulphur stretching frequencies are at lower energies, and the metal – halide stretches at higher energies, than in the thiourea compounds, then the higher energy band is assigned as the metal – chlorine stretching mode and the band at $196 \ cm^{-1}$ as the metal – sulphur stretching mode.

The position of the two lowest energy internal vibrations in the ligand are similar to those of the square planar compounds.

The infrared spectrum of the compound shows two marked differences from those of the other compounds (Table 20). The 1478 cm^{-1} band in free thioacetamide chiefly involves motion located in the methyl group[90] and as expected this band moves very little on coordination in the tetrahedral and planar compounds (Table 20). However, there is no absorption band close to 1480 cm^{-1} in the infrared spectrum of $Ni(tam)_4Cl_2$, and the band at 1446 cm^{-1} apparently corresponds to this absorption. This shift may be caused by steric interaction between the methyl groups and the chloride ion. The second difference is the appearance of a medium strength band at 611 cm^{-1}. This may be the NH_2 wag or torsion, the accidental degeneracy[90] of these modes being removed by steric or hydrogen bonding effects in the complex.

The electronic spectrum of $Ni(tam)_2(NCS)_2$ is typical of octahedrally coordinated nickel (II) with 10Dq = 9470 cm^{-1} and B = 770 cm^{-1} and the magnetic susceptibility obeys a Curie – Weiss law with μ_{eff}= 3.19 B.M., θ= –3°.

The infrared spectrum of the compound is similar to that of $Ni(tam)_4Cl_2$ (except for the absence of the band at 611 cm^{-1}.) with the addition of thiocyanate bands at 2118 cm^{-1}, 779 cm^{-1} and 466 cm^{-1}. These frequencies are typical of those found for bridging thiocyanate groups.[87]

The magnetic behaviour of the compound and the very close similarity of its infrared spectrum to those of compounds containing monodentate thioacetamide suggests that the compound does not have a structure similar to that of the analogous thiourea compound. It is likely, therefore, that this compound consists of $Ni(tam)_2$ units linked together by four thiocyanate bridges.

The far infrared spectrum (Table 23) can be interpreted in terms of this structure. The 268 cm^{-1} band is readily assigned as the nickel-thiocyanate stretching frequencies.

After this work was complete, Nardelli et al.[95] published brief preliminary details of their X - ray crystal structure determination on this compound. They find that the nickel is octahedrally coordinated with two axial thiocyanate groups and four sulphur atoms in the plane, two from the thioacetamide in cis positions and two from the thiocyanate groups.

Examination of the infrared spectrum of $Cd(tam)_4$ $(NO_3)_2$ (Fig 11.) does not lead to any definite conclusions concerning whether the nitrate ions are coordinated or not due to strong absorption by thioacetamide in the 1600 - 1200 cm^{-1} region. The spectrum is, however, appreciably different from that of $Ni(tam)_4(NO_3)_2$. The ν_1 (A_1) vibration of the nitrate ion (infrared inactive for the free ion) appears with medium intensity. The spectrum is, therefore, perhaps more consistent with the presence of coordinated nitrate. Assuming octahedral sterochemistry with coordinated nitrate ions, the doublet at 235,221 cm^{-1} in the far infrared spectrum can be assigned as metal-nitrate stretching modes, and the 173, 163 cm^{-1} bands as the metal-sulphur stretching modes of the octahedral complex. The far infrared spectra of the compound could also be interpreted in terms of a distorted tetrahedral structure, the higher energy doublet being metal - sulphur stretching modes and the lower energy bands being bending modes similar to those observed in $Co(tu)_4(NO_3)_2$ (Table 6.) The C - C out of plane deformation occurs at 397 cm^{-1} which is very similar to the position of this mode in tetrahedral compounds, but different from that found in octahedral $Ni(tam)_4Cl_2$. This is not necessarily indicative of tetrahedral

Fig.11

Infrared Spectra (1700 - 600 cm^{-1}) of some Thioacetamide Complexes
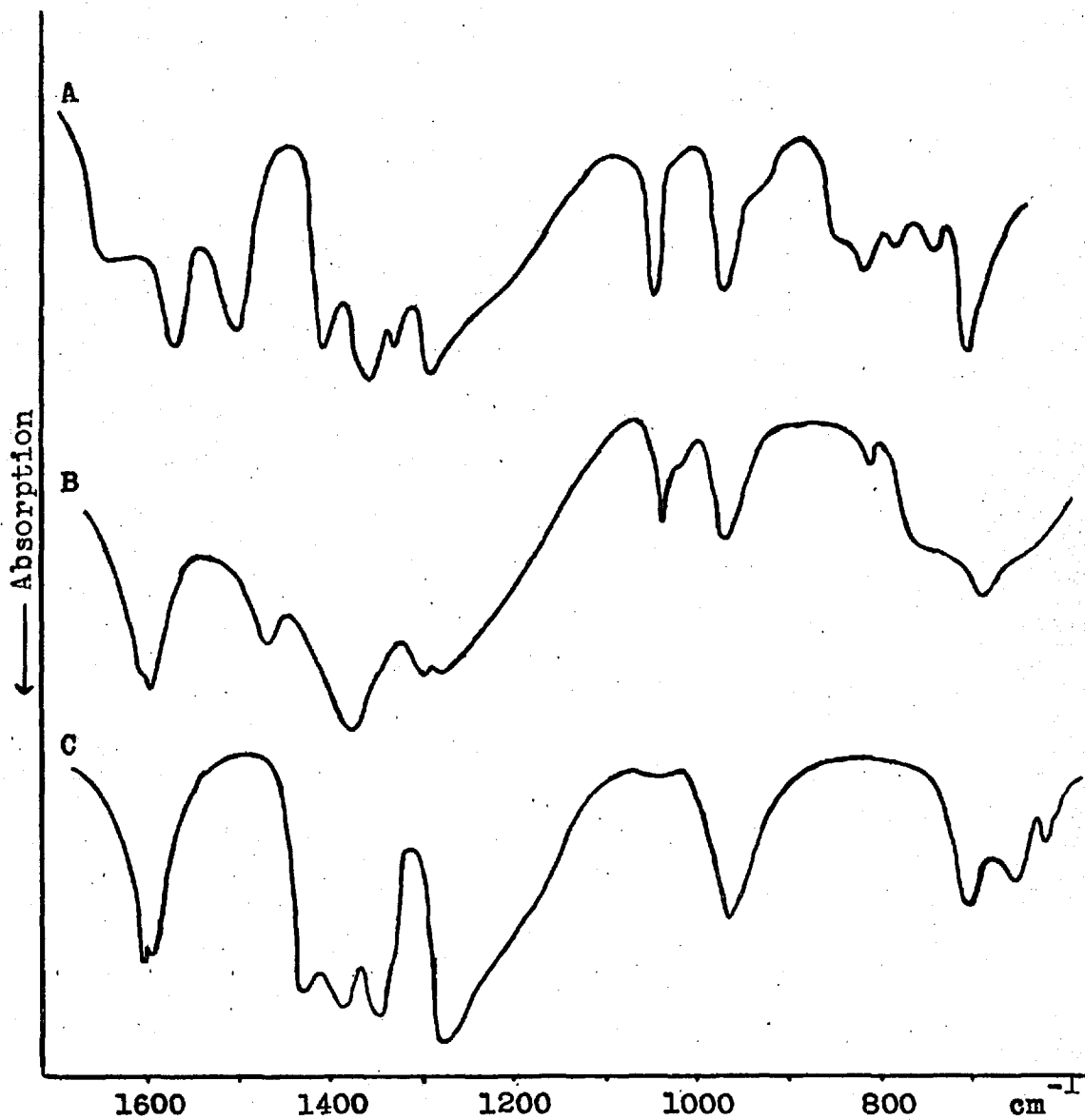
A $Cd(tam)_4(NO_3)_2$

B $Ni(tam)_4(NO_3)_2$

C $Ni(tam)_4Cl_2$

coordination however as the same band occurs at 393 cm^{-1} in octahedral $Ni(tam)_2(NCS)_2$. The balance of evidence therefore seems to support the octahedral structure for this compound.

Comparison of Thioacetamide and Thiourea Complexes

Thioacetacetamide has a greater tendency to form square planar compounds with nickel (II) than has thiourea; no compounds containing the $Ni(tam)_6^{2+}$ cation could be prepared. The position of the lowest spin allowed d – d bands of the square planar nickel compounds is similar for both ligands, indicating that the ligand fields produced by thiourea and thioacetamide are rather similar in these compounds.

The metal – sulphur stretching frequencies in the square planar thioacetamide complexes are consistently lower than those in the corresponding thiourea compounds. The most surprising feature of the far infrared spectra of the square planar thioacetamide complexes is the weakness of the bands assignable as the metal–sulphur stretching frequencies compared to those in the tetrahedral compounds and the square planar thiourea complexes. No explanation of this can be given, presumably the change in dipole moment during the vibration is small due to the particular values of the molecular parameters in these compounds.

Thioacetamide forms tetrahedral 2:1 complexes with cobalt(II), zinc(II) and cadmium(II) halides which are similar to those formed by thiourea, and the ligand field parameters are very similar for the two sets of cobalt compounds. The metal - halide stretching frequencies of the thioacetamide complexes are, however, somewhat lower than those of the corresponding thiourea compounds, whereas the metal-halide stretching frequencies are rather higher.

It is possible that these differences in metal-ligand stretching frequencies are due to small differences in the detailed stereochemistries of the compounds. There are no crystal structure determinations on these thioacetamide complexes but the Cu - S and the C - S distances and the Cu - S - C angles in Cu(tam)$_4$Cl[94] and Cu(tu)$_3$Cl[50] (non-bridging thiourea molecules) are similar. This, together with the fact that the trend in metal-sulphur stretching frequencies is observed in all compounds where a meaningful comparison can be made, suggests that the differences are due to actual changes in the bond strengths.

Nickel(II) has a greater tendency to adopt a square planar stereochemistry when the ligands are capable of forming strong π-bonds (assuming that steric effects are similar in the two sets of compounds). In Chapter Four it was shown that, in the trans-octahedral compounds $M(tu)_2(NCS)_2$, thiourea is acting as a π-acceptor relative to thiocyanate. The thiocyanate ion appears to have, in general, very little π-effect.[82] It is likely, therefore, that in the square planar $Ni(tu)_4^{2+}$ cation (where π-effects would be expected to be stronger than in the octahedral compounds), thiourea is acting as a π-acceptor.

This suggests that the reduction in the bond strengths of the thioacetamide complexes relative to those of the thiourea complexes is not due to a decrease in π-bonding. All the facts can be rationalised, however, if there is a decrease in σ-bond strength, accompanied by an increase in metal$\rightarrow$ligand π-bonding, resulting in a similar field strength and a greater tendency to form planar complexes. (This assumes that a change in π-bonding will have a relatively greater effect on the ligand field than it will have on the bond strength, but this is not unreasonable.) In thiourea compounds the factors affecting whether a square planar $Ni(tu)_4^{2+}$ cation

or an octahedral $Ni(tu)_6^{2+}$ cation is formed are rather finely balanced. A relatively small increase in the π-acceptor capacity of the ligand might result in square planar coordination being preferentially adopted. This is presumably what happens in thioacetamide complexes; this ligand would be expected to be a better π-acceptor than thiourea because the methyl group is a weaker π-donor than the amine group.

Conclusions

a)   The complexes $M(tam)_2X_2$ (M = Co, Zn, Cd; X = Cl, Br, I M = Fe; X = Cl, Br) are tetrahedrally coordinated; the complexes $Ni(tam)_4X_2$ (M = Br, NO_3, ClO_4, $\frac{1}{2}SO_4$), $M(tam)_4Cl_2$ (M = Pd, Pt) are planar; and the complexes $Ni(tam)_4Cl_2$ and $Ni(tam)_2(NCS)_2$ are octahedral. $Cd(tam)_4(NO_3)_2$ is also probably octahedral.

b)   The ligand field produced by thioacetamide is approximately equal to that produced by thiourea in similar complexes

c)   The metal-sulphur stretching frequencies of the thioacetamide complexes are somewhat lower than those of the corresponding thiourea compounds. This is probably due to a difference in bond strength.

d)   Thioacetamide appears to be a weaker σ-donor and a better π-acceptor than thiourea.

CHAPTER SIX

Some Complexes of Chelating Alkyl Sulphides

Metal complexes of 2:5 dithiahexane have been prepared by a number of workers [96, 97, 98] and their far infrared spectra have been interpreted as indicating the presence of the gauche form of the ligand. [99] Blackhouse, Foss, and Nyholm [97] have measured the room temperature magnetic susceptibility of some of the nickel complexes and conclude that the nickel atoms are octahedrally coordinated in each case. More recently, Carlin and Weisberger [98] have reported the magnetic susceptibility and electronic spectra of some cobalt and nickel complexes of 2:5 dithiahexane and 3:5 dithiaoctane. The results of these investigations suggested that a detailed study of the metal complexes of 2:5 dithiahexane and some more sterically hindered chelating alkyl sulphides would be of interest.

General

2:5 Dithiahexane forms a 3 : 1 complex with nickel perchlorate. 2 : 1 Complexes are formed with cobalt and nickel halides and thiocyanates, cobalt perchlorate, cobalt nitrate, copper(II) perchlorate and copper(II) borofluoride. Cobalt chloride, copper(II)

chloride, and the cadmium halides give 1 : 1 complexes
with dithiahexane. Some of these complexes have not been
described previously and the physical measurements on the
other compounds were not complete. In particular, there
is no infrared data for these compounds below 650 cm^{-1}.

The ligand 1:2 bis(isopropylthio)ethane forms 2 : 1
complexes with cobalt and nickel halides and thiocyanates.
No complexes of this ligand have been described previously.

Attempts to prepare solid complexes of first row
transition metals with 1:2 bis(tert-butylthio)ethane,
1:2 bis(phenylthio)ethane, and 1:2 bisthiocyanatoethane
were unsuccessful. (See Chapter Seven.)

Infrared Spectra
        2:5 Dithiahexane has three axes of internal
rotation (taking the methyl groups as symmetrical) and
can therefore exist in several molecular conformations
in the liquid state. However, the molecule cannot exist
in the trans form as a chelating ligand in coordination
complexes. There are, therefore, marked differences
between the infrared spectra of the ligand and the metal
complexes. These spectral differences have been studied
in some detail[99,100] and the results interpreted as

indicating the presence of the gauche form of the ligand
in the complexes. The infrared spectra of all the
dithiahexane complexes prepared in this work were rather
similar to those reported by Sweeny et al.[99] showing
that the ligand exists in the gauche form in these complexes
too. An X - ray crystal structure determination of the
compound $Co(DTH)_2(ClO_4)_2$,[101] which has infrared bands
due to dithiahexane similar to those in the other
complexes, confirms these conclusions.

The infrared spectrum of liquid 1:2 bis(isopropyl-
thio)ethane is distinctly different from the spectra of
its complexes and this probably indicates a similar
change in conformation.

Electronic Spectra

The electronic spectrum of $Ni(DTH)_3(ClO_4)_2$ (Table 24)
is characteristic of octahedrally coordinated nickel(II)
and the position of ν_1, ν_2, and ν_3 can be fitted by taking
$10Dq = 10,900$ cm^{-1} and $B = 740$ cm^{-1}. The ligand field
is much stronger than in $(Ni(tu)_6)(NO_3)_2$, in agreement
with Jørgensen's theory, and the nephelauxetic effect
is much less pronounced. (see Chapter One).

Table 24

Electronic Reflectance Spectra

Compound	Band Maxima (cm^{-1})
$Ni(DTH)_3(ClO_4)_2$	26,700; 17,100; 10,900.
$Ni(DTH)_2(NCS)_2$	26,000sh; 17,100; 11,000sh, 10,100.
$Ni(DTH)_2Cl_2$	24,400; 15,350; 10,600sh, 9100.
$Ni(DTH)_2Br_2$	23,100; 15,000; 10,600sh, 9000.
$Ni(DTH)_2I_2$	C.T.[*] 14,900; 10,900sh, 8650.
$Co(DTH)_2(ONO_2)_2$	C.T. 17,000sh; 9430.
$Co(DTH)_2(NCS)_2$	25,500, 23,800sh; (20,200sh)[+] 17,500, 16,200; 9610; (7,300sh).
$Co(DTH)_2Cl_2$	19,700, 18,900; (16,900) 15,500, 14,800sh; 8000.
$Co(DTH)_2Br_2$	18,900, 18,000sh; 15,750; 8550sh, 7690.
$Co(DTH)_2I_2$	C.T. 13,000sh; 8240, 6800sh.
$Co(DTH)_2(ClO_4)_2$	20,000; 7380.
$Co(DTH)Cl_2$	20,000sh, 18,500; 15,700, 14,900, 14,400; 6020, 5460, 5130, 4850, 4610.
$(n-Bu_4N)_2(CoCl_4)$	(18,800) 15,700, 14,800, 14,500; 5990, 5460, 5140, 4820, 4570.
$Cu(DTH)Cl_2$	12,000

Table   24 (cont.)

Compound	Band Maxima (cm^{-1})
$Ni(IPTE)_2(NCS)_2$	25,300sh; 15,400; 9400.
$Ni(IPTE)_2Cl_2$	23,400; 13,900; 9,800sh; 8480.
$Ni(IPTE)_2Br_2$	22,850; 13,900; 9900sh; 8250.
$Ni(IPTE)_2I_2$	C.T. 14,000, 13,500sh; 9700sh, 8250.
$Co(IPTE)_2(NCS)_2$	25,000sh; 14,900; 9900; (7810).
$Co(IPTE)_2Cl_2$	19,700, 18,800; 14,500; 8500sh, 7460.
$Co(IPTE)_2Br_2$	18,900sh, 18,000; 15,100,14,400; 7350.
$Co(IPTE)_2I_2$	C.T. 13,000sh; 7810, 6300sh.
$Ni(DTH)_2(NCS)_2I_4$	10,900
$Ni(DTH)_2Cl_2I_4$	9720, 8580
$Ni(DTH)_2Br_2I_4$	9180sh, 8600
$Ni(DTH)_2I_6$	10,000
$Ni(DTH)_3(ClO_4)_2I_6$	11,500

* C.T. indicates that ν_3 is obscured by charge transfer absorption.

+ Spin – forbidden bands in parentheses.

The electronic reflectance spectra of the compounds $Ni(DTH)_2X_2$ (X = NCS, Cl, Br, I) are readily interpreted in terms of octahedral stereochemistry. γ_1 is split into two components in these compounds, the upper, weaker, component at $\sim$10,800 cm^{-1} is assigned as the $^3B_{1g} \longrightarrow {}^3B_{2g}$ transition of a trans-octahedral complex. The energy of this transition gives the in-plane field, which is seen to be independent of the axial ligands. The axial fields due to the halide or pseudohalide ions are then; NCS,$^-$ 9,200, Cl$^-$, 7,600, Br,$^-$ 7,400, I$^-$, 6,400 cm^{-1}. These values are subject to some error but indicate that these ions are in their normal positions in the spectro-chemical series. In no case is any splitting of γ_2 observed and therefore values of $\delta\sigma$ and $\delta\pi$ cannot be calculated with any reliability.

A compound $Ni(IPTE)_3(ClO_4)_2$ could not be prepared. The reflectance spectra of the complexes $Ni(IPTE)_2X_2$ (X = NCS, Cl, Br, I) are rather similar to those of the corresponding dithiahexane compounds. The shoulder on the high energy side of γ_1 in the halide complexes gives the in-plane field (assuming a trans-octahedral structure) produced by 1:2 bis(isopropylthio) ethane as $\sim$ 9,900 cm^{-1}. Using this value, the axial fields due to the anions are found to be similar to those in the corresponding dithiahexane compounds.

The weaker ligand field produced by bis(isopropylthio)ethane relative to dithiahexane is probably caused by the bulk of the isopropyl groups causing an increase in the metal – sulphur distance.

A compound of stoichiometry $Co(DTH)_3(ClO_4)_2$ could not be prepared.

The electronic spectra of the cobalt-dithiahexane compounds cannot be accurately accounted for by the Tanabe-Sugano determinants; however, the positions of the bands in the halide complexes can be fitted by using the "complete" energy level diagram as calculated by Liehr.[102] Taking 10Dq as 8,300 cm^{-1} (B is fixed at 835 cm^{-1} in the calculation) the predicted positions of the spin-allowed transitions are ~8,000, 16,200, and ~19,500 cm^{-1} which is in reasonable agreement with the observed spectrum of $Co(DTH)_2Cl_2$. A similar fit may be found for the bromide by taking 10Dq = 8,000 cm^{-1}. The electronic spectrum of $Co(DTH)_2(NCS)_2$ cannot be accounted for by Liehr's diagram, the reason for this is obscure since this compound would be expected to have a ligand field of nearly O_h symmetry. It is possible that one or both of the bands in the 16,000 – 18,000 cm^{-1} region are due to a trace of a tetrahedral species. The absorption at 9,600 and ~24,000 cm^{-1} can then be accounted for by Liehr's diagram with 10Dq = 11,000 cm^{-1}.

The shoulder at 7,300 cm^{-1} in this compound is probably due to a transition to the ^2E_g level gaining intensity from ν_1.

The electronic spectra of the cobalt-bis(isopropylthio ethane complexes can be fitted to Liehr's diagram by taking values of 10Dq as 8,000, 7,800, 7,600, and 7,500 cm^{-1} for the thiocyanate, chloride, bromide, and iodide respectively. The band at ~ 8,500 cm^{-1} in the spectrum of the chloro-complex is probably due to a transition to the ^2E_g level. The splitting of ν_1 for both cobalt iodide complexes is as would be expected for a weak axial σ-donor and a stronger in-plane σ-donor (assuming that π-effects are smaller than σ-effects.)

The reflectance spectrum of Cu(DTH)Cl$_2$ consists of one very broad band at about 12,000 cm^{-1}. The absence of a band at about 6,000 cm^{-1} shows that the compound is not tetrahedral. In chloroform, acetone or nitromethane solution, the electronic band moves to about 13,500 cm^{-1} (ε =130 mole^{-1}) and there is again no absorption at lower energy. The shift in position of the d - d band on going from the solid state to solution presumably reflects a change in the axial bonding of the essentially square planar complex. The magnetic moment of the solid complex, 1.76 B.M. at 293°K, is normal for copper(II) compounds.

The electronic spectra of $Co(DTH)_2(ClO_4)_2$, $Co(DTH)_2(NO_3)_2$, $Cu(DTH)_2(ClO_4)_2$, $Cu(DTH)_2(BF_4)_2$ and $Co(DTH)Cl_2$ will be discussed separately below.

Far Infrared Spectra

Free 2:5 dithiahexane and 1:2 bis(isopropylthio) ethane are virtually transparent in the region 500 - 200 cm^{-1}. (The far infrared spectra of the compounds discussed in this chapter were not measured below 200 cm^{-1}.) Two weak bands are observed at 418 cm^{-1} and 219 cm^{-1} in dithiahexane using rather thick samples. Mitzushima et al.[100] have calculated that the C - C - S bend of symmetry B of the RS - CH_2 - CH_2 - SR group (R = CN) will occur at 410 cm^{-1} for the trans molecule (C_{2h}) and 222 cm^{-1} for the gauche molecule (C_2). The two bands that are observed probably represent these modes, however C - S - C bending modes may also occur in this region.

The far infrared spectrum of $Ni(DTH)_3(ClO_4)_2$ shows one strong band at 248 cm^{-1}, together with weak bands at 450 cm^{-1}, 350 cm^{-1}, and 230 cm^{-1}. The A C - C - S bending mode (infrared inactive for a centrosymmetric species), which occurs at 292 cm^{-1} in the Raman spectrum of solid 2:5 dithiahexane (i.e. the trans form), has been predicted[100] to occur at 251 cm^{-1} in the gauche form. The observed strong band may be this mode modified by the presence of the nickel atom.

Table 25

Far Infrared Spectra (500 – 200 cm^{-1}

Compound	Band Maxima (cm^{-1})				
Liquid DTH	417wbr			219w	
$Ni(DTH)_3(ClO_4)_2$	450m	350w	248s, 230sh		
$Ni(DTH)_2(NCS)_2$	443w	317w	281s,[*]	229s	
$Ni(DTH)_2Cl_2$	446w	–	264s,[*] 246s, 229s, 205w		
$Ni(DTH)_2Br_2$	442w	–	256s, 236w, ~200[*]		
$Ni(DTH)_2I_2$	450w	343vw, 300wbr, 255s, 240s			
$Co(DTH)_2(ONO_2)_2$	440w	327vw	264s,[*] 248s, 222br		
$Co(DTH)_2(NCS)_2$	440m	315w,	272br,[*] 230mbr		
$Co(DTH)_2Cl_2$	442m	295sh,	266s,[*] 236s		
$Co(DTH)_2Br_2$	440w	–	255s, 233s, ~200[*]		
$Co(DTH)_2I_2$	446m	342w	245s, 223s		
$Co(DTH)Cl_2$	393m	330w, 296s,[*] 281s,[*] 267s,[*] 242w			
$Co(DTH)_2(ClO_4)_2$	442w	343w, 329w, 277s, 255br, 235m			
$Cu(DTH)_2(ClO_4)_2$	455br	343w, 325w, 290s, 272s, 259s			
$Cu(DTH)_2(BF_4)_2$	455br	352w	291s, 274s, 255s		
$Cu(DTH)Cl_2$	464w	308s,[*] 288s, 272s.			
$Cd(DTH)Cl_2$	434m	324w,	259w, 226s, 212s		
$Cd(DTH)Br_2$	440w	–	238s, 220s		
$Cd(DTH)I_2$	440sh, 429m	322wbr	< 200		

[*]These bands probably represent predominantly metal–anion stretching modes.

Table 25 (cont.)

Compound	Band Maxima (cm^{-1})		
Liquid IPTE	430w,	350w,	335w
$Co(IPTE)_2(NCS)_2$	360w		271s*
$Co(IPTE)_2Cl_2$	360w		283s*
$Co(IPTE)_2Br_2$	362w		250m,220s*
$Co(IPTE)_2I_2$	360br		<200
$Ni(IPTE)_2(NCS)_2$	363w	300sh	279s*
$Ni(IPTE)_2Cl_2$	362w		273s*
$Ni(IPTE)_2Br_2$	361w	258m,	240m,216s*
$Ni(IPTE)_2I_2$	361w	250m	<200s*
$Ni(DTH)_2(NCS)_2I_4$	269m,*	235m, ~200	
$Ni(DTH)_2Cl_2I_4$	250m,*	240m 225m ·	
$Ni(DTH)_2Br_2I_4$	248br		
$Ni(DTH)_2I_6$	265w,	250mbr,220br	
$Ni(DTH)_3(ClO_4)_2I_6$	265m,	250sh,	

*These bands probably represent predominantly metal-anion stretching modes.

Examination of the spectra of the series of compounds $M(MTH)_2X_2$ (M = Co, Ni; X = Cl, Br, I, NCS) shows that they each have a weak band at ~ 455 cm^{-1}, a very weak band at 350 - 395 cm^{-1} and one or two fairly strong bands at 220 - 260 cm^{-1}. In addition, the two thiocyanates each have a strong band at about 275 cm^{-1} which is assigned as a metal - thiocyanate stretching mode, and the two chloro complexes each have a strong band at about 265 cm^{-1} which is assigned as a metal - chlorine stretching mode. The metal - chlorine stretches are rather higher than in most other octahedral cobalt and nickel complexes and this may reflect an interaction between the metal - chlorine stretches and the vibrations involving dithiahexane at slightly lower energy. In support of this, the strong "dithiahexane bends" occur at rather lower energy in the chloride complexes than in the bromide and iodide complexes.

The far infrared spectra of the complexes $M(IPTE)_2X_2$ (M = Ni, Co; X = Cl, Br, I, NCS) each have a weak band at 360 cm^{-1} together with one strong band which varies with the anion. (Fig.12). This strong band is assigned as a metal - anion stretching mode. The metal - halogen stretching modes are at rather high energy for octahedral complexes, but their relative frequencies for different halogens are similar to those usually found and no other assignment seems reasonable.

Fig.12

Far Infrared Spectra of Ni(IPTE)$_2$X$_2$ Complexes
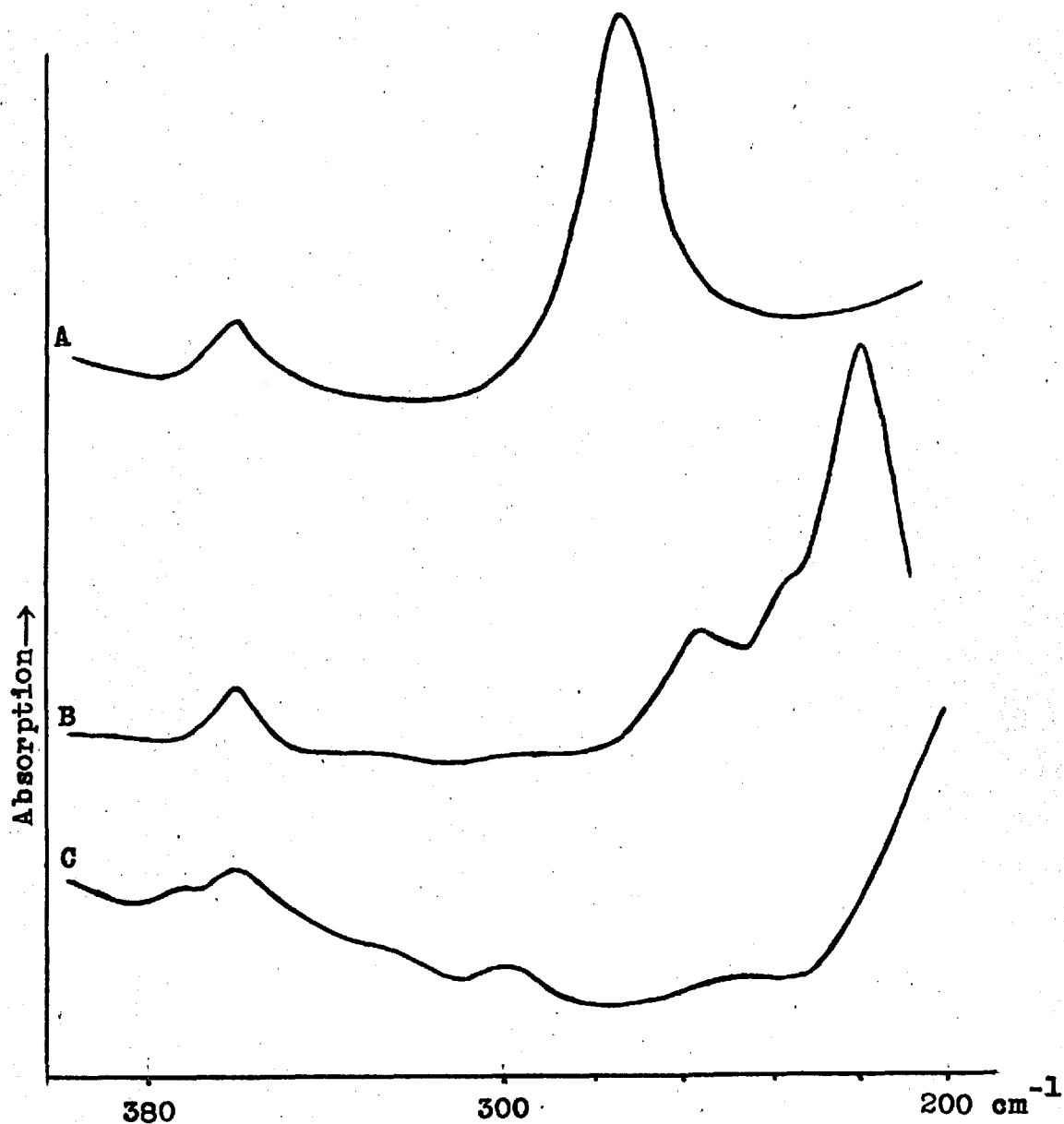
A   Ni(IPTE)$_2$Cl$_2$

B   Ni(IPTE)$_2$Br$_2$

C   Ni(IPTE)$_2$I$_2$

The shift of these modes to higher energy relative to the dithiahexane compounds possibly reflects the weaker in-plane field in the bis(isopropylthio)ethane complexes. (compare the $M(tu)_2(NCS)_2$ compounds described in Chapter Four).

The far infrared spectra of some other dithiahexane complexes will be discussed below.

The compounds $Co(DTH)_2(NO_3)_2$, $Co(DTH)_2(ClO_4)_2$ $Cu(DTH)_2$ $(ClO_4)_2$ and $Cu(DTH)_2(BF_4)_2$

The infrared spectrum of $Co(DTH)_2(NO_3)_2$ has bands due to the nitrate ion at 1372m, 1275s, 811m, and 727m cm^{-1} showing that the anion is coordinated. The bands due to dithiahexane indicate that this ligand is coordinated in the gauche conformation. The magnetic susceptibility of the compound (Table 26) supports the octahedral structure. The lowest energy electronic transition indicates that the ligand field is slightly weaker than that in $Co(DTH)_2(NCS)_2$. The far infrared spectrum is very similar to that of $Ni(DTH)_2Cl_2$ suggesting that the $Co - ONO_2$ stretch occurs at 264 cm^{-1}.

Cotton et al. have determined tht crystal structure of $Co(DTH)_2(ClO_4)_2$; the cobalt is octahedrally coordinated by four sulphur atoms at 2.29A$^{\circ}$ in the plane and two oxygen atoms from the perchlorate groups at 2.36 A$^{\circ}$; the

Table 26

Magnetic Properties of some Complexes of Chelating Alkyl

Sulphides

Compound	μ B.M.[*]	μ_{eff} B.M.[†]	θ
$Co(DTH)_2(NO_3)_2$	4.65	4.83	-23°
$Co(DTH)_2(ClO_4)_2$	see Table 28		
$Co(DTH)Cl_2$	4.73	4.70	$+5^o$
$Cu(DTH)_2(ClO_4)_2$	1.78	1.84	-18°
$Cu(DTH)Cl_2$	1.76		
$Ni(DTH)_2(NCS)_2$	3.08		
$Ni(IPTE)_2I_2$	3.10		

[*] measured at room temperature and corrected for diamagnetism

[†] calculated from the relationship $\mu_{eff} =$
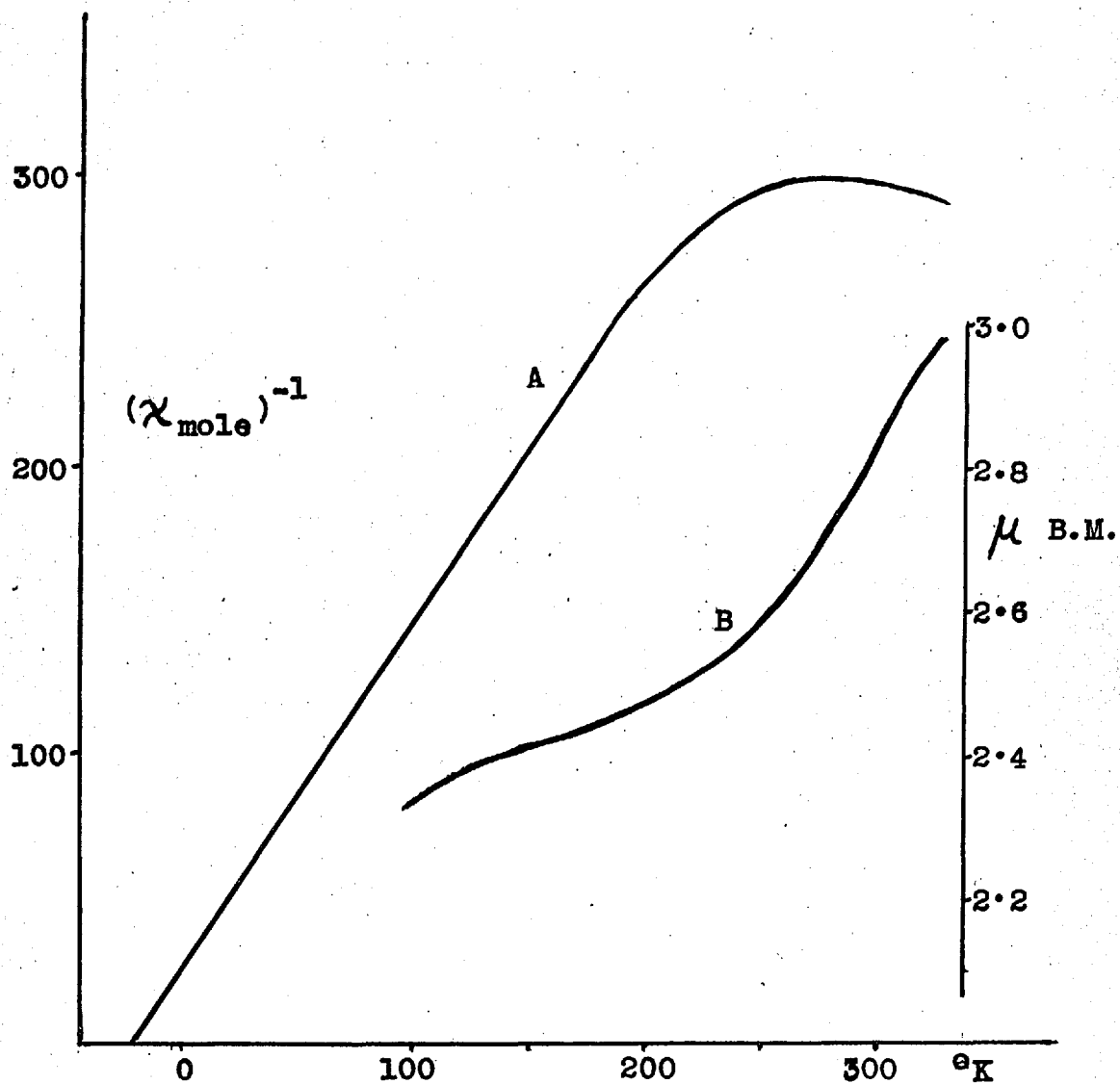$2.84(\chi_m(T-\theta))^{\frac{1}{2}}$, χ_m corrected for diamagnetism.

Table 27

Internal Vibrational Modes of the Perchlorate and Nitrate

Ions

Compound	Asymmetric Str.	Symm. Str.	Deform.
$Co(DTH)_2(NO_3)_2$	1372m, 1275s,	1038m[*]	811m, 727m
$Ni(DTH)_3(ClO_4)_2$	1075vsbr	927w	625s
$Co(DTH)_2(ClO_4)_2$	1105vs, 1037vs,	922m	625s, 618s
$Cu(DTH)_2(ClO_4)_2$	1100vs, 1050vs	930msp,916w,	625s, 621s

[*] Assignment uncertain due to DTH bands in this region.

long Co – O bond indicates relatively weak axial

coordination. The results of this study were not

available at the time this work was carried out. The

magnetic susceptibility of the complex follows a Curie – Weiss

law over the temperature range $78 - 200^{\circ}K$ with $\mu_{eff} = 2.46$ B.M.

$\theta = -21.^{\circ}$ Above $200^{\circ}K$ the magnetic moment increases rapidly

with increasing temperature (Fig.13, Table 28). It was

not possible to extend the magnetic measurements above

330° due to the dangerously explosive nature of the

compound. (see Chapter Seven). The most likely explanation

of this effect is that there is a quartet state just above

the doublet ground state in this compound. In systems

involving spin equilibria, it is difficult to differentiate

between an equilibrium involving two different chemical

species (with, for example, different metal – ligand bond

lengths) and a Boltzmann distribution between terms of

different spin multiplicity within a particular species.

In the latter case, for octahedral cobalt(II) compounds,

it is not possible to evaluate a meaningful value of the

separation of the doublet and quartet states from the

magnetic data as the two levels interact through spin-

orbit coupling. Assuming that two different species

are present, that the low spin form obeys the same Curie –

Weiss law over the range $200 - 330^{\circ}K$ as it does below

$200^{\circ}K$, and that the high spin form follows the same Curie –

Weiss law as $Co(DTH)_2(ONO_2)_2$; it is possible to evaluate

Fig. 13

Magnetic Properties of $Co(DTH)_2(ClO_4)_2$

Curve A - left hand axis. χ_{mole} (c.g.s. units)
corrected for diamagnetism.

Curve B - right hand axis. μ calculated from Curie law.

Table 28

Magnetic Properties of $Co(DTH)_2(ClO_4)_2$

Temperature $^\circ K$	χ_{mole}* c.g.s. units	μ B.M.[+]	K[ii]$_{equilibrium}$
77	8.46×10^{-3}	2.29	
80	8.20	2.30	
90.5	7.43	2.32	
120	5.87	2.38	
152	4.78	2.42	
168	4.38	2.43	
177	4.19	2.44	
201	3.80	2.48	
212	3.65	2.50	
231	3.48	2.55	0.027
249	3.38	2.60	0.045
265	3.32	2.68	0.066
290	3.32	2.78	0.115
319	3.36	2.94	0.185
333	3.44	2.99	0.241

*Corrected for diamagnetism

[+] Calculated from the Curie law

[ii] For the reaction   low-spin form $\rightleftharpoons$ high-spin form

the equilibrium constant in the temperature range 220 –
330°K. From the variation of this equilibrium constant
with temperature, values of $\triangle H$ and $\triangle S$ for the conversion
of the low spin form to the high spin form can be
calculated. A plot of log Kequilibrium against T^{-1} gives
an excellent straight line (Fig 14) corresponding to
$\triangle H$ = 3.42±0.1 Kcals/mole and $\triangle S$ = 7.4±0.3 cal/mole/deg.
A part of this entropy contribution represents the increase
in degeneracy on going to the quartet state. It is not
possible to detect the presence of a high spin species in
the complex from a study of the electronic spectrum since
even at the highest safe temperature only a small fraction
of the complex would be present in the high spin form.
An X-ray crystal structure determination on this compound
below 150°K and at the highest possible temperature would
be of great interest. The temperature of the published
structural study (preliminary details only have been
published to date) was not given. It was presumably
about 25°C.

Attempts to prepare the compound $Co(DTH)_2(BF_4)_2$
were unsuccessful.

Fig. 14
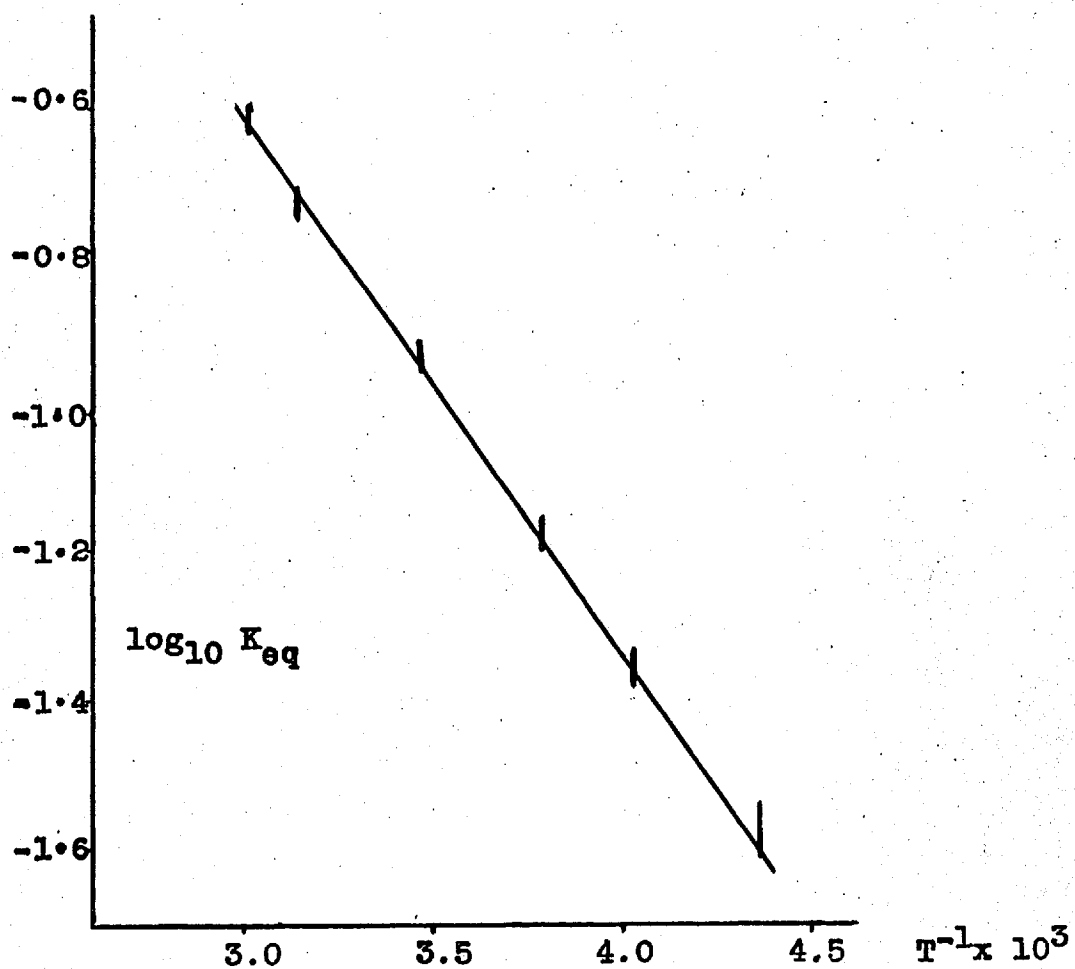
Graph of $\log_{10} K_{eq}$ against T^{-1} for the high spin - low spin equilibrium of $Co(DTH)_2(ClO_4)_2$

The infrared spectrum of $Cu(DTH)_2(ClO_4)_2$ is very similar to that of $Co(DTH)_2(ClO_4)_2$ (Table 27). The similarity of the splitting of asymmetric stretch of the perchlorate ions suggests that the anions are weakly coordinated in the copper compound as well. The $d \to d$ band of the copper compound is completely obscured by an intense charge transfer band which extends into the near infrared region. This charge transfer band, which is not observed in the cobalt and nickel compounds, probably reflects the tendancy of the sulphur-containing ligand to reduce copper(II) to copper(I). The reflectance spectrum of $Cu(DTH)_2(BF_4)_2$ is similar to that of the perchlorate compound. The far infrared spectra of $Cu(DTH)_2(ClO_4)_2$ and $Co(DTH)_2(ClO_4)_2$ are very similar, the three bands in the 200 - 300 cm^{-1} region being rather higher in the copper compound. The far infrared spectrum of $Cu(DTH)_2(BF_4)_2$ is identical to that of the corresponding perchlorate complex. The position of the strong bands in these spectra indicates that these bands have some metal - ligand stretching character since metal - ligand stretches for low spin cobalt(II) and for copper(II) would be expected to be at higher energy than for high spin cobalt(II) or nickel(II).
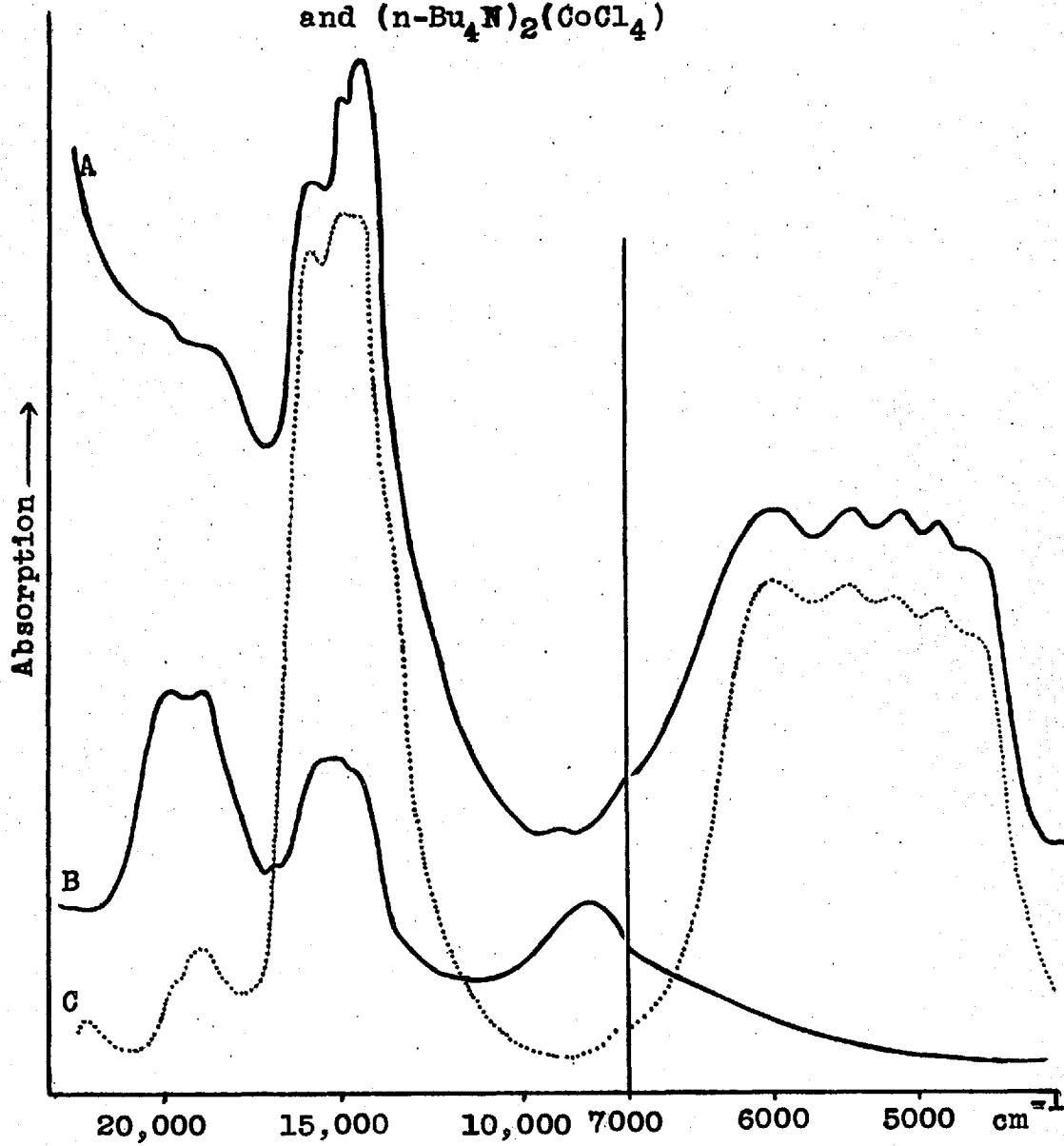
The Complex $Co(DTH)Cl_2$

The addition of 2:5 dithiahexane to anhydrous cobalt
chloride produced a green solid which, after washing with
dry benzene, had the stoichiometry $Co(DTH)Cl_2$. The
electronic reflectance spectrum of the compound in the
range 16,000 - 4,000 cm^{-1} is virtually identical to that
of the $CoCl_4^{2-}$ ion and strongly suggests the presence of
this species in the complex. The absorption in the
region 17,000 - 25,000 cm^{-1} cannot be attributed to a
tetrahedral cobalt(II) complex, but may be accounted for
by the presence of an octahedral cobalt(II) species.
Square planar cobalt(II) complexes can also cause
absorption in this region. Super-position of the
electronic spectra of $CoCl_4^{2-}$ and $Co(DTH)_2Cl_2$ gives a
spectrum very similar to that of $Co(DTH)Cl_2$ (Fig.15)

The magnetic susceptibility of the compound follows
a Curie-Weiss law with μ_{eff}= 4.70 B.M. θ =+5°. The value
of the magnetic moment indicates that very little of the
cobalt can be present in a low spin form. $Co(DTH)Cl_2$
thus probably has a structure consisting of $Co(DTH)_2$
units and tetrahedral $CoCl_4$ units, chloride ions from the
$CoCl_4$ units completing a distorted octahedron about the
cobalt atoms of the $Co(DTH)_2$ units.

Fig. 15

Reflectance Spectra of $Co(DTH)Cl_2$, $Co(DTH)_2Cl_2$, and $(n-Bu_4N)_2(CoCl_4)$

A $Co(DTH)Cl_2$

B $Co(DTH)_2Cl_2$

C $(n-Bu_4N)_2(CoCl_4)$

The far infrared spectrum of the complex tends to support this type of structure. The strong, complex, absorption band at 300 - 260 cm^{-1} (Fig.16.) is probably largely due to metal - chlorine stretching modes, the highest energy bands being due to vibrational modes involving predominately cobalt - free chlorine stretching, and the lowest energy bands to modes involving predominantly cobalt - bridging chloride stretching.

Iodine Adducts of 2:5 Dithiahexane Complexes

Blackhouse and Nyholm[98] have reported that $Ni(DTH)_2I_2$ forms a paramagnetic addition complex with molecular iodine.

Reaction of the complexes $Ni(DTH)_2X_2$ (X= NCS,Cl,Br,I) and $Ni(DTH)_3(ClO_4)_2$ with excess iodine in chloroform gave the paramagnetic complexes $Ni(DTH)_2X_2I_4$ and $Ni(DTH)_3(ClO_4)_2I_6$ as dark brown crystalline solids. These complexes slowly loose iodine at room temperature but even when they were warmed to 50° in vacuo for many hours only part of the iodine was lost. Attempts to prepare the corresponding adducts of the cobalt-dithiahexane complexes and the bis(isopropylthio)ethane complexes gave impure products.

Fig. 16

Far Infrared Spectra of $Co(DTH)Cl_2$ and $Co(DTH)_2Cl_2$
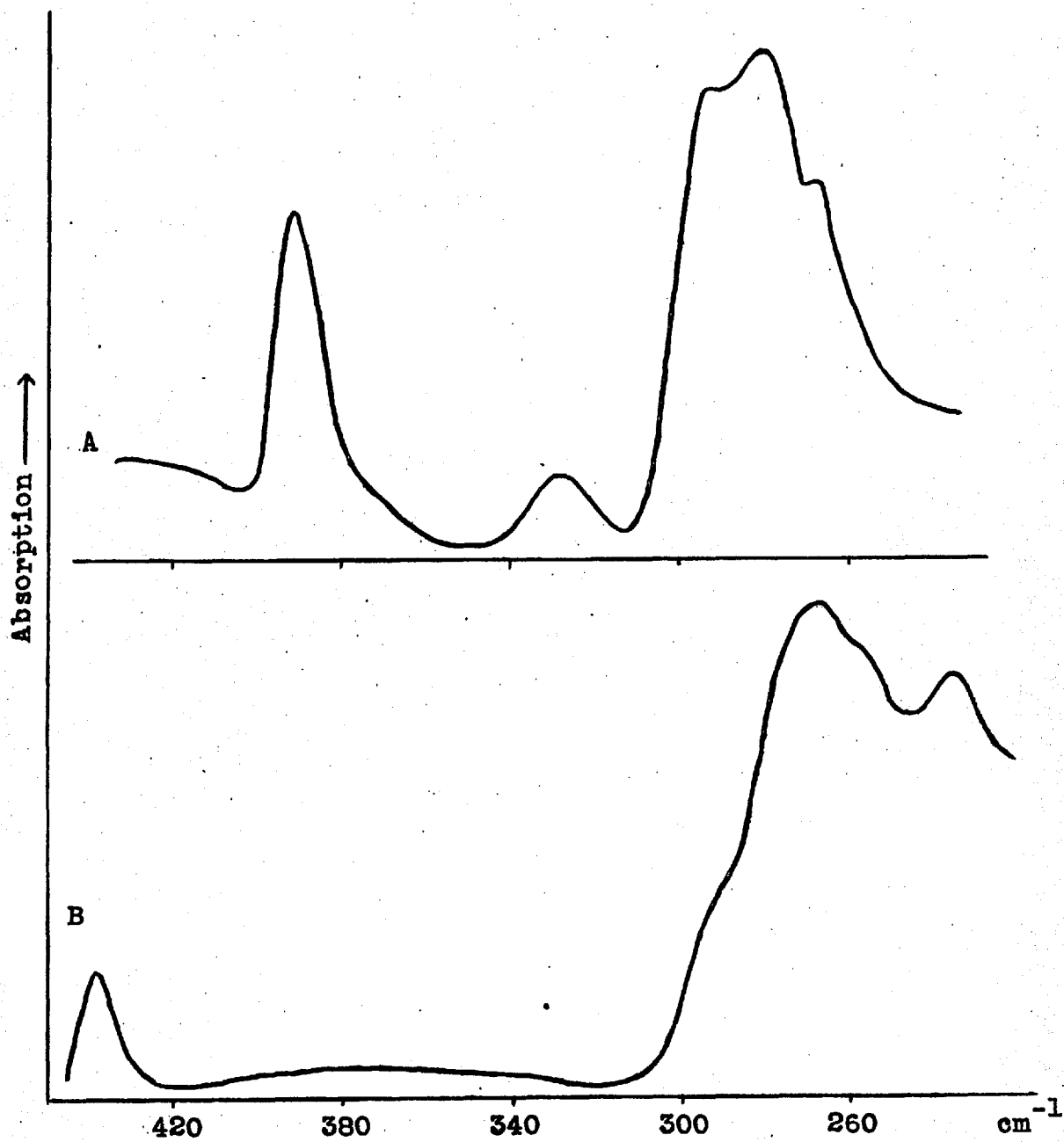
A $Co(DTH)Cl_2$ B $Co(DTH)_2Cl_2$

The infrared spectrum of $Ni(DTH)_3(ClO_4)_2I_6$ shows
that the perchlorate groups are not coordinated. The bands
due to dithiahexane, in particular the absence of a band
at about 1210 cm^{-1} and the presence of bands at 836 and
850 cm^{-1}, indicate that the ligand is present in the gauche
conformation.[99] The most significant differences between
the spectra of the adduct and the parent compound are the
shift of the C - S stretch from 646 cm^{-1} in $Ni(DTH)_3(ClO_4)_2$
to 613 cm^{-1} in the adduct, and of the CH_2 rock from 890 to
912 cm^{-1}. The only electronic transition that can be
observed is that corresponding to $\mathcal{V}_1$ at 11,500 cm^{-1}, $\mathcal{V}_2$
and $\mathcal{V}_3$ being obscured by the intense absorption of the
iodine. These results indicate that the iodine molecules
are coordinated to the sulphur atoms, the increase in
ligand field perhaps reflecting the absence of any lone
pairs available for π-donation to the nickel atom on half
of the sulphur atoms.

Considerable difficulty was experienced in obtaining
a satisfactory infrared spectrum of $Ni(DTH)_2(NCS)_2I_4$,
apparently due to strong absorption or scattering by the
iodine molecule. This effect was observed in the infrared
spectra of all the iodine adducts, but seems to be
particularly strong in this. However, it is clear that the

C – N stretching vibration shifts some 30 cm^{-1} to higher energy on formation of the adduct, (from 2082 to $\sim$2110 cm^{-1}) whilst the Ni – NCS stretch is lowered. The position of γ_1' shows that the ligand field in the adduct is slightly stronger than in the parent compound. These shifts are similar to those observed in the complex Ni(py)$_4$(NCS)$_2$I$_4$[75] and can be interpreted as showing that the iodine is bonded to the sulphur atom of the thiocyanate group.

Addition of iodine to a solution of Ni(DTH)$_2$I$_2$ in chloroform causes the appearance of two strong bands in the electronic spectrum at 28,900 cm^{-1} and 34,100 cm^{-1}. The intensity of these bands increases rapidly with the concentration of added iodine up to a nickel/iodine molar ratio of about 1:3, the molar extinction coefficient (per nickel) of the strongest band being about 25,000 at this point. Further addition of iodine causes the appearance of a strong band at 34,000 cm^{-1} which increases rapidly in strength with added iodine. The two bands at 28,900 and 34,100 cm^{-1} are similar in position and relative intensity to those observed in the I$_3^-$ ion[103] and indicate the presence of this species (either ionic or coordinated) in the solution at this point. The change in the spectrum of the solution on addition of large

quantities of iodine is due to the formation of a second type of iodine complex. These spectral changes suggest that addition of iodine to $Ni(DTH)_2I_2$ in chloroform first gives a complex containing the triiodide ion but further addition of iodine caused the iodine to bond to the sulphur atoms.

It was not possible to observe d – d transitions in the iodine adduct in solution. The reflectance spectrum of the solid adduct indicates that the ligand field is rather stronger than in the parent compound (Fig.17) and the bands due to dithiahexane in the infrared spectrum of the adduct more closely resemble those of the parent compound and $Ni(DTH)_3(ClO_4)_2$ than they do those of $Ni(DTH)_3(ClO_4)_2I_6$. The absence of any splitting of ν_1 suggests that in this complex the triiodide produces a stronger field than that usually produced by the iodide ion. It is possible, however, that the triiodide ions are not coordinated in this complex and a complicated structure is adopted. Alternatively it is possible that the iodine adduct has the stoichiometry $Ni(DTH)_2(H_2O)_2I_6$. If the water molecules are coordinated and the triiodide ions ionic, all the observed data can be rationalised in terms of this formulation.

Fig. 17

Electronic Spectra of $Ni(DTH)_2I_2$ and $Ni(DTH)_2I_6$

178.
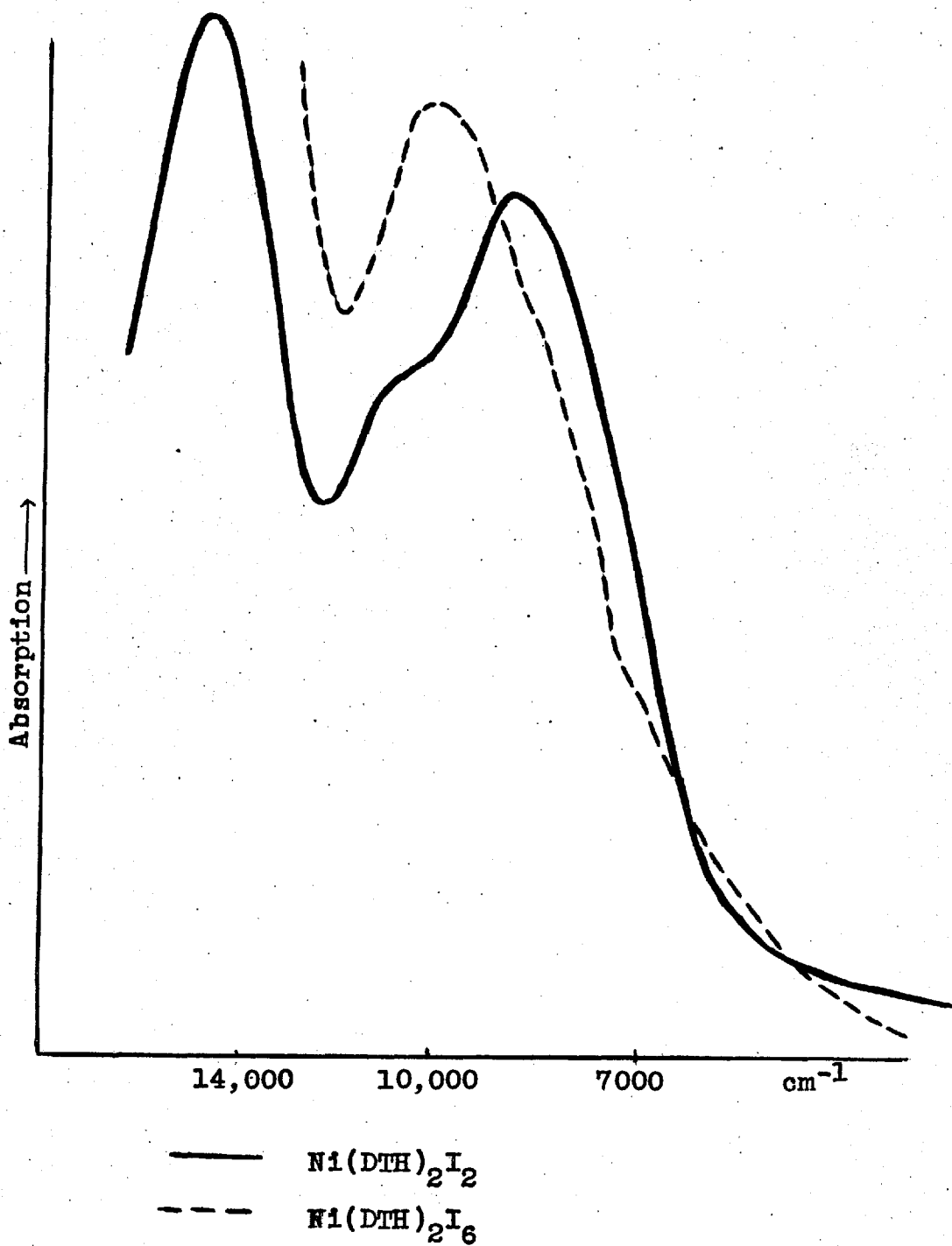
The infrared spectra of dithiahexane in the complexes $Ni(DTH)_2Br_2I_4$ and $Ni(DTH)_2Cl_2I_4$ are more like those of the parent compounds than that of $Ni(DTH)_3(ClO_4)_2I_6$, suggesting that the iodine is bonded to the anion in these compounds. The nickel – chlorine stretch is at lower energy in the adduct than it is in $Ni(DTH)_2Cl_2$ but, since this mode in the latter compound is rather higher than usual, little importance can be attached to this observation. The average 10Dq values for the iodine adducts of the bromide and chloride complexes are lower than those of the parent compounds (Figs 18 and 19) and this tends to suggest that the iodine is not attached to the sulphur atoms. It is surprising that the average ligand field in the iodine adducts of the chloride and bromide complexes is weaker than in the iodine adduct of the iodide complexes, but the structures adopted by and bonding in these iodine adducts must be strongly dependent on steric factors. In the absence of further data on the donor properties of the ClI_2^-, BrI_2^- and I_3^- ions no definite conclusions can be reached.

Fig. 18

Electronic Spectra of $Ni(DTH)_2Cl_2$ and $Ni(DTH)_2Cl_2I_4$

Absorption ⟶

14,000   10,000   7000 cm^{-1}

——— $Ni(DTH)_2Cl_2$

- - - - $Ni(DTH)_2Cl_2I_4$
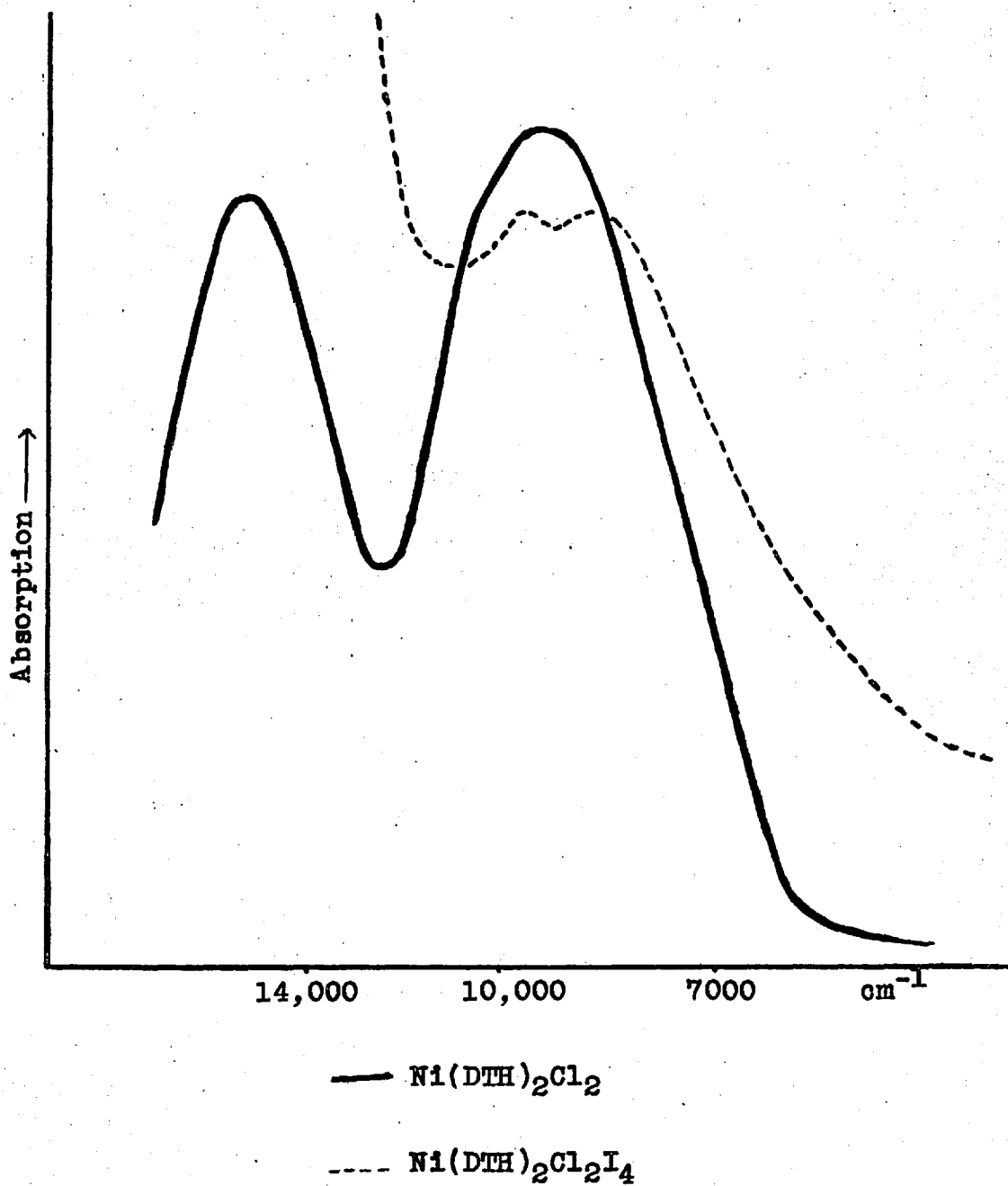
Fig. 19

Electronic Spectra of $Ni(DTH)_2Br_2$ and $Ni(DTH)_2Br_2I_4$

— $Ni(DTH)_2Br_2$

---- $Ni(DTH)_2Br_2I_4$
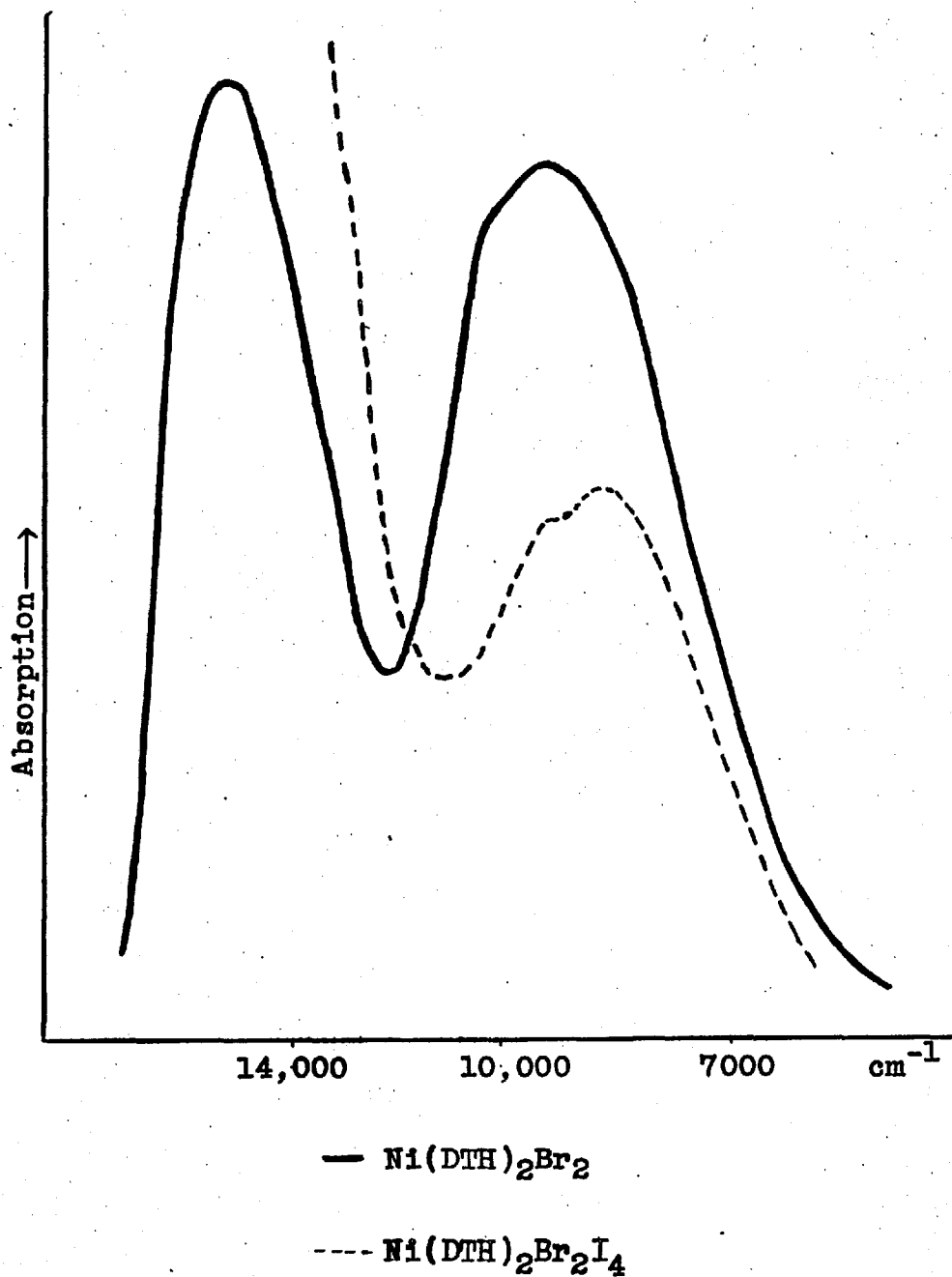
Conclusions

a)   The compounds $M(DTH)_2X_2$ (M = Ni, Co; X = Cl, Br, I, NCS), $M(IPTE)_2X_2$ (M = Ni, Co; X = Cl, Br, I, NCS), $Ni(DTH)_3(ClO_4)_2$ and $Co(DTH)_2(ONO_2)_2$ are high-spin and octahedrally coordinated. The highest energy infrared bands having appreciable metal - sulphur stretching character are at about 250 cm^{-1}. in the dithiahexane complexes. The ligand field produced by 1:2 bis(isopropylthio)ethane is considerably weaker than that by 2:5 dithiahexane.

b)   The complexes $Co(DTH)_2(ClO_4)_2$, $Cu(DTH)_2(ClO_4)_2$ and $Cu(DTH)_2(BF_4)_2$ are essentially square planar with weak axial bonding. The cobalt perchlorate complex exhibits an equilibrium between spin doublet and spin quartet ground states.

c)   The complex $Co(DTH)Cl_2$ consists of octahedral $Co(DTH)_2Cl_2$ units and tetrahedral $CoCl_4$ units linked together by two common chloride ions.

d)   The reaction of iodine with some dithiahexane complexes produces the iodine adducts $Ni(DTH)_3(ClO_4)_2I_6$ and $Ni(DTH)_2X_2I_4$ (X = Cl, Br, I, NCS). In the perchlorate complex the iodine is bonded to the sulphur atoms and in the thiocyanate, to the sulphur atoms of the thiocyanate groups. In the halide complexes the iodine is probably bonded to the halide ion, but definite conclusions cannot be reached in these cases.

CHAPTER SEVEN

Experimental Methods

Preparation of Compounds

Many of the compounds prepared in this work have not been made previously and most of the others were prepared by methods which were more convenient or gave purer products than the original procedure. For those compounds which have been described previously reference to the original preparation will be given. The absence of such a reference indicates that no earlier synthesis could be found.

Analytical Methods

Carbon, hydrogen, nitrogen, and a few of the halogen and sulphur analyses were performed by the Microanalytical Laboratory, Imperial College.

Cobalt, nickel, manganese, iron, zinc, and cadmium were determined by titration with EDTA solution, following standard procedures.[104,105] In the case of the thioacetamide and thioether complexes it was necessary to destroy the ligand by treatment of the complex with nitric acid. In a few cases cobalt and nickel were determined gravimetrically as $Co(py)_4(NCS)_2$ and nickel dimethylglloxime[106] respectively. Copper was determined gravimetrically as cuprous thiocyanate.[106]

Selenium was determined gravimetrically as the element
after reduction of the selenate with hydrazine
hydrochloride.[106]

Thiocyanate in the absence of other sulphur-
containing species was determined by Volhard's' method.[106]
In a few cases the sulphur in the thiourea compounds was
determined by oxidation to sulphate with bromine,
followed by precipitation of barium sulphate. Iodine
was determined by the method of Liepert.[114]

Ethanol and methanol were determined as the
weight loss on heating the complex to constant weight
at 110° in vacuo over phosphorus pentoxide.

The following procedure for the determination of
chloride and bromide in the presence of a sulphur-
containing ligand was found to rapid and accurate. The
compound (0.02 -0.1 g.) was covered with 10 - 20 ml. of
water and 5 - 10 drops of 100 volume hydrogen peroxide
added. The stoppered flask was allowed to stand for
10 - 20 minutes with occasional shaking, and then made
slightly alkaline. One drop of very dilute cobalt nitrate
solution was added (to catalyse the decomposition of the
peroxide) and the solution warmed on a steam bath until no
more oxygen was evolved.

The solution was cooled and acidified with nitric acid. Chloride and bromide were then determined by Volhard's method.

Molecular iodine in the alkyl sulphide complexes was determined as follows. The finely ground compound (0.03 - 0.1 g.) was covered with water (10 - 20 ml.) and 5 ml. of dichloromethane added. The mixture was shaken for 10 minutes in a stopped flask, and the iodine titrated with 0.02N sodium thiosulphate solution until the colour of the iodine in the dichloromethane layer did not reappear after shaking for a few minutes. The compounds were decomposed rather slowly under these conditions, so that towards the end of the titration it was necessary to add the thiosulphate dropwise and shake vigorously between each addition.

Preparations: Chapter Two

Analyses, melting points, and reference to the preparation of the compounds are given in Table 30. The new preparations are as follows.

$Co(tu)_2I_2$

Thiourea (1.52 g., 0.02 mole) was added to a solution of cobalt iodide dihydrate (3.48 g., 0.01 mole) in n-butanol (20.ml.). The mixture was heated until

Table 30

Preparation and Analytical Results for some Thioure..

Complexes

Compound	Prep.	M.P. °C Found	M.P. °C Lit.	C	H	N	X
Co(tu)$_2$Cl$_2$	a	146	148	9.0*	2.8	–	25.1
				8.5	2.9	–	25.2
Co(tu)$_2$Br$_2$	a	163–165	163	6.9	2.4	–	42.9
				6.5	2.2	–	43.1
Co(tu)$_2$I$_2$	b	172–174		5.8	1.9	11.7	54.1
				5.2	1.7	12.1	54.6
Zn(tu)$_2$Cl$_2$	c	158	159	8.8	2.9	–	.24.3
				8.3	2.8	–	24.6
Zn(tu)$_2$Br$_2$	b	158–160	–	6.7	2.2	–	43.1
				6.4	2.1	–	42.6
Zn(tu)$_2$I$_2$	b	170–174	–	5.5	1.8	–	52.6
				5.1	1.7	–.	53.8
Cd(tu)$_2$Cl$_2$	c	210 dec.	–	7.7	2.3	–	21.2
				7.1	2.4	–	21.1
Cd(tu)$_2$Br$_2$	b	197–199	–	5.9	1.7	–	37.8
				5.7	1.9	–	37.7
Cd(tu)$_2$I$_2$	b	230 dec.	–	5.0	1.4	–	48.6
				4.6	1.6	–	49.0
Ni(tu)$_6$(NO$_3$)$_2$	a	166	168	10.8	3.9	30.7	–
				11.2	3.8	30.6	–
Ni(tu)$_6$Br$_2$	d	dec.		10.9	3.6	–	23.7
				10.7	3.6	–	23.7
Ni(tu)$_4$Cl$_2$	c	dec.		10.8	3.3	–	16.4
				11.1	3.7	–	16.3

Table 30 (cont.)

Compound	Prep.	M.P. ^{o}C	C	H	N	X
$Mn(tu)_4Cl_2$	c	193-195	11.3	4.0	–	16.5
			11.1	3.8	–	16.5
$Ni(tu)_4SO_4 \cdot MeOH$	b	dec.	12.0	4.0	22.1	32.1[e]
			12.2	4.1	22.7	32.6
$Pd(tu)_4Cl_2$	f	dec.	–	–	23.3	15.0
			–	–	23.2	14.7
$Pd(tu)_4SO_4$	f	dec.	9.6	3.3	22.4	–
			9.5	3.2	22.2	–
$Pt(tu)_4Cl_2$	f	dec.	8.6	2.8	19.3	–
			8.4	2.8	19.6	–
$Pt(tu)_4SO_4$	f	dec.	8.0	2.6	18.9	–
			8.1	2.7	18.8	–

*Upper figure; found (%).

Lower figure; required or calculated (%).

a,	ref. 43	e,	X = S;
b,	this work.		found: Ni, 11.8%
			calc: Ni, 11.9%
c,	ref. 70.		
d,	ref. 68.	f,	ref. 107.

all the solid had dissolved and chlorobenzene added. The
hot solution was filtered and allowed to evaporate slowly
at room temperature for several days. The dark green
crystals (3.2 gl) are filtered off and dried at 50°
in vacuo.

$Zn(tu)_2I_2$

A solution of zinc iodide in ethanol (20 ml.)
was prepared metathetically from zinc nitrate hexahydrate
(2.97 g., 0.01 mole) and sodium iodide, (3.00 g., 0.02 mole).
Thiourea (1.52 g., 0.02 mole) was added, and the solution
heated until all of the solid had dissolved. On cooling,
a white solid slowly separated. This was filtered off and
dried at 50° in vacuo. Yield 0.9 g. This compound could
not be obtained quite pure; a number of samples prepared
by this and other methods were all slightly defficient in
iodine.

$Cd(tu)_2X_2$ (X = Cl, [70] Br, I)

The cadmium halide (0.01 mole) was dissolved in a
small volume of hot water, and thiourea added. The mixture
was heated until all of the solid has dissolved, filtered,
and allowed to cool. The resulting white crystals were
recrystallized from water and dried at 50° in vacuo.
Yields $Cd(tu)_2Cl_2$ 1.7 g., $Cd(tu)_2Br_2$ 2.3 g., $Cd(tu)_2I_2$ 3.4 g.

$Ni(tu)_6Br_2$ [68.]

A solution of nickel bromide hexahydrate (3.27 g., 0.01 mole) in ethanol (20 ml.) was added to a boiling solution of thiourea (4.55 g., 0.06 mole) in ethanol (100 ml.) The green solution was kept overnight at 0° and the green crystals filtered off, twice recrystallised from ethanol and dried in vacuo at 95°. Yield 1.8 g.

$Ni(tu)_4SO_4.MeOH$ [68]

Nickel sulphate heptahydrate (7.0 g., 0.025 mole) was dissolved in hot dry methanol (100 ml.) and finely ground thiourea (7.5 g., 0.1 mole) added with rapid mechanical stirring. The deep violet complex was filtered off, dried in vacuo, finely ground, and boiled with methanol (50 ml.). The mixture was filtered hot, and the deep violet crystalline complex dried in vacuo.

$Ni(tu)_4SeO_4.MeOH$

This complex was prepared in the same way as the sulphate compound except that it was recrystallized from methanol, rather than extracted from methanol. (Found Ni, 10.8. $C_5H_{20}N_8O_4SeNi$ requires: Ni, 10.9%) This compound slowly decomposes over the course of a few weeks.

Preparations: Chapter Three

$\underline{Co(tu)_2(CH_3COO)_2}$ [58]
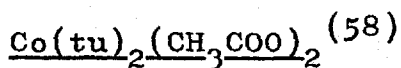
Cobalt acetate tetrahydrate (2.49 g., 0.01 mole) was dissolved in dry methanol (50 ml.) and the solution was filtered. Thiourea (1.52 g., 0.02 mole) dissolved in hot methanol (15 ml.) was added, and the deep blue solution was stored at 0° for several days. The blue crystals were filtered off and dried at 50° in vacuo. Yield 1.3 g., m.p. 169 - 170°. (Found: Co, 17.9; N,17.0. Calc.for $C_6H_{14}CoN_4O_4S_2$: Co,17.9; N,17.0%).

$\underline{Zn(tu)_2(CH_3COO)_2}$ [58]
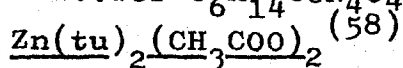
Zinc acetate dihydrate (2.20 g., 0.01 mole) was dissolved in hot ethanol (20 ml.) and thiourea (1.52 g., 0.02 mole) was added. The white crystals which separated on cooling to 0° were filtered off and dried at 50° in vacuo. Yield 1.9 g., m.p. 177°. (Found: N, 16.2; Zn,20.2. Calc. for $C_6H_{14}N_4O_4S_2Zn$: N, 16.7; Zn 19.5%).

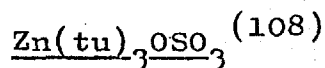$\underline{Cd(tu)_2(CH_3COO)_2}$ [58]
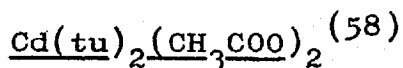
This complex was prepared as described for the zinc compound. Yield 3.4 g., m.p. 166° dec. (Found: C, 18.9; H, 3.55; Cd, 29.4; N, 14.7. Calc. for $C_6H_{14}CdN_4O_4S_2$: C, 18.8; H, 3.7; Cd, 29.4; N, 14.6%).
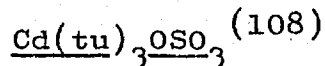
$\underline{Co(tu)_3OSO_3}$
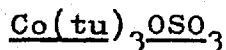
This complex was prepared by the method of Cotton et al. [43] (Found: C, 9.0; H, 3.2; Co, 15.5; N, 22.2.

Calc. for $C_3H_{12}CoN_6O_4S_4$: C, 9.4; H, 3.2; Co, 15.4; N, 21.9%).

$\underline{Zn(tu)_3OSO_3}$ [108]

This complex was prepared as described for the cobalt compound, using 2.87 g. of zinc sulphate pentahydrate. Yield 1.9 g., m.p. 155°. (Found: C, 91; H, 3.3; N, 21.8; Zn, 16.7. Calc. for $C_3H_{12}N_6O_4S_4$ Zn: C, 9.2; H, 3.1; N, 21.6; Zn, 16.8%).
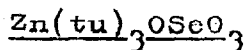
$\underline{Cd(tu)_3OSO_3}$ [108]

Cadmium sulphate (2.56 g., 0.01 mole) was dissolved in a small volume of hot water and thiourea (2.28 g., 0.03 mole) dissolved in a little hot water added. The hot solution was filtered and allowed to cool. The white crystals were filtered off and dried at 50° in vacuo. Yield 1.6 g., m.p. 215° dec. (Found: C, 8.6; H, 2.8; 25.7; N, 18.7. Calc. for $C_3H_{12}CdN_6O_4S_4$: C, 8.2; H, 2.8; Cd, 25.8; N, 19.2%).

$\underline{Co(tu)_3OSeO_3}$
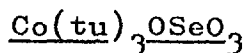
Cobalt selenate heptahydrate (1.64 g., 0.005 mole) was dissolved in a few mls. of cold water, and the solution was filtered. Finely powdered thiourea (10.g) was added, and the resulting blue slurry was stirred for 10 minutes. Methanol (200 ml.) was added slowly with rapid stirring.

A green solid separated, but on stirring overnight, this
changed to blue crystals, which were filtered off and dried
in vacuo. Yield 1.6 g. (Found: Co, 13.6; Se, 19.1.
$C_3H_{12}CoN_6O_4S_3Se$ requires Co, 13.6; . Se, 18.4%).

$\underline{Zn(tu)_3OSeO_3}$

Zinc selenate pentahydrate (1.49 g., 0.005 mole)
was dissolved in 15 ml. of water, and thiourea (1.52 g.
0.02 mole) dissolved in a little hot water added. The
warm solution was filtered, and 20 ml. of methanol was
added. The white compound which separated on cooling
was washed with methanol and dried in vacuo. Yield 1.5 g.
(Found: Se, 18.0; Zn, 15.0. $C_3H_{12}N_6O_4S_3SeZn$ requires:
Se,18.1; 15.0%).

$\underline{Co(tu)_3SSO_3.H_2O}$[109]
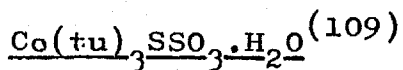
Finely ground barium thiosulphate hydrate
(2.94 g., 0.01 mole) was stirred overnight with a
solution of cobalt sulphate heptahydrate (2.81 g., 0.01 mole)
in 30 ml. water, and the precipitated barium sulphate
was filtered off. Thiourea (2.28 g., 0.03 mole) was
added to the solution, with slight warming. The solution
was then evaporated at 30° in vacuo to small bulk, and
the large hexagonal, deep blue crystals were filtered
off, washed with a little acetone, and air dried. Yield
0.5 g. (Found; C, 8.4; H, 3.2; Co, 14.3; N, 19.6.

Calc. for $C_3H_{14}CoN_6OS_5$; C, 8.6; H, 3.4; Co, 14.1; N, 20.1%).

$\underline{Co(tu)_3SSO_3}$

On storing a sample of the monohydrate for 2 days in vacuo over phosphorus pentoxide, the anhydrous compound was formed as a fine blue powder. Wt.loss: 4.2 Calc. 4.3% (Found: C, 8.7; H, 3.2; Co, 14.6; N, 21.2. $C_3H_{12}CoN_6O_3S_5$ requires: C, 9.0; H, 3.0; Co, 14.8; N, 21.0%).

$\underline{Zn(tu)_3SSO_3 \cdot H_2O}$ (109)

This complex was prepared as described for the hydrated cobalt compound, except that the large white hexagonal crystals separated out on cooling the solution to 0°. Yield 0.8 g. (Found: C, 8.7; H, 3.5; N, 19.9; Zn, 15.3. Calc. for $C_3H_{14}N_6O_4S_5Zn$: C, 8.5; H, 3.4; N, 19.9; Zn, 15.4%).

$\underline{Zn(tu)_3SSO_3}$

This complex was prepared as described for the anhydrous cobalt compound. (Found: C, 9.2; H, 3.0; N, 20.7; S, 39.1; Zn, 16.1. $C_3H_{12}N_6O_3S_5Zn$ requires: C, 8.9; H, 3.0; N, 20.7; S, 39.7; Zn, 16.1%).

$\underline{Cd(tu)_3SSO_3}$ (109)

This anhydrous compound was prepared as described for the monohydrate complex of zinc, and the long white needles were recrystallised from water.

(Found: C, 8.1; H, 2.6; Cd, 24.7; N, 18.8. Calc. for $C_3H_{12}CdN_6O_3S_5$: C, 8.0; H, 2.7; Cd, 24.8; N, 18.6%).

$\underline{Co(tu)_4(ClO_4)_2}$

This complex was prepared as described by Cotton et al.[43] (Found: C, 8.7; H, 2.8; Co, 10.2; N, 19.9. Calc. for $C_4H_{16}Cl_2CoN_8O_8S_4$: C, 8.5; H, 2.9; Co, 10.5; N, 20.0%).

$\underline{Zn(tu)_4(ClO_4)_2}$

Thiourea (3.05 g., 0.04 mole) was added to a solution of zinc perchlorate hexahydrate (3.72 g., 0.01 mole) in the minimum quantity of n-butanol. The solution was heated until all the solid had dissolved, filtered hot, and allowed to cool. The resulting white crystals were filtered, washed with chloroform, and dried at 50° in vacuo. Yield 2.9 g., m.p. 118 - 122°. (Found: C, 8.9; H, 2.9; N, 2 0.2; Zn, 11.3. $C_4H_{16}Cl_2N_8O_8S_4Zn$ requires: C, 8.5; 2.8; N, 19.7; Zn, 11.5%).

$\underline{Cd(tu)_4(ClO_4)_2}$

This complex was prepared in the same way as the corresponding zinc compound. Yield 3.6 g., m.p. 110°. (Found: C, 8.0; H, 2.9; Cd, 18.1; N, 18.4. $C_4H_{16}CdCl_2N_8O_8S_4$ requires: C, 7.8; H, 2.6; Cd, 18.3; N, 18.2%).

Co(tu)$_4$(NO$_3$)$_2$
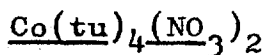
Following the procedure of Cotton et al., [43]
three different products of this composition were
obtained (see Chapter Three). In seven attempts, the
A form was obtained three times, and the B and C forms
twice each. (Found for form A: Co, 12.1; S, 26.1. For
form B: C, 9.8; H, 3.2; Co, 11.7; S, 25.9. For form
C: Co, 11.9; S, 25.7. Calc. for C$_4$H$_{16}$CoN$_{10}$O$_6$S$_4$:
C, 9.85; H, 3.3; Co, 12.1; S, 26.3%).

Zn(tu)$_4$(NO$_3$)$_2$
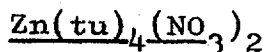
Zinc nitrate hexahydrate (2.97 g., 0.01 mole)
was dissolved in a small volume of hot ethanol (50 ml.)
was added. The solution was filtered hot, and the white
crystals which deposited on cooling were filtered off,
and dried at 50° in vacuo. Yield, 2.8 g., m.p. 141 – 142°.
(Found: C, 10.0; H, 3.2; N, 28.2; Zn, 13.1. C$_4$H$_{16}$N$_{10}$O$_6$S$_4$Zn
requires: C, 9.7; H, 3.3; N, 28.4; Zn, 13.2%).

Cd(tu)$_4$(NO$_3$)$_2$

This complex was prepared as described for the zinc
compound. m.p. 140 – 142°. (Found: Cd, 21.0; N, 26.2.
C$_4$H$_{10}$CdN$_{10}$O$_6$S$_4$ requires: Cd, 20.8; N, 26.0%).

Preparations: Chapter Four

$\underline{M(tu)_2(NCS)_2 \quad (M = Ni, \ Co, \ Cd, \ Zn)}$

A solution of the metal thiocyanate in water (50 ml.)
was prepared metathetically from the metal sulphate (0.02
mole) and barium thiocyanate dihydrate (5.8 g., 0.02 mole).
Thiourea (3.04 g., 0.04 mole) was added, and the solution
was heated until all the solid had dissolved. The solution
was filtered and allowed to cool. The cadmium and cobalt
cpmplexes crystallised out from the cooling solutions,
but it was necessary to allow the solutions of the other
complexes to evaporate to small bulk in order to obtain
a satisfactory yield. The crystalline complexes were
filtered off and dried at 50° in vacuo. (Found for
$Ni(tu)_2(NCS)_2$: C, 15.1; H, 2.5; N, 25.8; Ni, 18.0.
Calc. for $C_4H_8N_6NiS_4$: C, 14.7; H, 2.5; N, 25.7; Ni, 18.0%..
Found for $Co(tu)_2(NCS)_2$: C, 15.1; H, 2.3; N, 25.1;
Co, 18.1. Calc. for $C_4H_8CoN_6S_4$: C, 14.7; H, 2.5; N, 25.7;
Co, 18.0%. Found for $Cd(tu)_2(NCS)_2$: C, 12.9; H, 1.8;
N, 22.4; Cd, 29.5. Calc. for $C_4H_8CdN_6S_4$: C, 12.6; H, 2.1;
N, 22.1; Cd, 29.5%. . Found for $Zn(tu)_2(NCS)_2$: C, 14.5;
H, 2.6; N, 25.4; Zn, 19.3. Calc. for $C_4H_8N_6S_4Zn$:
C, 14.4; H, 2.4; N, 25.2; Zn, 19.6%.).

$Mn(tu)_2(NCS)_2$

This complex was prepared in the same way as the nickel compound, except that 1.1 g., 0.0145 mole of thiourea was used. (Found: C, 15.0; H, 2.1; N, 25.9; Mn, 17.3. Calc. for $C_4H_8MnN_6S_4$: C, 14.9; H, 2.5; N, 26.0; Mn, 17.0%.).

$Fe(tu)_2(NCS)_2$

A solution of ferrous thiocyanate in water (20 ml.) was prepared metathetically from ferrous sulphate (2.78g., 0.01 mole) and barium thiocyanate (2.90 g., 0.01 mole) and the solution was shaken with finely divided iron until it was green. The ferrous thiocyanate solution was filtered under an atmosphere of nitrogen into a deoxygenated solution of thiourea (1.52 g., 0.02 mole) in water (10 ml.) and the solution was concentrated in vacuo until the yellow crystalline complex was deposited. The complex was filtered off under nitrogen and dried in vacuo. (Found: C, 14.9; H, 2.5; N, 25.7, Fe, 17.3. Calc. for $C_4H_8FeN_6S_4$: C, 14.8; H, 2.5; N, 25.9; Fe, 17.3%.).

$M(MeOH)_2(NCS)_2$ (M = Co, Ni, Mn)

A solution of the metal thiocyanate in methanol was prepared metathetically from the metal nitrate and potassium thiocyanate. A few ml. of 1:2 dimethoxypropane was added and, after standing for a few hours, the solution was evaporated to small bulk at room temperature

in vacuo. The complexes which separated were filtered

off in a dry-box and dried in vacuo for a few minutes.

(Found for $Co(MeOH)_2(NCS)_2$: Co, 24.5; NCS, 48.6; CH_3OH,

26.8. $C_4H_8CoN_2O_2S_2$ requires: Co, 24.7; NCS, 48.5;

CH_3OH, 26.8%. Found for $Ni(MeOH)_2(NCS)_2$: Ni, 25.2;

NCS, 49.1; CH_3OH, 26.0. $C_4H_8N_2NiO_2S_2$ requires: Ni, 24.6;

NCS, 48.6; CH_3OH, 26.8. Found for $Mn(MeOH)_2(NCS)_2$:

Mn, 23.1; NCS, 49.7; CH_3OH, 27.4. $C_4H_8MnN_2O_2S_2$ requires:

Mn, 23.4; NCS, 49.4; CH_3OH, 27.2%.).

$M(EtOH)_2(NCS)_2$ (M = Co, Ni, Mn)

A solution of the metal thiocyanate in ethanol

was prepared metathetically from the metal nitrate and

potassium thiocyanate. Benzene (about one-third of the

volume of the alcohol) was added and the mixture distil-

led slowly at atmospheric pressure. When the bulk of

the solution had been reduced to one-third, the source

of heat was removed and the distillate discarded. The

solution was allowed to cool and then concentrated in

vacuo. The complexes which separated were filtered off

in a dry-box and dried in vacuo for a few minutes.

(Found for $Co(EtOH)_2(NCS)_2$: Co, 22.1; NCS, 43.9; C_2H_5OH;

34.2. $C_6H_{12}CoN_2O_2S_2$ requires: Co, 22.0; NCS, 43.6;

C_2H_5OH; 34.4. Found for $Ni(EtOH)_2(NCS)_2$: Ni, 22.6;

NCS; 43.5; C_2H_5OH; 33.7. $C_6H_{12}N_2NiO_2S_2$ requires:

Ni, 22.0; NCS, 43.6, 44.3; C_2H_5OH, 34.4. Found for

$Mn(ETOH)_2(NCS)_2$:   Mn, 20.6; NCS, 44.3; C_2H_5OH, 34.3;

$C_6H_{12}MnN_2O_2S_2$ requires: Mn, 20.8;   NCS, 44.2;

C_2H_5OH, 35.0%.).

Anhydrous Metal Thiocyanates

The alcohol adducts were heated at 110° in vacuo

over phosphorus pentoxide to give the corresponding

anhydrous metal thiocyanates.   (Found for $Co(NCS)_2$:

Co, 33.4. $C_2CoN_2S_2$ requires: Co, 33.6.   Found for

$Ni(NCS)_2$:   Ni, 33.8. $C_2N_2NiS_2$ requires: Ni, 33.6.

Found for $Mn(NCS)_2$:   Mn, 32,0; $C_2MnN_2S_2$ requires:

Mn, 32.1%.).

It was necessary to use a thoroughly baked out

apparatus for the preparation of anhydrous cobalt thio-

cyanate if contamination of the product with the hemi-

hydrate was to be avoided.

Anhydrous ferrous thiocyanate was prepared in

the same way as the ethanol complexes, except that the

vacuum evaporation was carried out at 50°.   The yellow-

brown solid was dried in vacuo over phosphorus pentoxide

at 110°.   The weight loss during this drying was small.

(Found for $Fe(NCS)_2$:   NCS, 65.2. $C_2FeN_2S_2$ requires:

NCS, 67.6%.).   This compound could not be obtained

free from ferric iron.

Anhydrous zinc thiocyanate was prepared in the same way as the ethanol complexes and was dried at 110° in vacuo over phosphorus pentoxide. There was no evidence for the existence of an ethanol adduct. (Found for $Zn(NCS)_2$: NCS, 63.4. $C_2N_2S_2Zn$ requires: NCS, 64.2%.).

Anhydrous cadmium thiocyanate crystallised directly from a concentrated aqueous solution which was prepared metathetically from solutions of barium thiocyanate and cadmium sulphate. (Found for $Cd(NCS)_2$: Cd, 48.8; NCS, 50.6. $C_2CdN_2S_2$ requires: Cd, 49.2; NCS, 50.8%.).

The cadmium and zinc thiocyanates were stable indefinately to air, and the nickel compound was only slightly hygroscopic. The ferrous compound was rather rapidly oxidized by air. Manganese thiocyanate rapidly picks up water from moist air and eventually dissolves Cobalt thiocyanate is extremely unstable towards moist air.
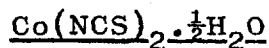
$Co(NCS)_2 \cdot \frac{1}{2}H_2O$

Exposure of anhydrous cobalt thiocyanate to moist air for a few minutes, followed by heating the resultant brown solid at 110° in vacuo gave cobalt thiocyanate hemihydrate. (Found for $Co(NCS)_2 \cdot \frac{1}{2}H_2O$: Co, 31.7; NCS, 62.6; H_2O, 4.9. Calc. for $C_2HCoN_2O_{\frac{1}{2}}S_2$: Co, 32.0; NCS, 63.1; H_2O, 4.3%.).

Preparations: Chapter Five

$Co(tam)_2Cl_2$[88] and $Co(tam)_2Br_2$
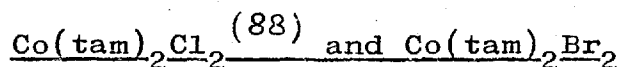
The hydrated cobalt halide (0.01 mole) was dissolved in warm acetone (15 ml.) and a warm solution of thioacetamide (1.50 g., 0.02 mole) in acetone added. On cooling to 0° the solution deposited deep blue crystals which were filtered off, washed with ether and dried in vacuo. Yields: $Co(tam)_2Cl_2$ 1.9 g., $Co(tam)_2Br_2$ 1.3 g. Analyses of the halide complexes are given in Table 31.

$Co(tam)_2I_2$
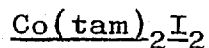
Cobalt iodide dihydrate (3.4 g., 0.01 mole) was dissolved in a small volume of isopropanol and a solution of thioacetamide (1.50 g., 0.02 mole) in a little 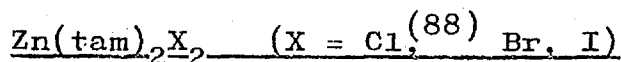warm isopropanol added. The solution was rapidly filtered, chloroform (20 ml.) was added, and the mixture allowed to stand at 0° for three hours. (Longer standing causes the product to be contaminated with cobalt sulphide.) The green crystals (1.6 g.) were filtered off, washed with ether and dried in vacuo.

$Zn(tam)_2X_2$ (X = Cl,[88] Br, I)

These complexes were prepared in the same way as the cobalt chloride complex, but using isopropanol as solvent. The zinc iodide was prepared metathetically

Table 31

Analytical Results for some Thioacetamide Complexes with

Metal Halides

Compound	Found (%)		Reqd or Calc. (%)	
	Metal	Halide	Metal	Halide
$Cc(tam)_2Cl_2$	21.3	25.4	21.1	25.5
$Cc(tam)_2Br_2$	15.8	42.8	16.0	43.3
$Co(tam)_2I_2$	12.6	54.3	12.7	54.8
$Zn(tam)_2Cl_2$	22.9	24.6	22.8	24.8
$Zn(tam)_2Br_2$	18.0	42.2	17.4	42.6
$Zn(tam)_2I_2$	13.6	53.4	13.9	54.0
$Cd(tam)_2Cl_2$	33.5	21.1	33.7	21.3
$Cd(tam)_2Br_2$	26.6	37.2	26.6	37.8
$Cd(tam)_2I_2$	21.2	49.3	21.8	49.1
$Fe(tam)_2Cl_2$	20.0	25.7	20.2	25.6
$Fe(tam)_2Br_2$	15.1	43.3	15.3	43.7
$Ni(tam)_4Cl_2$	13.6	16.3	13.7	16.5
$Ni(tam)_4Br_2$	11.2	30.9	11.3	30.8

from zinc nitrate (2.61 g., 0.01 mole) and sodium iodide

(3.00 g., 0.02 mole) in isopropanol. The volume of this

solution was reduced to 15 ml. before adding the thio-

acetamide.   Yields: $Zn(tam)_2Cl_2$ 1.2 g., $Zn(tam)_2Br_2$

1.2 g., $Zn(tam)_2I_2$ 2.2 g.

$Cd(tam)_2Cl_2$[88]

This compound was prepared by the same method,

as $Co(tam)_2Cl_2$ except that the cadmium chloride was dis-

solved in methanol.   Yield 0.8 g.

$Cd(tam)_2Br_2$ and $Cd(tam)_2I_2$

These compounds were prepared by the same method

as $Co(tam)_2I_2$ except that the final solution was allowed

to stand overnight at 0° before filtering off the product.

Yields: $Cd(tam)_2Br_2$ 2.0 g., $Cd(tam)_2I_2$ 2.5 g.

$Fe(tam)_2Cl_2$[88]

Ferrous chloride (2.00 g., 0.01 mole) was dis-

solved in a little hot ethanol and the solution shaken

with finely divided iron until the solution was green.

The ferrous chloride solution was filtered in a atmos-

phere of nitrogen into a warm, deoxgenated solution of

thioacetamide (1.50 g., 0.02 mole) in a little isopropanol.

Chloroform was added and the solution cooled to 0°. The

cream coloured crystals were filtered off under nitrogen,

washed with ether and dried in vacuo.   Yield: 0.9 g.

Fe(tam)$_2$Br$_2$
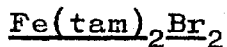
This compound was prepared in the same way as the chloride complex but using acetone as solvent for both components.   Yield: 1.1 g. of yellow crystals.

These ferrpus compounds are stable to air for a few days at room temperature, but their solutions in alcohols etc. are very rapidly oxidized.

Ni(tam)$_4$X$_2$ (X = ClO$_4$, NO$_3$, Br)

The nickel salt (0.005 mole) was dissolved in a little warm isopropanol and thioacetamide (1.50 g., 0.02 mole) dissolved in a little warm isopropanol added.   The blue or purple complex crystallised immediately.   It was filtered off, washed with ether and dried in vacuo. Yields: Ni(tam)$_4$(NO$_3$)$_2$ 1.4 g., Ni(tam)$_4$(ClO$_4$)$_2$ 0.7 g., Ni(tam)$_4$(NO$_3$)$_2$ 1.4 g.,   Analyses for the thioacetamide complexes other than those derived from the halides of cobalt, iron, zinc, and cadmium are given in table 32.

In one case the nitrate complex was initially precipitated as a brown compound, but on standing under the mother liquor for a few hours it changed to a blue solid identical to the nitrate complex prepared as above.

Table 32

Analytical Results for some Thioacetamide Complexes[*]

Compound	Found (%)				Reqd. or Calc.(%)			
	C	H	N	M	C	H	N	M
$Co(tam)_2(NCS)_2$	22.4	3.3	17.0	18.4	22.1	3.1	17.2	18.1
$Ni(tam)_2(NCS)_2$	21.7	3.1	17.1	18.2	22.1	3.1	17.2	18.1
$Ni(tam)_4(NO_3)_2$	19.6	4.2	16.8	12.2	19.9	4.2	17.4	12.2
$Ni(tam)_4(ClO_4)_2$	17.5	3.4	9.9	10.3	17.2	3.6	10.0	10.5
$Ni(tam)_4SO_4$	21.3	4.5	12.4	12.5	20.9	4.4	12.2	12.8
$Pd(tam)_4Cl_2$	20.2	4.1	11.6	–	20.1	4.2	11.7	–
$Pd(tam)_4Cl_2$	16.9	3.6	9.7	–	16.9	3.7	9.9	–
$Cd(tam)_4(NO_3)_2$	18.4	3.7	15.4	20.9	17.9	3.8	15.6	20.9

[*]Data for the complexes with cobalt, zinc, cadmium, nickel, and iron(II) halides are given in Table 31.

The reason for this change could not be ascertained since the preparation of the brown compound could not be repeated.

$Ni(tam)_4SO_4$

· This compound was prepared in the same way as $Ni(tu)_4SO_4 \cdot MeOH$ (page 188.). The precipitated complex was shaken with methanol (instead of boiling) and dried in vacuo.

$Pd(tam)_4Cl_2$

Palladous chloride (0.18 g., 0.001 mole) was dissolved in a few drops of dilute hydrochloric acid, and thioacetamide (0.30 g., 0.004 mole) dissolved in a little ethanol added. The yellow precipitate was filtered off, washed with ethanol and ether, and dried in vacuo. Yield 0.4 g.

$Pt(tam)_4Cl_2$

A concentrated aqueous solution of potassium tetrachloroplatinite was prepared from potassium hexa-chloroplatinate (0.5 g., 0.001 mole) according to the method in Inorganic Syntheses.[112] Thioacetamide (0.30 g., 0.004 mole) dissolved in a little water was added, and the fawn coloured precipitate was filtered off, washed with ethanol and ether, and dried in vacuo. Yield: 0.3 g.

Ni(tam)$_4$Cl$_2$ [(88)]
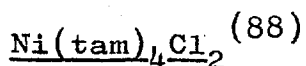
Hydrated nickel chloride (1.01 g. 0.005 mole) was dissolved in a little isopropanol and thioacetamide (1.50 g., 0.02 mole) dissolved in a little isopropanol added. The solution was allowed to stand overnight at 0° and the green crystalline solid was filtered off and dried in vacuo. Yield: 1.4 g.

Cd(tam)$_4$(ONO$_2$)$_2$
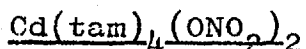
Cadmium nitrate (1.24 g., 0.005 mole) was dissolved in a small volume of hot isopropanol and the solution allowed to cool. A warm solution of thioacetamide (1.50 g. 0.02 mole) in a little isopropanol was added, followed by chloroform (20 ml.). On standing overnight, the solution deposited colourless crystals which were filtered off and dried in vacuo. Yield: 1.8 g.

Ni(tam)$_2$(NCS)$_2$ [(89)]
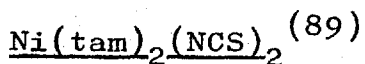
A solution of nickel thiocyanate in isopropanol was prepared metathetically from nickel nitrate (2.91 g., 0.01 mole) and potassium thiocyanate (1.94 g., 0.02 mole) and the solution concentrated to 20 ml in vacuo. A few ml. of 2:2 dimethoxypropane was added, the solution was allowed to stand for a few hours and then concentrated to about 10ml. in vacuo. Solid thioacetamide (1.50 g.,0.02 mole) was added, and the mixture warmed to about 40°.

The suspension was shaken until the solid was homogeneous (about 10 minutes) and then for a further hour. The green crystalline precipitate was filtered off, washed with ether and dried in vacuo.   Yield: 2.4 g.

$Co(tam)_2(NCS)_2$ [89]
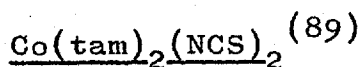
This compound was prepared by the method of Nardelli et al. [89] The crystals were washed with a little acetone and dried in vacuo.

Attempts to prepare thioacetamide complexes of metal salts of oxyacids were unsuccessful with the exception of $Cd(tam)_4(ONO_2)_2$.   The metal sulphide was precipitated in these cases.

All the thioacetamide complexes showed some tendency to decompose to the metal sulphide, this being most marked with the cobalt compounds. The decomposition was slowed down considerably by keeping the compounds at 0° in a refridgerator,   under these conditions all of the compounds were stable for at least several weeks.

Preparations: Chapter Six

Many of the compounds were prepared by published methods. (Table 33). The other complexes were prepared as described below.

$Ni(DTH)_3(ClO_4)_2$ [97]
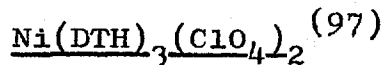
Finely divided nickel perchlorate hexahydrate was covered with 2:5 dithiahexane and the mixture was allowed to stand over phosphorus pentoxide in a vacuum desiccator for a few weeks. The resultant blue solid was ground with more dithiahexane and the slurry replaced in the vacuum desiccator over fresh phosphorus pentoxide. This procedure was repeated until the infrared spectrum of the product showed that no water was present. The complex was washed with dry benzene and dried in vacuo at 50°. Analytical results for most of the complexes of chelating alkyl sulphides are given in Table 33.

$Co(DTH)_2(ClO_4)_2$ [101]
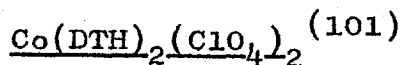
This compound was prepared in the same way as $Ni(DTH)_3(ClO_4)_2$ starting from cobalt perchlorate hexahydrate. (Found: Co, 11.8. Calculated for $C_8H_{20}Cl_2CoO_8S_4$: Co, 11.7%.). The infrared spectrum of this compound was similar to that reported by Cotton[101].

This compound detonates violently at about $180^\circ C$

Table 33

Preparations and Analytical Results for some 2:5 Dithia-
hexane Complexes

Compound	Prep.	Found (%)			Reqd. or Calc.(%)		
		C	H	X	C	H	X
$Ni(DTH)_3(ClO_4)_2$	a	23.5	5.0	$-^f$	23.1	4.8	$-^f$
$Ni(DTH)_2Cl_2$	a	25.5	5.4	19.4	25.7	5.4	19.0
$Ni(DTH)_2Br_2$	a	20.8	4.3	34.2	20.7	4.4	34.5
$Ni(DTH)_2I_2$	a	17.2	3.6	45.9	17.2	3.7	45.6
$Ni(DTH)_2(NCS)_2$	b	28.4	4.7	14.0^j	28.7	4.8	14.0^j
$Co(DTH)_2Cl_2$	c	25.3	5.6	18.8	25.7	5.4	18.9
$Co(DTH)_2Br_2$	c	20.7	4.2	35.0	20.7	4.4	34.5
$Co(DTH)_2I_2$	c	17.7	3.7	45.4	17.2	3.7	45.5
$Co(DTH)_2(NCS)_2$	d	28.2	4.4	6.9^g	28.6	4.8	6.7^g
$Co(DTH)_2(NO_3)_2$	d	22.0	5.0	6.8^g	22.4	4.7	6.5^g
$Co(DTH)Cl_2$	d	19.7	4.3	$-^h$	19.1	4.0	$-^h$
$Cu(DTH)Cl_2$	e	18.5	3.9	$-^i$	18.7	3.9	$-^i$
$Cd(DTH)Cl_2$	e	15.3	3.4	23.4	15.7	3.3	23.2
$Cd(DTH)Br_2$	e	12.5	2.8	40.0	12.2	2.6	40.4
$Cd(DTH)I_2$	e	9.6	2.2	51.1	9.8	2.1	52.0

a, ref. 97.   b, ref. 120.   c, ref. 98.   d, This work.

e, ref. 96.   f, found Ni, 9.6; calc. Ni, 9.4%.

g, X = N.   h, found Co, 23.0; calc. Co, 23.4%.

i, found Cu, 24.8; Calc. Cu, 24.8%.   j, X = Ni.

For this reason reliable C, H, and S analyses could not be obtained, and no attempt was made to measure the properties of this complex at temperatures greater than $60^{\circ}C$.

$\underline{Co(DTH)_2(NO_3)_2}$
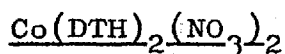
This complex was prepared in the same way as $Ni(DTH)_3(ClO_4)_2$ starting from cobalt nitrate hexahydrate.

$\underline{Cu(DTH)_2(ClO_4)_2}$
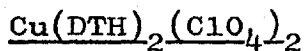
Cupric perchlorate (3.70 g., 0.01 mole) was dissolved in ethanol (50 ml.) and dithiahexane (3.7 g., 0.03 mole) was added dropwise. The brown precipitate was filtered off, washed with ethanol and dried in vacuo. (Found: Cu, 12.6. $C_8H_{20}Cl_2CuO_8S_4$: Cu, 12.6%.).

This compound detonates violently at about $160^{\circ}C$ (Compare $Co(DTH)_2(ClO_4)_2$.).

$\underline{Cu(DTH)_2(BF_4)_2}$
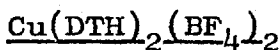
This compound was prepared in the same way as the corresponding perchlorate complex. (Found: Cu, 13.2. $C_8H_{20}B_2CuF_8S_4$ requires: Cu, 13.2%.).

Co(DTH)Cl$_2$

Anhydrous cobalt chloride (0.01 mole) was prepared by the thionyl chloride method[110] but no attempt was made to remove the final traces of thionyl chloride. A solution of dithiahexane (0.03 mole) in sodium dry benzene was added and the mixture shaken for some hours. The resultant green solid was filtered off in the dry-box, washed with dry benzene and dried in vacuo at 50°.

Attempts to prepare 1:1 complexes with the other nickel and cobalt halides were unsuccessful.

Co(DTH)$_2$(NCS)$_2$

Commercial "cobalt thiocyanate" (1.75 g.) was dissolved in a small quantity of hot absolute alcohol and the solution filtered. Dithiahexane was added and the solution concentrated in vacuo until green crystals were deposited. The complex was filtered off, washed with a little acetone, and dried at 50° in vacuo. Yield 2.4 g.

1:2 Bis(isopropylthio)ethane[111]

Isopropyl mercaptan (15 g., 0.2 mole) was dissolved in ethanol (100 ml.) and 4.5 g. (0.2 mole) of sodium added in small pieces with stirring. Ethylene dibromide (18.5 g., 0.1 mole) dissolved in 100 ml. of ethanol was added dropwise to this solution so as to maintain a gentle

reflux. After all the ethylene dibromide had been added the mixture was refluxed for two hours and then allowed to cool. The ethanol was distilled of in vacuo and the resultant oily solid extracted with diethyl ether. The ethereal solution was washed with water and dried over calcium chloride. The ether was removed in vacuo and the resultant yellow oil was distilled in vacuo collecting the fraction distilling from $90^{\circ}-100^{\circ}$ under 1 mm pressure. Yield 15 g.

$M(IPTE)_2X_2$ (M = Co, Ni; X = Cl, Br, I)
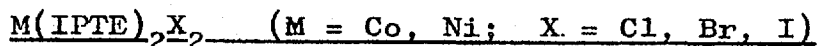
The hydrated metal halide (0.01 mole) was dis-solved in the smallest possible amount of ethanol and 1:2 bis(isopropylthio)ethane (0.03 mole) added. The complexes precipitated immediately and were filtered off and dried in vacuo. (Analytical results for these com-pounds are given in Table 34.).

$M(IPTE)_2(NCS)_2$ (M = Ni, Co)

The ethanol complexes $M(EtOH)_2(NCS)_2$ (page 197.) were finely ground in a dry-box and covered with an excess of 1:2 bis(isopropylthio)ethane. The slurry was placed in a vacuum desiccator over phosphorus pentoxide for several days and the resultant green complex was washed with a little dry benzene and dried in vacuo.

Table 34

Analytical Results for some 1:2 Bis(isopropylthio)etane

Complexes

Compound	Found (%)			Required (%)		
	C	H	X	C	H	X
$Ni(IPTE)_2Cl_2$	39.4	7.4	-	39.5	7.4	-
$Ni(IPTE)_2Br_2$	33.2	6.1	28.0	33.4	6.3	27.8
$Ni(IPTE)_2I_2$	28.3	5.1	-	28.7	5.4	-
$Ni(IPTE)_2(NCS)_2$	40.4	6.6	5.6*	40.7	6.8	5.3*
$Co(IPTE)_2Cl_2$	39.8	7.6	14.6	39.5	7.4	14.6
$Co(IPTE)_2Br_2$	33.8	5.8	-	33.4	6.3	-
$Co(IPTE)_2I_2$	29.5	5.5	37.0	28.7	5.4	37.9
$Co(IPTE)_2(NCS)_2$	40.1	6.5	5.5*	40.7	6.8	5.3*

*X = N.

1:2 Bis(tert-butylthio)ethane[111]

This compound was prepared as a colourless liquid b.p. $75 - 80°/ 0.1$ mm by the same method as was used for 1:2 bis(isopropylthio)ethane. No solid complexes of this ligand with cobalt(II), nickel(II), copper(II) or cadmium(II) could be prepared in a pure state; although there was some indication of complex formation with nickel and copper.

1:2 Bis(phenylthio)ethane[82]

This was prepared as a white solid, m.p. $70°$ by the method of Bell and Bennett.[82] No evidence for formation of complexes of this ligand with cobalt(II) nickel(II), copper(II), or cadmium(II) was found.

Iodine Adducts of Dithiahexane Complexes

The metal complex (0.002 mole) and iodine (2.54 g., 0.01 mole) were refluxed together in chloroform (20 ml.) for a few hours and the solution set aside for two or three days. The dark solid was filtered off washed with a little diethyl ether and dried in air. Only the nickel dithiahexane complexes gave stoichiometric iodine adducts. Yields $Ni(DTH)_2(NCS)_2I_4$ 0.5 g.; $Ni(DTH)_2Cl_2I_4$ 0.4 g.;

$Ni(DTH)_2Br_2I_4$ 0.3 g.; $Ni(DTH)_2I_6$ 0.8 g.;

$Ni(DTH)_3(ClO_4)_2I_6$ 0.3 g.

Table 35

Analytical Results for the Iodine Adducts of Dithiahexane

Complexes

Compound	Found (%)		Required (%)	
	Ni	I	Ni	I
$Ni(DTH)_2(NCS)_2I_4$	6.2	55.0	6.4	54.8
$Ni(DTH)_2Cl_2I_4$	7.0	56.1	6.7	57.6
$Ni(DTH)_2Br_2I_4$	6.1	51.6	6.1	52.6
$Ni(DTH)_2I_6$	5.0	72.8	5.5	71.6
$Ni(DTH)_3(ClO_4)_2I_6$	4.3	54.0	4.2	55.1

All of the complexes tend to loose iodine at room temperature, also it is difficult to ensure that the product is not contaminated with molecular iodine. This probably accounts for the differences between the found and required Iodine analyses.

Physical Measurements

Electronic reflectance spectra were measured over the range 20,000 – 3700 cm^{-1} on a Beckman DK 2 spectrophotometer using magnesium oxide as reference and over the range 33,000 – 10,000 cm^{-1} on a Unicam S.P. 500 spectrophotometer using magnesium carbonate as reference.

Electronic solution spectra were measured over the range 40,000 – 3700 cm^{-1} on a Perkin-Elmer 350 spectrophotometer, and in the range 40,000 – 10,000 on a Unicam S.P. 500 spectrophotometer.

Magnetic susceptibility measurements at room temperature were made using a Gouy balance of conventional design. Magnetic measurements over the temperature range 77° – 370° K were made on a Gouy balance similar to that described by Figgis and Lewis.[115] For the compounds which obeyed a Curie-Weiss law measurements were made at 8 – 12 temperatures equally spaced over the temperature range studied (80 – 300°K or 80 – 370°K); in other cases more points were taken in the region of the abnormality. All measurements were made with the temperature being reduced, although in most cases (including all of the unstable compounds) one or more points were taken with the temperature being increased from 80°K.

At each temperature measurements were made at 3 - 6 field strengths in the range 2,000 - 6,500 gauss, but in no case was a significant field dependance detected. At least two separate magnetic "runs" were made on each compound, each run involving a fresh packing (and in the case of the unstable compounds, a new preparation) of the sample. The field strength and the thermocouple were calibrated every few months against $HgCo(NCS)_4$.[116]

Mossbauer Spectra were determined at 295°K with a standard Elron spectrometer using an Intertechnique SA40B Analyser in the multichannel mode with pulse height analysis and standard counting equipment. The source ^{57}Co - Pd was obtained from the Radiochemical Centre, Amersham. Isomer shifts are given relative to the source and the compound $Na_2(Fe(CN)_5NO).2H_2O$ was used as calibrant.[117]

Powder patterns were obtained using an Enraf - Nonius Guinier - De Wolff Camera No.II.

Raman spectra of aqueous solutions were obtained on a Cary 81 spectrometer using the mercury 4358 A° line. 7 mm sample tubes were used throughout. The spectral slit width used was 10 cm^{-1} and the double slit mode was used for all measurements above 200 cm^{-1}.

Infrared Spectra in the range 4000 – 400 cm^{-1} were measured on a Grubb-Parsons "Spectromaster" grating instrument using Nujol, hexachlorobutadiene, or "Fluorolube" mulls between potassium bromide plates.

Far infrared spectra in the range 500 – 200 cm^{-1} were measured on Grubb-Parsons DM 2 and DM 4 double beam grating instruments. The DM 4 instrument (this was used for most of the compounds) was flushed with air from a "Dryad" unit. This reduced the water vapour level in the instrument such that the strongest rotational bands absorbed less than 20% of the radiation. Under these conditions the double beam background was virtually flat. All of the compounds were measured as nujol mulls between polythene discs and a compensating film of nujol between polythene discs was placed in the reference beam. The spectra were usually run at 20 cm^{-1} per minute and in most cases the absorption bands were run over at 10 cm^{-1}/min. The narrow slit cams were used throughout.

Far infrared spectra in the range 260 – 130 cm^{-1} were measured on a single beam vacuum grating instrument designed and constructed in this department by Drs.J.L. Wood, H.G. Silver and P.Tamsalu. In a few cases the spectra were also run from 390 – 240 cm^{-1} on this instrument.

The spectrometer (which has been described in detail elsewhere[118], has a high pressure mercury lamp as source and a Golay detector. Two echdette gratings with 200 and 80 lines/cm, blaised at 225 cm^{-1} and 90 cm^{-1}, are available. The filter system used consists of a potassium bromide chopper, black polythene transmission filter, and two crossed restallen reflectors. In this work, the ranges covered by the different restallen filters were as given below.

Grating	Restrallen	Frequency Range
80 line/cm	2 KCl	125 - 190 cm^{-1}
200 line/cm	2 NaCl	160 - 270 cm^{-1}
200 line/cm	2 NaF	240 - 390 cm^{-1}

These filters eliminate virtually all the higher order radiation down to 130 cm^{-1}.

The spectral slit width used was less than 2 cm^{-1} over the whole range and less than 1 cm^{-1} between 200 and 160 cm^{-1}. The instrument was evacuated down to about 0.2 mm; this removed all bands due to water vapour from the spectra except that at 202.7cm^{-1} which appeared weakly. This band did not, however, affect the derived spectra of the compounds and provided a convenient check on the calibration in the "2 NaCl" region.

The samples were measured as nujol mulls sealed into polythene bags, interference effects being eliminated by using polythene with an uneven finish. A spectrum of nujol in polythene was first measured, and the spectrum of the mull was then run without altering the instrument settings. A pipper gave calibration lines at $2 - 5$ cm^{-1} intervals on the spectra. The ratio of the signal levels for the mull and the nujol reference at each pipmark (at closer intervals near the maxima of sharp bands) was plotted against wavelength to give the absorption spectrum.

In a few cases, far infrared spectra were measured over the range $200 - 65$ cm^{-1} on a Grubb-Parsons GM 3 single beam grating instrument flushed with dry air from a "Lectrodryer".

Each of the far infrared instruments was calibrated by reference to the water vapour spectrum. [119]

REFERENCES

(1) S. E. Livingstone, Quart. Revs., (1965) 19, 386.

(2) S. Ahrland, J. Chatt, and N. R. Davies,
             Quart. Revs., (1958) 12, 265.

(3) C. K. Jørgensen, J. Inorg. Nuc. Chem., (1962) 24, 1571.

(4) R. E. Carlin and E. Weissberger,
             Inorg. Chem., (1964) 3, 611.

(5) F. A. Cotton, O. D. Faut, and J. T. Mague,
             Inorg. Chem., (1964) 3, 17.

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

(7) Y. Shimura and R. Tsuchida,
             Bull. Chem. Soc. Japan, (1956) 29, 311.

(8) C. K. Jørgensen, Prog. Inorg. Chem., (1963) 4, 73.

(9) Y. Tanabe and S. Sugano,
             J. Phys. Soc. Japan, (1954) 9, 753.

(10) C. E. Shaffer, Abstracts, 140th National Metting of
the American Chemical Society, Chicago, 1961 p. 24N.

(11) C. K. Jørgensen, Adv. Chem. Phys., (1963) 5, 33.

(12) S. Koide and M. H. L. Pryce, Phil. Mag., (1958) 116, 607.

(13) L. E. Orgel, "Transition Metal Chemistry", 2nd Ed.
             Metheun, London. (1966).

(14) B. N. Figgis, "Introduction to Ligand Fields",
             Interscience, New York, (1965).

(15) C. J. Ballhausen, "Introduction to Ligand Field Theory",
             McGraw-Hill, New York. (1962).

(16) B. N. Figgis and J. Lewis, Technique of Inorganic
             Chemistry, (1965) 4, 137.

(17) B. N. Figgis and J. Lewis,
             Prog. Inorg. Chem., (1964) 6, 37.

(18) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, (1955).

(19) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York, (1963).

(20) F. A. Cotton, "Chemical Applications of Group Theory", Interscience, New York, (1963).

(21) J. F. Duncan and R. M. Golding, Quart. Revs., (1965) 19, 37.

(22) P. J. Hendra, Nature, (1966) 212, 179.

(23) J. R. Allan, D. H. Brown, R. H. Nutell, and D. W. A. Sharp, J. Inorg. Nuc. Chem., (1965) 27, 1305.

(24) D. H. Adams, J. Chatt, J. M. Davisson, and J. Gerratt, J. Chem. Soc., (1963), 2189.

(25) R. J. H. Clark and T. M. Dunn, J. Chem. Soc., (1963), 1189.

(26) A. Sabatini and L. Sacconi, J. Amer. Chem. Soc., (1964) 86, 17.

(27) D. B. Powell and N. Sheppard, J. Chem. Soc., (1956), 3108.

(28) L. Sacconi, A. Sabatini, and P. Gans, Inorg. Chem., (1964) 3, 1772.

(29) R. J. H. Clark and C. S. Williams, Inorg. Chem., (1965) 4, 350.

(30) D. Forster and D. M. L. Goodgame, J. Chem. Soc., (1965), 262; 1286.

(31) D. Forster and D. M. L. Goodgame, Inorg. Chem., (1965) 4, 715.

(32) R. J. H. Clark and C. S. Williams, Spectrochim. Acta, (1966) 22, 1081.

(33) D. Forster and D. M. L. Goodgame, Inorg. Chem., (1965) 4, 1712.

(34) K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martel,
J. Amer. Chem. Soc., (1961) 83, 1066.

(35) J. Fujita, A. E. Martel, and K. Nakamoto,
J. Chem. Phys., (1962) 36, 324, 331.

(36) K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto,
J. Chem. Phys., (1963) 39, 423.

(37) I. S. Ahuja, D. H. Brown, R. H. Nuttall, and D. W. A.
Sharp.   J. Chem. Soc. A., (1966), 938.

(38) C. W. Frank and L. B. Rogers,
Inorg. Chem., (1966) 5, 615.

(39) H. Siebert,   Z. Anorg. Chem., (1954) 275, 225.

(40) J. E. Stewart,   J. Chem. Phys., (1957) 26, 248.

(41) L. J. Belamy, "The Infrared Spectra of Complex
Molecules", 2nd. Ed. Methuen, London. (1958) and
references therein.

(42) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane,
C. Curran, and J. V. Quagliano,
J. Amer. Chem. Soc., (1958) 80, 527.

(43) F. A. Cotton, O. D. Faut, and J. T. Mague,
Inorg. Chem., (1964) 3, 17.

(44) M. J. Janssen,   Spectrochim. Acta, (1961) 17, 475.

(45) B. H. Robinson, Abstracts, Chemical Society Autumn
Meeting, (1965) Paper B2.

(46) N. R. Kunchur and M. R. Truter
J. Chem. Soc., (1958) 2551.

(47) J. W. Emsley and J. A. S. Smith,
Trans. Faraday Soc., (1961) 57, 893.

(48) N. R. Kunchur and M. R. Truter,
J. Chem. Soc., (1958), 3478.

(49) M. Nardelli, L. Cavalca, and A. Braibanti,
Gazzetta, (1957) 87, 137.

(50) A. Lopez-Castro and M. R. Truter,
J. Chem. Soc., (1963), 1309.

(51) C. B. Knobler, Y. Okaya, and R. Pepinsby,
Z. Krist., (1959) 111, 385.

(52) S. Oi, T. Kawase, K. Nakatsu, and H. Kuroya,
Bull. Chem. Soc. Japan, (1960) 33, 861.

(53) A. Sabatini and I. Bertini,
Inorg. Chem., (1965) 4, 959.

(54) D. M. Adams and D. M. Morris, Nature, (1965) 208, 283.

(55) B. N. Figgis, Trans. Faraday Soc., (1960) 56, 1553.

(66) R. L. Carlin and S. L. Holt, Jr.,
Inorg. Chem., (1963) 2, 849.

(57) M. Nardelli, L. Cavalca, and A. Braibanti,
Gazzetta, (1956) 86, 867.

(58) M. Nardelli, I. Chierici, and G. V. Gasparri,
Ricerca Sci., (1959) 29, 1731.

(59) L. Cavalca, D. Andreeti, and P. Domiano,
Acta. Cryst., (1967) 22, 90.

(60) C. D. Flint and M. Goodgame.
J. Chem. Soc., submitted for publication.

(61) H. Siebert, Z. Anorg. Chem., (1953) 275, 225.

(62) I. S. Ahuja, D. H. Brown, R. H. Nuttall, and D. W. A.
Sharp. J. Chem. Soc. A, (1966), 938.

(63) R. E. Hester, R. A. Plane, and G. E. Walrafen
J. Chem. Phys., (1963) 38, 249.

(64) A. Simon and D. Kunath, Chem. Ber., (1961) 94, 1980.

(65) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran,
and J. V. Quagliano, J. Amer. Chem. Soc., (1959) 81, 3818.

(66) A. V. Babaeva, I. B. Baranovskii, and Y. Y. Kharitonov,
Russ. J. Inorg. Chem., (1963) 8, 307.

(67) J. A. Costamagna and R. Levitus,
                    J. Inorg. Nucl. Chem., (1966) <u>28</u>, 1116.

(68) A. V. Babaeva and Yan Vei-Da,
                    Russ. J. Inorg. Chem., (1960) <u>5</u>, 1320.

(69) D. A. Long, T. V. Spencer, D. N. Waters, and L. A.
      Woodward,   Proc. Roy. Soc., (1957) <u>240A</u>, 499.

(70) A. Rosenheim and V. J. Meyer,
                    Z. Anorg. Chem., (1906) <u>49</u>, 13.

(71) M. Nardelli, L. Cavalca, and A. Braibanti,
                    Gazzetta, (1956) <u>86</u>, 867.

(72) M. Nardelli, L. Cacalca, and A. Braibanti,
                    Gazzetta, (1957) <u>87</u>, 917.

(73) M. Nardelli, A. Braibanti, and G. Fava,
                    Gazzetta, (1957) <u>87</u>, 1209.

(74) M. Nardelli, G. F. Gasparri, G. G. Battistini, and
      P. Dominio   Acta Cryst., (1966) <u>20</u>, 349.

(75) D. Forster and D. M. L. Goodgame,
                    J. Chem. Soc. A, (1966), 170.

(76) C. J. Ballhausen and C. R. Hare,
                    J. Chem. Phys. (1964) <u>40</u>, 788.

(77) D. S. Mclure in "Advances in the chemistry of Co-
      ordination Compounds". Editor S. Kirschner, Macmillan,
      New York,   (1961).

(78) C. Burbridge, D. M. L. Goodgame, and M. Goodgame,
                    J. Chem. Soc. A, (1967), 349.

(79) R. M. Golding, K. F. Mok, and J. F. Duncan,
                    Inorg. Chem. (1966) <u>5</u>, 774.

(80) G. Yagupsky, R. Negretti and R. Levitus,
                    J. Inorg. Nuc. Chem.,(1965) <u>27</u>,2603.

(81) M. J. Weeks,   Thesis, University of London, (1966).

226.

(82) E. V. Bell and G. M. Bennett,
J. Chem. Soc., (1928), 319Q.

(83) R. W. Asmussen and H. Soling,
Acta Chem. Scand., (1957) 11, 745.

(84) G. Goodenough, "Magnetism and the Chemical Bond",
Interscience, New York. (1963).

(85) H. D. Noether,   J. Chem. Phys,, (1942) 10, 693.

(86) G. M. Barrow,   J. Chem. Phys., (1952) 20, 1739.

(87) J. Lewis, R. S. Nyholm, P. W. Smith,
J. Chem. Soc., (1961), 4590.

(88) M. Nardelli and I. Chierici,
Gazzetta, (1957) 87, 1478.

(89) M. Nardelli and I. Chierici,
Gazzetta, (1958) 88, 359.

(90) I. Suzuki,   J. Chem. Soc. Japan, (1962) 35,1449.

(91) M. R. Truter,   J. Chem. Soc., (1960) 997.

(92) K. A. Jensen and P. H. Nielsen,
Acta Chem. Scand., (1966) 20, 597.

(93) W. Kutzelnigg and R. Mecke,
Spectrochim. Acta, (1961) 17, 530.

(94) M. R. Truter and K. W. Rutherford,
J. Chem. Soc., (1962), 1748.

(95) M. Nardelli, G. F. Gasparri, A. Musatti and
A. Manfredotti,   Acta Cryst., (1966), 21, 910.

(96) G. T. Morgan and W. Ledbury,
J. Chem. Soc., (1922), 2886.

(97) R. Blackhouse, M. E. Foss, and R. S. Nyholm,
J. Chem. Soc., (1957), 1714.

(98) R. E. Carlin and E. Weissberger,
Inorg. Chem., (1964) 3, 611.

(99)   D. M. Sweeny, S. Mizushima, and J. V. Quagliano,
                J. Amer. Chem. Soc., (1955) 77, 6521.

(100)   S. Mitzushma, I. Ichishima, I. Nakagawa, and
        J. V. Quagliano, J. Amer. Chem. Soc., (1955) 77, 293.

(101)   F. A. Cotton and D. L. Weaver,
                J. Amer. Chem. Soc., (1965) 87, 4190.

(102)   A. D. Liehr,   J. Phys. Chem., (1963) 67, 1314.

(103)   A. I. Popov and R. F. Swensen,
                J. Amer. Chem. Soc., (1955) 77, 3724.

(104)   G. Schwarzenbach, "Complexometric Titrations",
        Methuen,   London,   1957.

(105)   F. J. Welcher,   "The Analytical Uses of ETTA",
        Van Nostrand. New York, (1957).

(106)   A. I. Vogel, "A Textbook of Quantitative Inorganic
        Analyses",   3rd. Edition,   Longmans,   (1961).

(107)   N. Kurnakow,   J. Prakt. Chem.(2), (1894) 50, 485.

(108)   M. Nardelli and I. Chierici,
                Ricerca Sci., (1958) 28, 1016.

(109)   M. Nardelli and I. Chierici,
                Gazzetta, (1958) 88, 832.

(110)   R. N. Keller, "Inorganic Syntheses" (19) 5, 153.

(111)   D. Welti and D. H. Whittaker,
                J. Chem. Soc., (1962), 4372.

(112)   R. N. Keller, "Inorganic Syntheses" (1946) 2, 247.

(113)   Beilstein's "Handbuch der Organischen Chemie",
        Supp. III,   Vol. 3,   p, 300.

(114)   J. Grant, "Quantitative Organic Microanalysis",
        4th. Ed. Churchill, London, 1945.

(115)   B. N. Figgis and R. S. Nyholm,
                J. Chem. Soc., (1959), 331.

(116) B. N. Figgis and R. S. Nyholm,
                    J. Chem. Soc., (1958), 4190).

(117) B. Fluok, W. Kerler, and W. Neawirth,
            Angew. Chem. Int. Ed.,   (1963) 2, 277.

      J. J. Spijkerman and J. R. De Voe,
            Nat. Bur. Standr. Tech. Notes, (1966) 276,80

(118) P. Taimsalu, Thesis, University of London, (1963).

(119) L. R. Blaine, E. K. Plyer, and W. S. Benedict,
            J. Res. NBS.,   (1962) 66A,   223.