DEPARTMENT OF CHEMISTRY

METAL COMPLEXES
OF SELECTED ORGANIC LIGANDS CONTAINING SULPHUR AND PHOSPHORUS

by

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ABSTRACT

An industrial problem concerning a pesticide product, ®Tinox, lead to the work described in this thesis. This included the study of the chelating properties of six sulphur and oxygen ligands and five phosphoryl sulphur and oxygen ligands with nickel(II) and cobalt(II) halides. Thirty two complexes of nickel(II) and cobalt(II) halides were prepared and are reported in this thesis.

The ligands used in the investigation are

1. 3-thiabutanol
2. 1-mercapto-3-thiabutane
3. 1-mercapto-2-methoxyethane
4. 1-methoxy-3-thiabutane
5. Di-(2-methylthioethyl) disulphide
6. Di-(2-methoxyethyl) disulphide
7. 0,0-dimethyl methyl phosphorodithioate
8. 0,0-dimethyl (2-methylthioethyl) phosphorodithioate
9. 0,0-dimethyl 0-(2-methylthioethyl) phosphorothionate
10. 0,0-dimethyl S-(2-methylthioethyl) phosphorothiolate
11. 0,0-dimethyl (2-methylthioethyl) thiophosphonate

The complexes were investigated by magnetic, spectrophotometric (infrared, ultraviolet) and conductiometric measurements.

The stereochemistry of the complexes prepared depended on the particular ligand used and examples of octahedral, tetrahedral and square planar complexes of nickel (II) halides and tetrahedral and square planar of cobalt halides complexes were obtained.

A comparison between the co-ordinating properties of sulphur and oxygen in their analogous forms i.e. thiol with hydroxyl, thioether with ether and thiophosphate with phosphate was made.

A preliminary study on the use of ferric salt in the stablisation of ®Tinox was conducted. No conclusion could be established at this stage and further experimental work is required for a proper evaluation on the potential use of the ferric salt.

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DEDICATED

TO

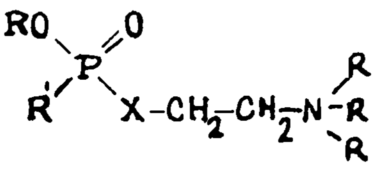
MY PARENTS

I

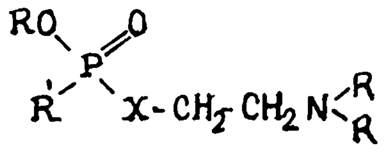
INTRODUCTION

®Tinox is an organophosphorus pesticide belonging to a larger group of compounds, the ®Systox, which is derived by replacing the basic choline nitrogen of the Tammalin esters[1] of the general structure as shown in (I) by a less basic atom such as sulphur.

Tammelin esters



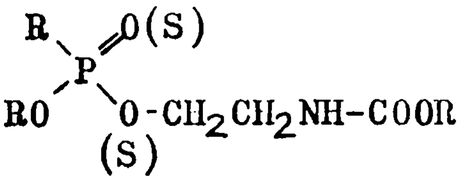
(Ia)



(Ib)

X=oxygen or sulphur R'=alkyl, alkoxy or fluorine

Though the Tammalin esters have excellent insecticidal activities, they also exhibit high mammalian toxicity. The latter property is attributed to the basicity of the nitrogen which is considered to be the primary factor in the interaction with the active sites of the enzyme cholinesterase[2,3]. For practical application as insecticides, active substances with such unfavourable toxicological properties are out of the question. The toxicity of these compounds may be reduced in two ways (i) by the reduction of the basicity of the choline nitrogen by using alkoxycarbonyl[4] or alkoxy-sulfonyl[5] group as shown in structures II and III, respectively; (ii) by replacing the basic choline nitrogen by less basic atoms such as sulphur. The second method results in the larger of the ®Systox compounds.



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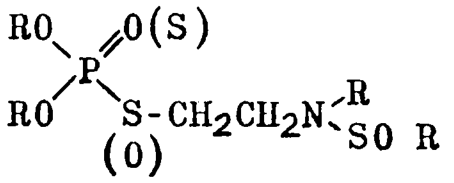
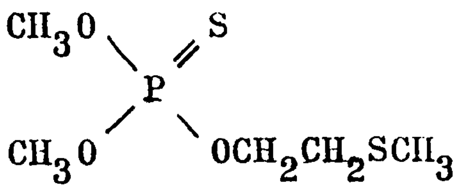
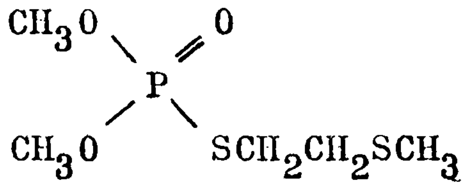


(III)

®Tinox is a commercial product which acts as a selective systemic and contact insecticide especially against aphids (Macrosiphon Solanifolii) and spider mites (Tetranychus Unticae)[6]. It is essentially a mixture of 0,0-dimethyl 0-(2-methylthioethyl) phosphorothionate (IVa, Thiono-Tinox) and 0,0-dimethyl S-(2-methylthioethyl) phosphorothiolate (IVb, Thiolo-Tinox). Both isomers of ®Tinox exhibit insecticidal activities. However, due to the higher dissolution rate of the thiolo isomer in aqueous system, which allows it to be absorbed into the plant system more quickly than the thiono isomer, the former isomer has overall activity more than ten times greater than that of the thiono form[7] and is largely responsible for the systemic activities of the product[8,9].


(IVa)


(IVb)

The product is manufactured from the acyl chloride (dimethyl chlorothiophosphonate) and 3-thiabutanol in chlorobenzene[10].

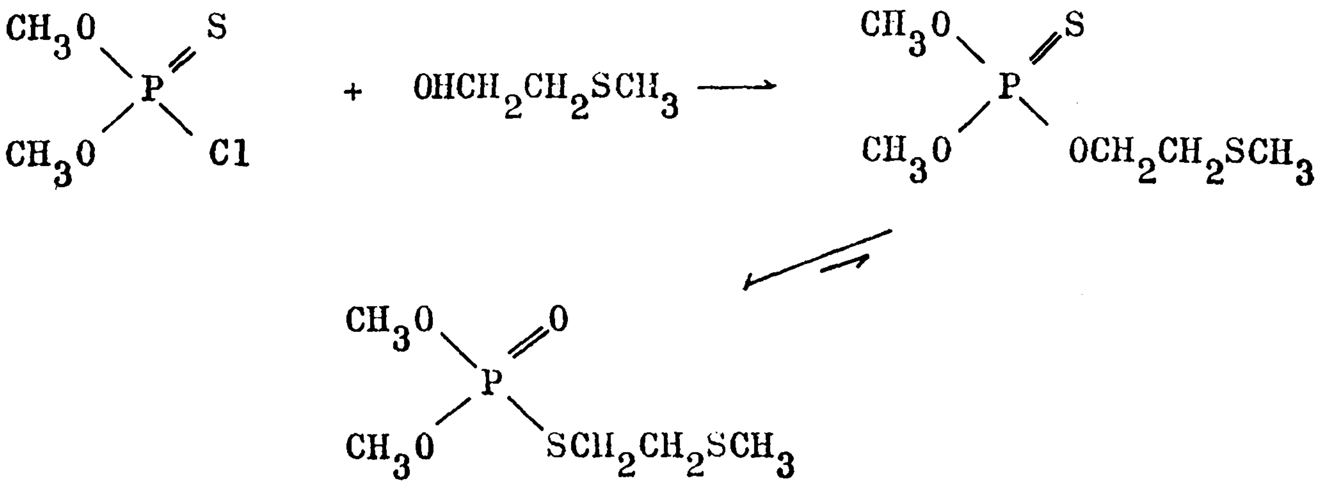
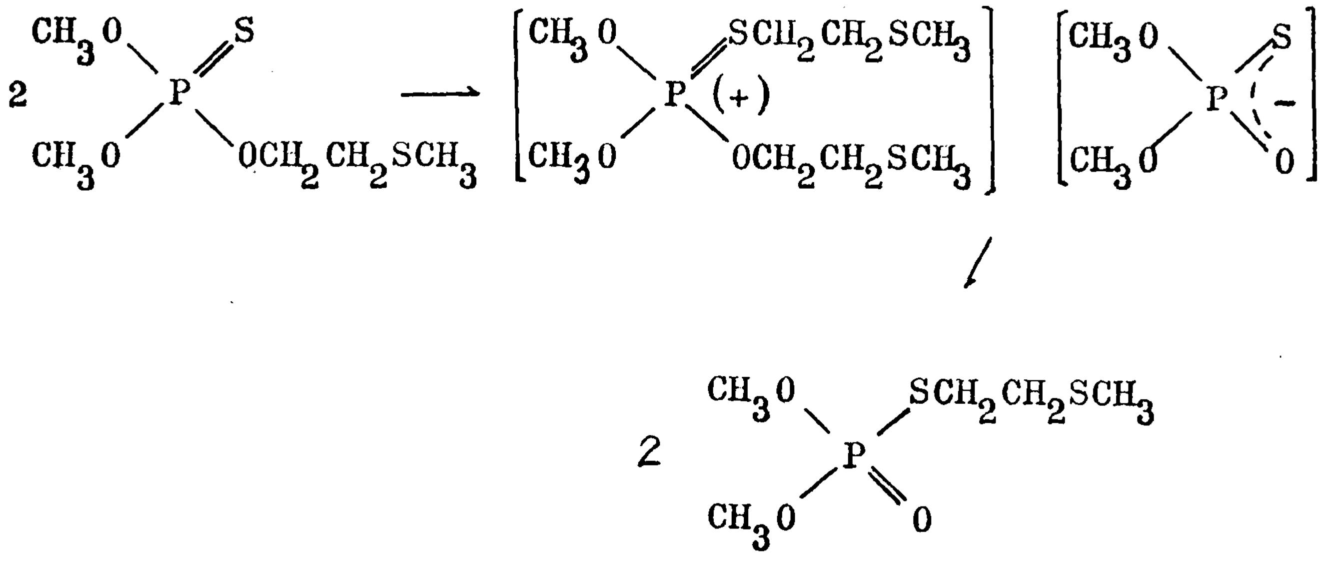


Figure 1.1 Reaction Scheme of Tinox Production

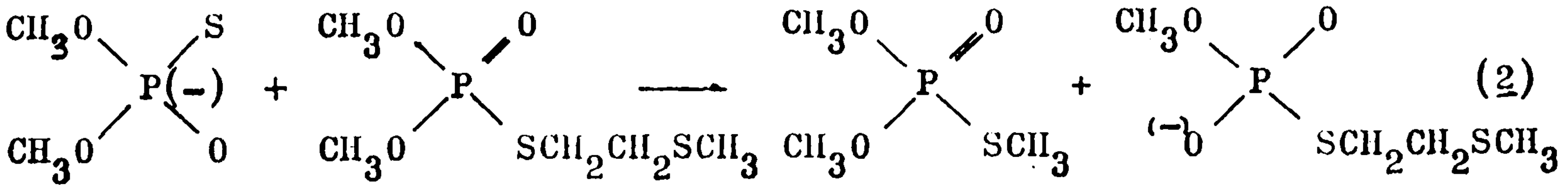
The thiono form of ®Tinox is first formed in this reaction and this is subsequently converted to the thiolo form by heat treatment. The conversion to the thiolo form does not go to completion and the final product consists of a mixture of the two isomers in the ratio of thiolo:thiono = 2:1[10]. The product is concentrated by vacuum distillation to the technical grade ®Tinox, which normally contains an average of 70-80% of the active material.

The isomerisation process utilizes the self-alkylating properties of the thiono-phosphoric ester[11-13]. Even without nucleophilic partners thiono-phosphoric acid esters themselves can participate in alkylation reactions. In order to obtain intermolecular C-O cleavage, vigorous reaction conditions are required, but such conditions (prolonged reaction time high temperature) are readily achieved in technical synthesis. In the case of ®Tinox production the nucleophilic centre is the thiono-isomer:



(1)

Though severe conditions are normally needed for the self-alkylation reaction, the process occurs at a very much lower temperature and is thought to be responsible for the gradual loss of the insecticidal activities of most ®Systox compounds on long storage due to the breakdown of the active substances by formation of other unwanted products. This deterioration is highlighted in ®Tinox by the formation of trimethyl phosphonate in the ®Tinox formulation represented by the following reaction:


(2)

Furthermore the thiolo-isomer is even stronger alkylating agent and would alkylate the sulfur atom in the side chain[14-16].

Identification of all the chemical components found in the formulation of ®Tinox after long term storage lends further support to the proposed breakdown mechanism. With the aid of gas liquid chromatography Wold-Dieter Spiethoff[17] has successfully identified all the components in samples of ®Tinox after a storage period of one year. The compounds found in these samples are listed in Table 1.1, p. 6.

Apart from the compounds which are inherent to the industrial process i.e. the ®Tinox isomers, chlorobenzene from the residual solvent, and 3-thiabutanol from the starting material, the origin of the various chemical substances may be traced back to the isomerisation process of thiono-isomer to thiolo-isomer. The following explanations were proposed by Wold-Dieter Spiethoff to account for the chemical components.

<u>0,0-Dimethyl S-methyl phosphorothioate (no.6)</u>

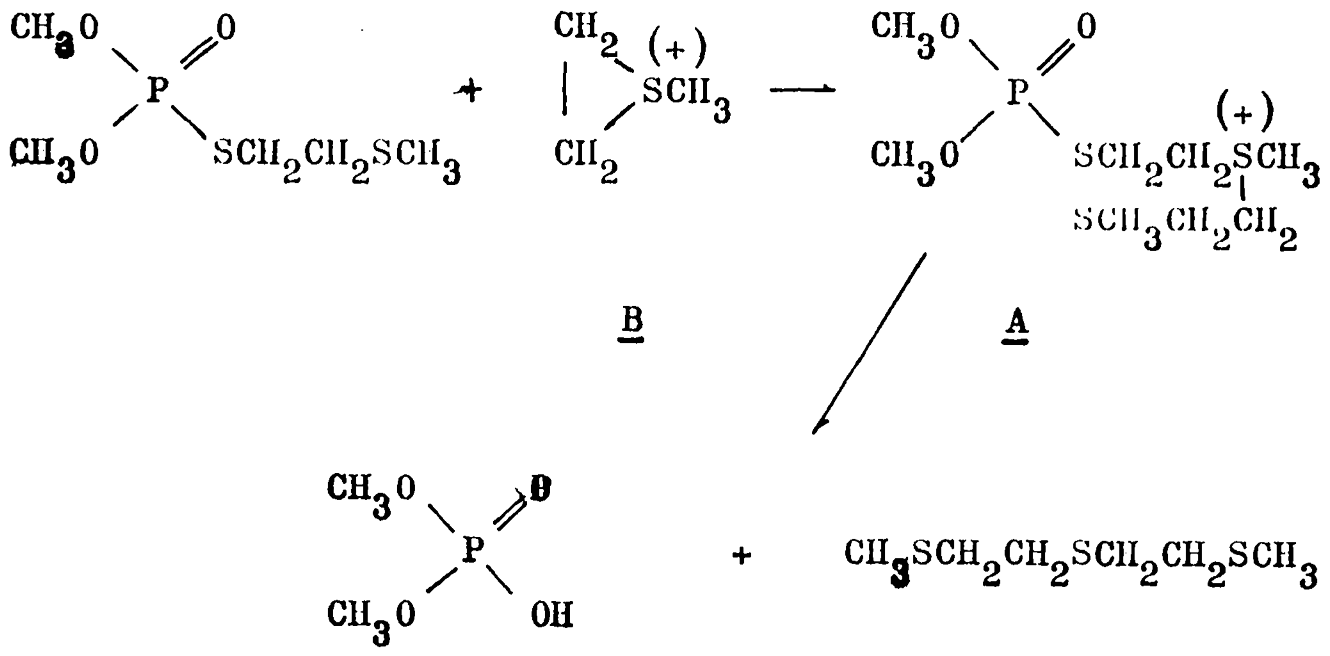
This has been dealt with above in equation (2).

Table 1.1

		Approx. %
1.	Thiolo-Tinox $(CH_3O)_2P(O)(SCH_2CH_2SCH_3)$	61.7
2.	Thiono-Tinox $(CH_3O)_2P(S)(OCH_2CH_2SCH_3)$	12.1
3.	Chlorobenzene C_6H_5Cl	6.6
4.	Trimethyl thiophosphate $(CH_3O)_3PS$	5.2
5.	3-Thiabutanol $CH_3SCH_2CH_2OH$	0.3
6.	O,O-Dimethyl S-methyl phosphorothioate $(CH_3O)_2P(O)(SCH_3)$	1.9
7.	Di-(methylthioethyl) sulphide $(CH_3SCH_2CH_2)_2S$	1.3
8.	1-Mercapto-3-thiabutane $CH_3SCH_2CH_2SH$	0.5
9.	Di-(methylthioethyl) disulphide $(CH_3SCH_2CH_2S)_2$	1.0
10.	2,5-dithiahexane $CH_3SCH_2CH_2SCH_3$	0.6
11.	Dimethyl sulphide $(CH_3)_2S$	0.5
12.	Phosphoric acid	8.3
13.	Polyphosphate	
14.	Sulphonium salts	

Di-(methylthioethyl) sulphide (no.7)

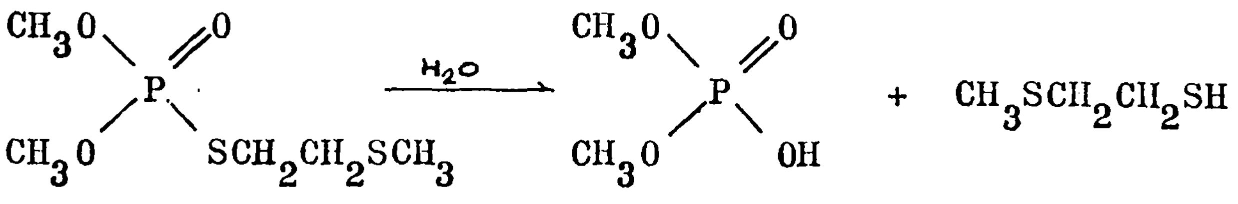
This is probably caused by the splitting of the ion product **A** from the reaction of thiolo-Tinox and the ion **B** of the isomerisation process. In this reaction phosphoric acid (no.12 in Table 1.1,p.6) is formed as well.



(3)

1-Mercapto-3-thiabutane (no.8)

Thiolo-Tinox hydrolyses rapidly in alkaline medium forming dimethyl phosphoric acid and 1-mercapto-3-thiabutane. The occurence of small quantities of these hydrolysis products in Tinox formulation is therefore readily explicable.



(4)

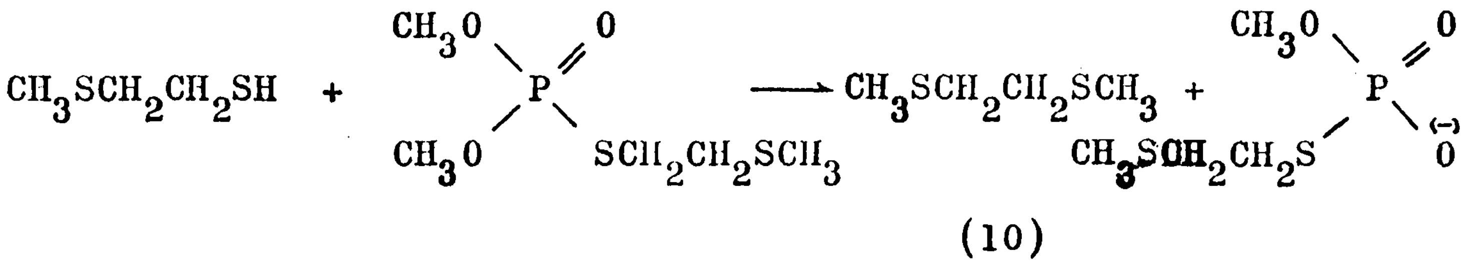
Di-(methylthioethyl) disulphide (no. 9)

The ease of oxidation of thiols accounts for the presence of the disulfide which arises from the oxidation of 1-mercapto-3-thiabutane.

$$CH_3SCH_2CH_2SH \xrightarrow{(O)} (CH_3SCH_2CH_2S)_2 \qquad (5)$$

2,5-Dithiahexane (no.10)

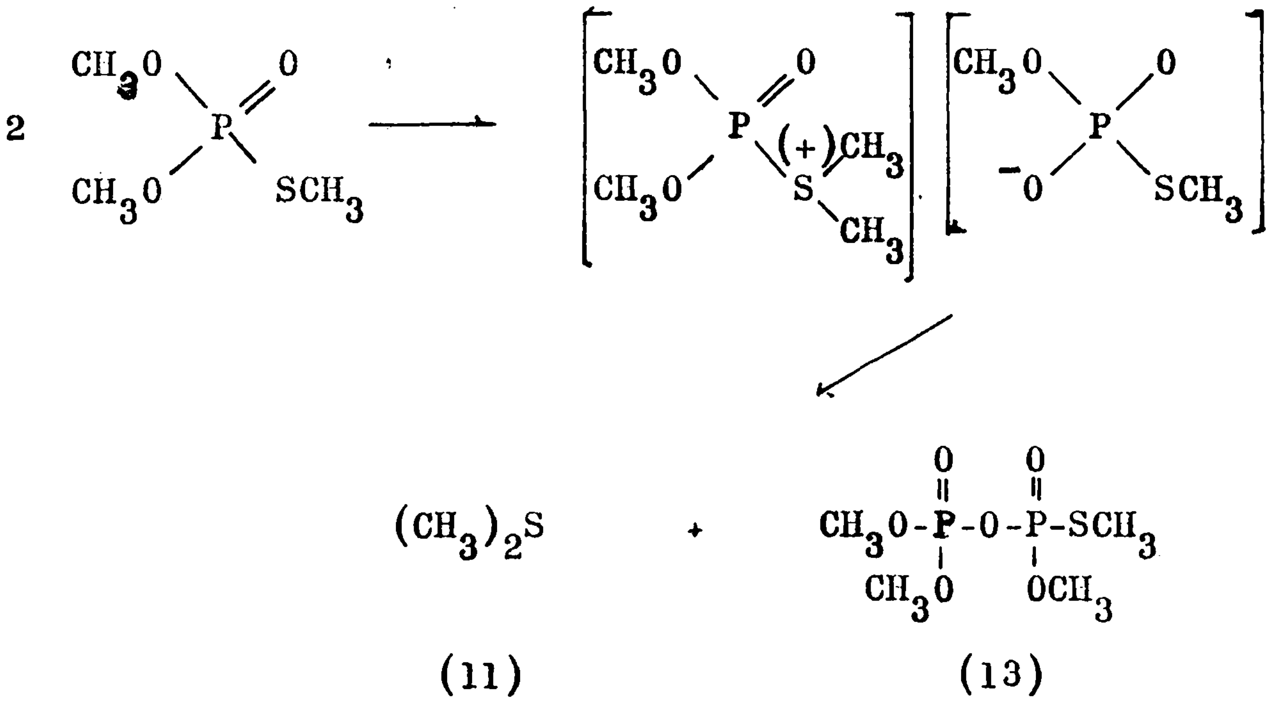
This compound is the product of methylation of 1-mercapto-methylthio-ethane by thiolo-Tinox.



(6)

Dimethyl sulphide (no.11), polyphosphate (no.13) and sulphonium salts (no.14).

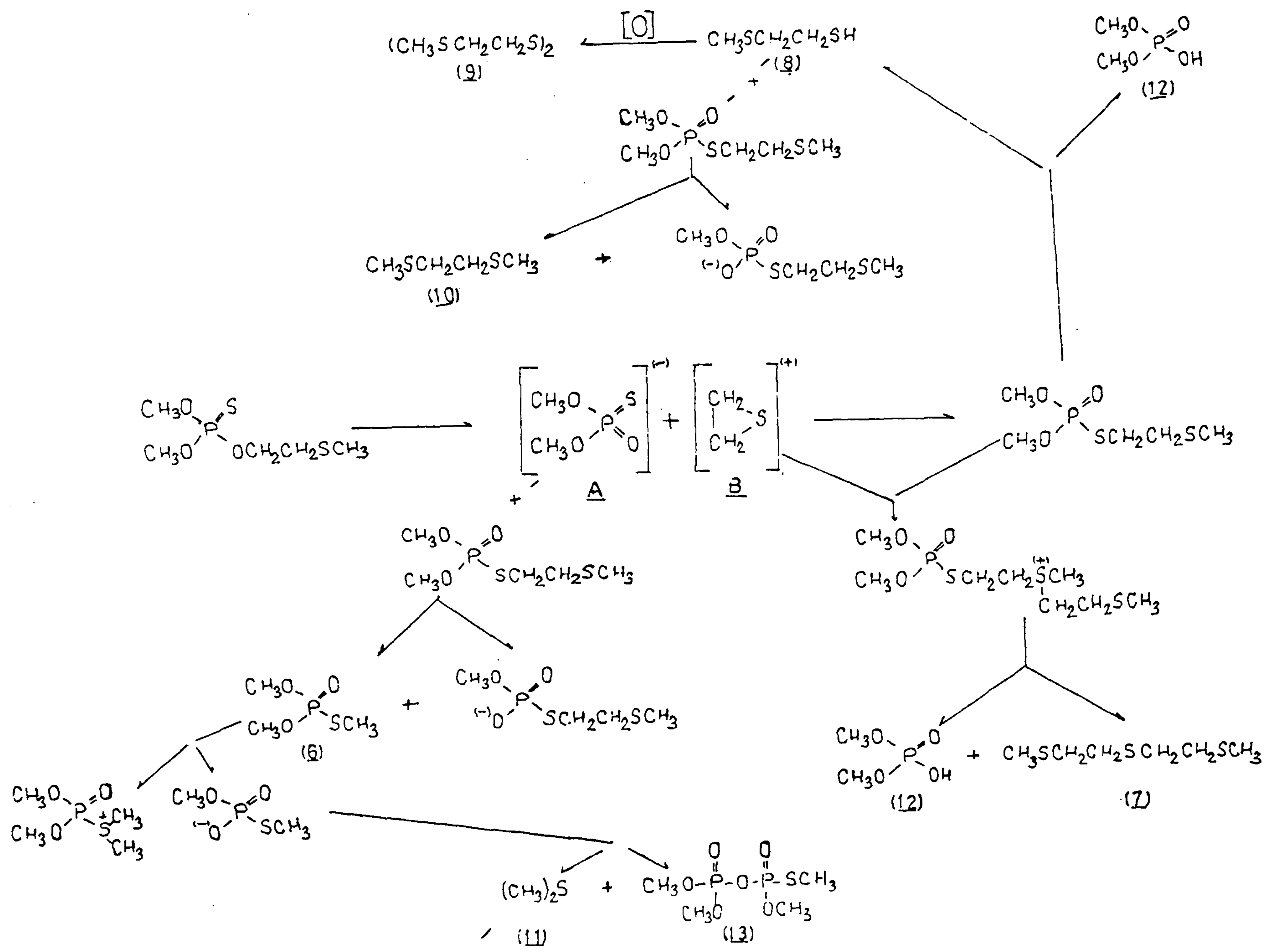
The acyl cleavage reaction of the O,O-dimethyl S-methyl phosphorothioate is responsible for the formation of dimethyl sulphide. Sulphonium ions and readily hydrolysable polyphosphate are formed in parallel with this reaction.



(7)

A schematic representation encompassing all the suggested reactions outlined above is shown in Figure 1.2, p.9.

FIG. 2.1 Schematic representation of ®Tinox breakdown processes



The instability of the active ingredients on long storage presents a serious technical problem in the accurate formulation of ®Tinox for commercial sale. Usually additional amount of ®Tinox is added to compensate for any decomposition of the active ingredient from the time of formulation to the actual field application of the insecticide. Apart from the fact that this method may lead to inaccuracy in the dilution process before spraying, it would impose additional cost to the manufacturer. Hence, there is urgency to find a way to stabilise the active ingredient after it has being formulated to prevent wastage of the valuable material.

One of the possible approaches to the problem of stabilisation of the active ingredients may be by metal chelation. As ®Tinox contains potential co-ordination sites, the phosphoryl oxygen and sulphur and the thioether group the possibility of ®Tinox forming metal complexes is high. It is well known that an unstable compound may be stabilised by chelate formation with the appropriate metal under the right conditions[18-19], hence, it is hoped that with a thorough understanding of the chelating properties of ®Tinox, a method may be developed to stabilise the compound through chelation with metal. The final solution would of course involves investigation of the thermodynamic properties of the complex if formed. However, the first stage of the investigation should concern mainly on whether metal complex could be formed with the ®Tinox isomers and the conditions favourable for the formation. A structural analysis on any complex formed by spectroscopic means would also be of great value to the full understanding of the chelation properties.

An additional problem in handling ®Tinox formulation is the cumbersome method of analysis[20]. The method consists of the determination of total active isomer content i.e. the thiolo and thiono isomer content together and a separate determination of the thiolo isomer content. Subtraction of the two results leads to the thiono isomer content.

The determination of total isomer content requires the removal of phosphorus containing impurities (mainly trimethyl thionophosphate) which are removed by azeotropic distillation with chlorobenzene. To ensure complete removal of this type of impurity, it is necessary to repeat the distillation for ten times or more, thus making the method tediously time consuming. The residue which contains only thiolo and thiono-isomer is saponified with sodium hydroxide. The excess sodium hydroxide is then determined using standard hydrochloric acid.

The thiolo isomer is determined iodometrically as 1-mercapto-3-thiabutane after saponification in the presence of lead acetate solution.

The thiono isomer is given by the difference of the total isomer content and thiolo isomer content.

Due to the large number of experimental steps involved in the analysis, the accuracy of this method is poor with an estimated percentage error of ± 15%.

It is hoped that the study of the chelating properties of the ®Tinox isomers may also lead to the development of a more convenient method for the analysis, such as direct photometric determination of the isomers of ®Tinox replacing the present inaccurate and time consuming method. For this purpose, an understanding of the chelation properties and the conditions for metal-complex formation of other chemical components present in the formulation are essential, so that any photometric method which might be developed would be guarded against any possible interference from these compounds. To this end, the Wold-Dieter Spiethoff analysis (p.4) may be used to elucidate the nature of the remaining components in the formulation. However, it must be pointed out, that the method used by Spiethoff for the identification of the chemical components may lead to mis-interpretation of the actual contents in the ®Tinox formulation. This is because of the high temperature employed in the analysis. At the temperature used (150°), it is certain that further isomerisation would take place and also other side reactions could not be ruled out entirely. Despite this criticism, the analysis is useful as a guide for the present investigation.

In order to formulate the right approach to the solution of the present problem, it is necessary to know about the work done up to date concerning the chelating properties of sulphur and phosphoryl sulphur and oxygen which are relevant to the problem. In this, it is convenient to divide the compounds in the formulation into two groups,(i) compounds which contain thioether group but no phosphorus and (ii) compounds which contain phosphorus as well as the thioether group. The first group provides a set of compounds for the study of sulfur as co-ordination centre in thiols and thioethers.

The remaining chemicals in the formulation of ®Tinox are the sulphonium salts, phosphoric acids, polyphosphates, trimethyl thionophosphate, trimethyl thiolophosphate, chlorobenzene and the two ®Tinox isomers. The first three substances are omitted in the study as these are insoluble in organic solvents and can be taken out of the system easily by first dissolving the formulation in ether and subsequently filtering off the insoluble materials. Chlorobenzene can be ignored in the chelation study as it is an inert solvent and does not interfere with the results obtained. Thus the second group contains only the two isomers of ®Tinox.

Due to the similarity between oxygen and sulphur as co-ordinating centres in ligands, the properties of the latter in complex behaviour is often compared with those of analogous oxygen complexes. The position of the sulphur in the electronegativity series does not reflect its true ability as a donor atom[21,22] mainly because its effective electronegativity will be influenced by the presence of other atoms or groups attached to the donor atom. From a consideration of an electrostatic model, it can be said that, for a unidentate ligand the co-ordinating ability depends not only on the electronegativity but on the total dipole moment (μ) of the ligand:

$$\mu = P + p' = P + \alpha E$$

where P=the permanent dipole moment, p'=the induced dipole moment, α=the polarisability and E=the inducing electrostatic field[23].

Thus, although the permanent dipole of NH_3 is less than that of H_2O, the total dipole moment of NH_3 may be greater in the presence of a cation with a high polarising power. The larger size and smaller dipole moment of H_2S reduces its co-ordinating ability below that of water for ions of low field strength. However, H_2S is more polarisable than water and with ions of high charge density H_2S co-ordinates strongly and protons are forced off to give insoluble sulphide.

On both the electrostatic and covalent models, for an uncharged ligand, it is expected that the co-ordinating tendency would follow the sequence of $R_2O > R_2S > R_2Se > R_2Te$.

Ahrland, Chatt and Davies[24] made an extensive study on the relative affinities of ligand atoms for metal ions. They divided metal into two classes:(a) those which form the most stable complexes with the first ligand atom of each group in the Periodic Table; (b) those which form the most stable complexes with the second or subsequent ligand atom. This is quite often used as a guide in deciding the metal ions used for studying complex behaviour of ligand. Another method of classification of metal ions and ligands has been suggested by Pearson[25]. He has classified metal ions and ligands into "hard" and "soft" Lewis acids and bases and has suggested as a general rule that hard acids bind strongly to hard bases and soft acids to soft bases.

Sulphur ligands are generally soft bases. However, it is possible for a soft base e.g. the highly polarisable S^{2-} and RS^- ions, to be strongly bonded to the proton which is itself a hard acid.

The ligand field strength of sulphur ligands may be compared with other ligands using the spectrochemical series[26]. This is arranged according to the spectroscopic splitting parameter Δ, as given by the frequencies of ligand field absorption bands in transition metal complexes. The position of sulphur ligand in the series is still not very clear, as sulphur has vacant d orbitals which can be used for $d_\pi - d_\pi$ bonding. The extent to which such π-bonding occurs is difficult to assess but available evidence suggests that, in favourable circumstances, it does occur with ligands containing sulphur[27]. As the parameter Δ is dependent on the overall electrostatic state of the bonding, it varies according to the degree of π-bonding.

The series of sulphur ligands to be studied may be divided into the thiols (RSH) and the thioether (RSR).

The behaviour of the thiols as a donor in transition metal complexes has not been subjected to such detailed study as a number of other donor groups. The thiol group often gives metal ions derivatives that are extremely insoluble, bridged, or even polymeric. Also thiols are good reducing agents. These properties greatly complicate the characterization of thiol complexes.

One of the most important properties associated with the thiol donor is its ability to form complexes containing sulphur bridges. This tendency is illustrated by the nickel(II) complex of ethyl mercaptan, which has been found to be diamagnetic, polymeric complex and the structure in Figure 1.3,p.16 was suggested[28], If other strong ligands are introduced e,g. tri-n-butylphosphine polymeric products can often be avioded and sulphur bridging is confined to the dimeric structure shown in Figure 1.4, p.16. Thus, Chatt and Mann[29] prepared the <u>cis</u> and <u>trans</u> forms of dichlorobis(tri-n-butylphosphine)-μ-ethyl-

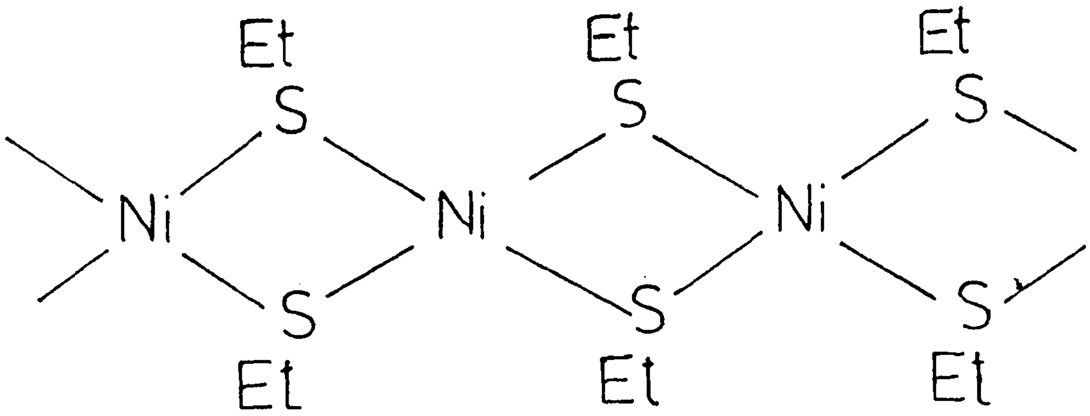


Figure 1.3

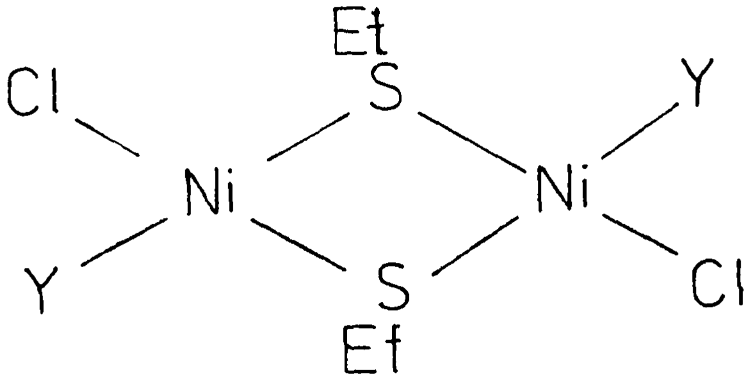


Figure 1.4

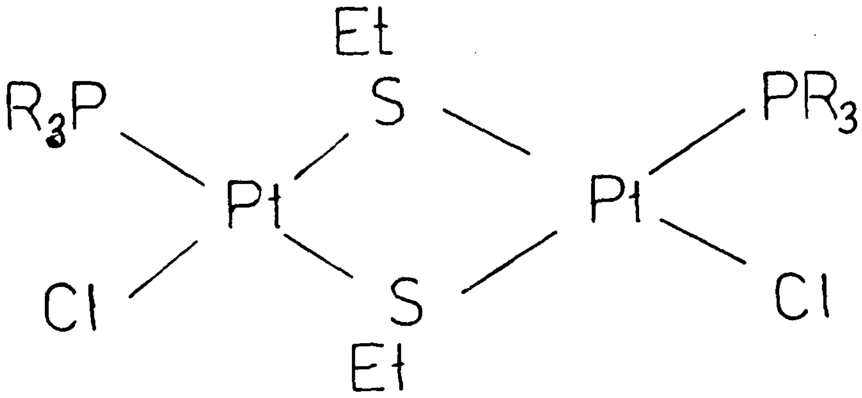


Figure 1.5

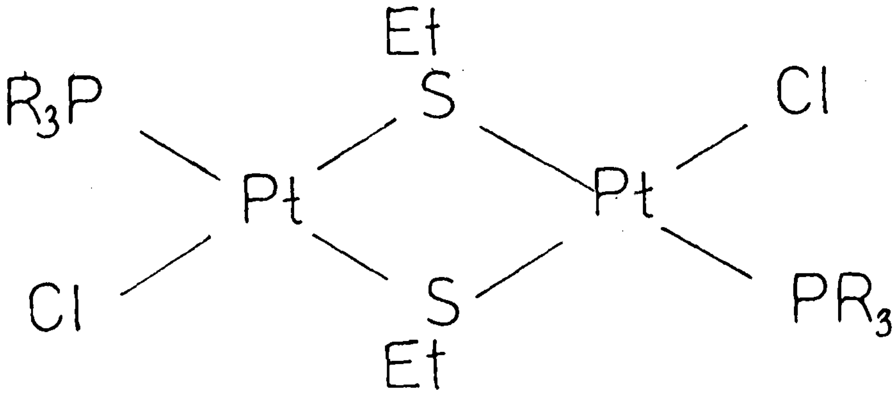


Figure 1.6

thiolodiplatinum(II) (structures in Figures 1.5 and 6, p.16, respectively) and other similar complexes. The linear structure can be terminated by the use of bidentate ligands containing the thiol and another donor e.g. nitrogen.

Several bidentate thiol ligands have been studied by Jicha, Busch and co-workers[30-33]. They found that with nickel and cobalt divalent ions, a number of complexes with different stoichiometric formula could be obtained depending on the experimental conditions. Thus, β-mercaptoethylamine forms two distinct types of compounds with nickel and cobalt divalent ions. In strong basic solution the well defined monomeric complex bis-(β-mercaptoethyl) amine nickel(II), ML_2 is obtained. The complex is diamagnetic and has a square stereochemistry. The high stability of this complex is illustrated by the reaction with pyridine. Four co-ordinated square complex of nickel usually expands its co-ordination number to six when treated with pyridine (i.e. a change from the square planar system to the octahedral by the attachment of two pyridine molecules on the z axis). This is not observed with the bis-(β-mercaptoethylamine) nickel(II) complex indicating the strength of the complex in resisting a change to its stereochemistry.

The tendency for sulphur ligands to form square planar diamagnetic complexes might seem surprising in that it is generally believed that square planar co-ordination is favoured by the high field ligand such as nitrogen. Such complexes probably occur because the nephelauxetic effect of sulphur greatly reduces the pairing energy (the interelectronic repulsion within the d shell) of the d electrons, allowing pairing to occur at a lower crystal field splitting energy. This results in the formation of a diamagnetic low spin complex. This behaviour is confined to thiol ligand and not to sulphur ligand as a whole e.g. thioether metal complexes are usually high spin and octahedral in stereochemistry[34]. This reflects on the different bonding behaviour of the sulphur ligand when present in different electronic state. Williams[35] has suggested that the principal difference between thiols and thioethers as ligands is that the former are more highly polarisable but not as effective *d* electron acceptors as the latter.

In neutral or slightly acidic solution a nickel complex formulated as $M(ML_2)_2Cl_2$ is formed[32]. The complex is diamagnetic indicating that all three nickel atoms are contained in planar co-ordination polygons. A structure for this compound involving a third nickel utilizing to full advantage the strong donor properties of the co-ordinated sulphur atoms of two uncharged *cis*-bis-(β-mercaptoethylamine) nickel(II) molecules as shown in Figure 1.7, below, has been proposed.

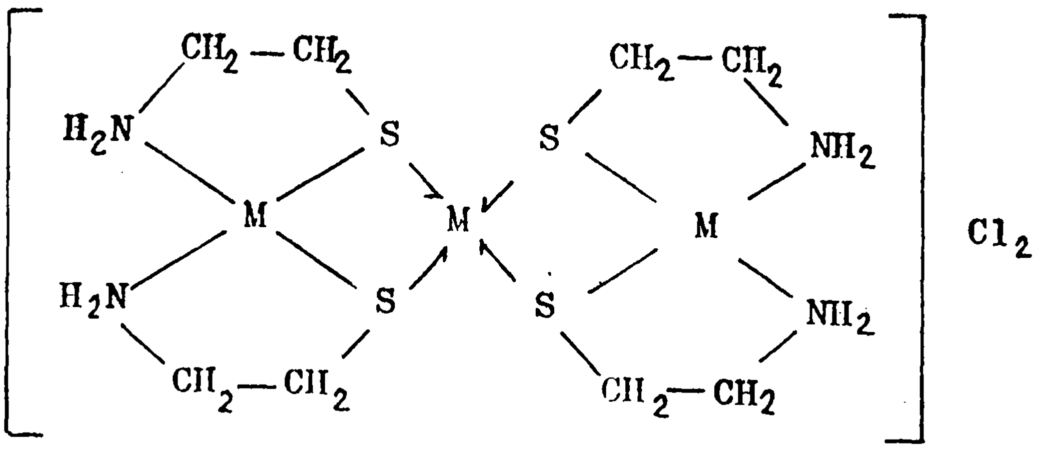


Figure 1.7

Despite the uncertainty associated with the actual geometric form for the uncharged species, the configurational stability of the <u>cis</u>-isomer receives some theoretical justification from the premise that two π-bonding sulphur atoms would not be expected to enter into competition for the $\underline{d}_{\pi}$ electrons of the nickel(II)[36] as would be required for the <u>trans</u>-isomer.

A change in the nature of the second donor atom may affect the chelating properties of the thiol chelates. This is reflected in the ligand 2-(2-mercaptoethyl) pyridine. This ligand is similar to β-mercaptoethyl amine in its donor atoms but differs in stereochemistry and type of nitrogen atom and in the size of the chelate ring it may form.

With this ligand, in addition to the two types of complexes ML_2, $M(ML_2)_2Cl_2$ formed by the β-mercaptoethyl amine described above, another type of complex with stoichiometric formula of $M_2L_2Cl_2$ is formed with nickel chloride when the preparation is done in ethanol. The complex is dimeric and as the structure involved sulfur bridging[31], two possible structures in Figure 1.8 and 9 illustrated below are proposed. No definite assignment of one of these structures was then possible.

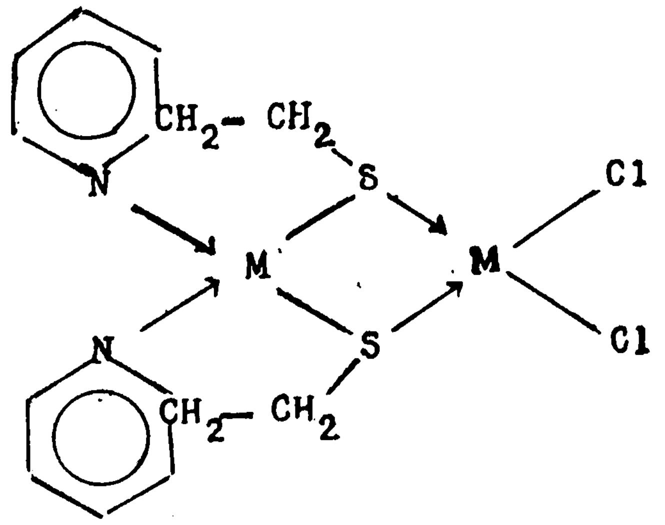


Figure 1. 8

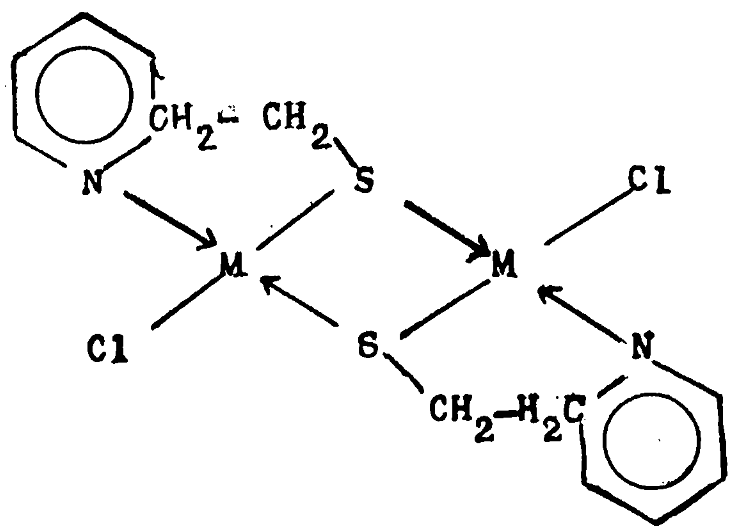


Figure 1. 9

Unlike the mercaptide ion (RS^-), complexes of sulphur as thioether (RSR) have been studied less extensively[27,37,38]. Most of the work done are with typical class 'b' metals such as Pt(II), Pd(II), Rh(III), Ir(III) and Hg(II)[39–41]. It is of interest to note that, though thioether proves to have spectrochemical field strength that is 'fairly strong'[42] or almost as strong as ammonia, the thioether chelates of typical class 'a' metals e.g. Co(II) and Ni(II) are quite unstable towards displacement by water[43]. This makes it necessary to prepare the complexes under non-aqueous conditions.

Bidentate ligands with sulphur atoms at both of the co-ordination sites e.g. 2,5-dithiahexane, have been studied in some detail[44]. There are indications that the nature of the alkyl group attached to the sulphur affects the general stability and ease of formation of complexes. With bulkier terminal alkyl group complexes of lower stability are obtained. With 2,5-dithiahexane, complexes of nickel and cobalt divalent halides, thiocyanates and perchlorates were obtained; with 1,2-di(isopropylthio)ethane complexes were formed with cobalt and nickel halides and thiocyanates but no complexes could be obtained from the perchlorates; with 1,2-di(t-butylthio)ethane, no solid complexes were obtained in pure states, though there were colour changes indicating some complex formation. No evidence of complex formation was obtained with 1,2-di(phenylthio)ethane.

The usual stoichiometry of the complexes with Ni(II) and Co(II) salts of the bidentate sulphur ligands mentioned above is ML_2X_2 (M=Ni, Co; L=bidentate ligand; X=anion e.g. Cl, Br, I), though other metal to ligand ratio may sometimes be obtained. The stereochemistry of these complexes is generally tetragonal with the anions co-ordinated in the axial positions.

With the exception of the disulphide ligands, the series of sulphur ligands under study are all bidentate with one co-ordination site occupied by a thioether and the other either by oxygen as hydroxyl or ether, and by sulfur as thiol. It would be interesting to compare the co-ordinating behaviour of the dithia-ligands with these substituted thia-ligands and to see whether the substitution of the sulphur by other co-ordinating ligands would affect the co-ordination behaviour of the sulphur atom.

The di-(methylthioethyl) disulphide, one of the compounds under investigation is of great interest. Unlike other ligands which are bidentate, this compound has four possible co-ordination centres. During the last decade there has been a great deal of interest in the synthesis and complex formation of multi-dentate ligands containing heavy atoms[45]. These have mainly been of the tripod quadridentate type e.g. the 2,3-butanedionebis (2-diphenylphosphinoethylimine) and trigonal symmetry of these ligands most frequently gives rise to trigonal bipyramidal complexes with Co(II) and Ni(II) metal ions. Comparatively few complexes of tetradentate thioether have been reported. The cyclic tetradentate ligand 1,4,8,11-tetrathiacyclotetradecane forms paramagnetic tetragonal complexes with nickel(II) halides[46] and the open chain which also forms tetragonal paramagnetic complexes have been reported[47]. A comparison of the Dq^{xy} values (1070 cm^{-1} for the tetracyclic and 1020 cm^{-1} for the open chain) showed that the open chain ligand is lower in the spectrochemical series than the cyclic ligand.

The list of compounds containing phosphorus and thioether may be divided into the phosphoryl $R_3P=O$ and thiophosphoryl $R_3P=S$ groups.

Ligands co-ordinating by the phosphoryl oxygen, such as phosphine oxide, phosphonate and phosphinate esters[48-52], have been studied quite extensively and with the use of infrared spectroscopy (the shift of the P=0 band) it is proved that co-ordination of these type of compounds is via the phosphoryl oxygen[53].

The position of absorption band attributed to the ν(P=0) stretching frequency limits varies within 1100-1300 cm^{-1} depending on the substituents on the phosphorus atom[54]. There is an increase in the frequency of ν(P=0) with increasing electronegativity of the substituents. This is said to be caused by the increase of partial charge on phosphorus which would result an increase in $p\pi - d\pi$ back bonding from the phosphoryl oxygen to phosphorus (i.e. an increase in bond strength) which is reflected by the shift of the ν(P=0) to higher frequency[55,56]

On co-ordination to the metal the oxygen loses part of its negative charge which would result a decrease in the availability of the oxygen electrons for back-bonding to the phosphorus. This is reflected by a shift of the absorption band to lower frequency by about 20-70 cm^{-1}.

The number of phosphorus monodentate ligands which would co-ordinate to a given metal is not very clear[57,58]. The evidence suggests that, in general, the co-ordination number of the metal varies with the chemical nature of the phosphorus atom and to a small extent the size of the substituent groups.

For a given metal, the co-ordination number increases with the number of the methoxy substituents[56]. Thus, trimethyl phosphinic oxide forms complexes of the type (MX_4^{z+})[57,58] and $[ML_4(OClO_3)]^+$ (M=Ni, Co and Fe; L=$(CH_3)_3P{=}O$)[59,60], while for dimethyl methyl phosphonate complexes of the types $[FeL_5]^{2+}$, $[ML_4]^{2+}$ (M=Ni or Cu) and $[ML_4(H_2O)_2]^{2+}$ (M=Co or Zn; L=ligand) have been isolated[58]. With trimethyl phosphate the divalent 3*d* metal ions easily form complexes of the type $[ML_5(H_2O)]^{2+}$ and trivalent metal ions form complexes of the type $[ML_6]^{3+}$.

Steric hindrance as a factor limiting the co-ordination number of the metal ion, is reflected by the tendency for the divalent metal complexes of di-isopropyl methyl phosphonate (DIMP) not to exceed a co-ordination number of four even in the presence of excess ligand. The steric effect is manifested by the fact that the tetra-co-ordinated ion does not have tetrahedral cationic configuration[58]. Magnetic moments and electronic spectra of the transition metal complexes indicate a ligand field symmetry intermediate between distorted T_d and D_{4h}.

Phosphoryl ligands with more than one co-ordination centre have not been studied in such detail as the monodentate ligands[61]. It has been recently reported[61] that bifunctional ligands such as $Ph_2P(O)(CH_2)_nP(O)Ph_2$ reacting with nickel(II) and cobalt(II) halides differ in their co-ordination properties depending on the length of the aliphatic chain and on the nature of the metal ion. The ligand 1,2-bis(diphenylphosphine oxide) ethane (DPEO) with nickel(II) and cobalt(II) perchlorate forms octahedral cationic complexes with the formula $M(DPEO)_3(ClO_4)_2$ (M=Ni or Co). Similar complexes are obtained with ligands $(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$[61] and $(Me_2N)_2P(O)N(CH_3)P(O)(NMe_2)_2$[62].

However with the halides of cobalt(II) and nickel(II) mixed octahedral-tetrahedral complexes are obtained having the formula $\left[M(DPEO)_3\right]^{2+}\left[(MX_4)\right]^{2-}$ (X=Cl, Br and I). The electronic spectra of the $\left[Co(DPEO)_3\right]^{2+}$ $(MX_4)^{2-}$ complexes show characteristic absorption bands for both the tetrahedral and octahedral cobalt(II) ions. However, in the analogous nickel(II) complexes the high intensity and complexity of the $(NiX_4)^{2-}$ spectrum obscures the low intensity bands of the octahedral nickel(II) cation, but the magnetic moments of the complex after subtracting the contribution due to the tetrahedral $(NiX_4)^{2-}$ anion is 3.22 B.M. which agrees with other octahedral nickel(II) complexes.

In contrast to the numberous metal complexes of phosphine oxides, very few phosphine sulphide complexes have been reported[63-67]. Under favourable conditions phosphine sulphides form stable complexes with metals that normally bond with easily polarized donor atoms i.e. class 'b' metal ions.

The co-ordination site is readily determined in the phosphoryl sulphide complexes by consideration of the $\nu(P=S)$ stretching frequency (500-700 cm^{-1}) in cases where this weak to medium strength band is observed. A shift of about 30 cm^{-1} in the $\nu(P=S)$ band to lower energy is indicative of the bonding through the sulphur atom[67].

Although some workers[66] reported unsuccessful attempts in preparing alkyl phosphine sulphide metal complexes, D. Meek and W.E. Slinkard[68] have reported the synthesis of several different metal co-ordination complexes with a series of tertiary phosphine sulphides. Trimethylphosphine sulphide $(CH_3)_3P=S$ forms white crystalline complexes with Cu(I), Cd(II), Hg(II) and Zn(II) salts by the direct reaction of the appropriate metal salt with the ligand in absolute ethanol.

Attempts to prepare complexes of the typical class 'a' metals such as Co(II), Ni(II) and Fe(II) with $R_3P=S$ ligands have not been successful[65]. Complex formation obviously depends on the polarisability and basic character of the P=S group. This could be altered by replacing the alkyl group with more basic substituents. W.E. Slinkard[68] isolated complexes of Co(II) and Ni(II) using $\left[(CH_3)_2N\right]_3P=S$ tris(dimethylamino) phosphine sulfide, as ligand. The possible co-ordination through nitrogen atom of the molecule is ruled out on the evidence that the ν(P=S) stretching frequency (565 cm^{-1}) in the free ligand is shifted to lower energy by 15-20 cm^{-1} in the complex spectra indicating that co-ordination has occured through the sulfur atom in the ligand. Co-ordination through the nitrogen atom would have raised the ν(P=S) stretching frequency.

The favoured stereochemistry of divalent transition metal complexes with phosphine sulphide is tetrahedral. With tris(dimethylamino) phosphine sulphide (TDPS) cobalt(II) salts form paramagnetic complexes of the type $\left[Co(TPDS)_4\right](ClO_4)_2$ and $Co(TDPS)_2X_2$ (X=Cl, Br, I). Nickel(II) salts have similar stereochemistry and nickel perchlorate complex of TDPS $\left[Ni(TDPS)_4\right](ClO_4)_2$ is one of the few known cationic tetrahedral nickel complex[58].

In the case of bidentate ligand containing phosphine sulfide as one of the co-ordination sites, Ojima and co-workers[69] reported the complex properties of a series of new thiourea derivative, 3-diphenyl-phosphinothioyl-1-phenylthioura (PTTU-A), 3-diphenyl-phosphinothioyl-1,1-diethylthiourea (PTTU-B), 3-diphenylphosphinothioyl-1-dimethylthiourea (PTTU-C) with transition metals such as Ni(II), Pd(II), Co(II) and Cu(II). The authors suggested that the thiourea derivatives could act as sulphur donor chelating reagents because their structures include both enolizable P=S and C=S bonds

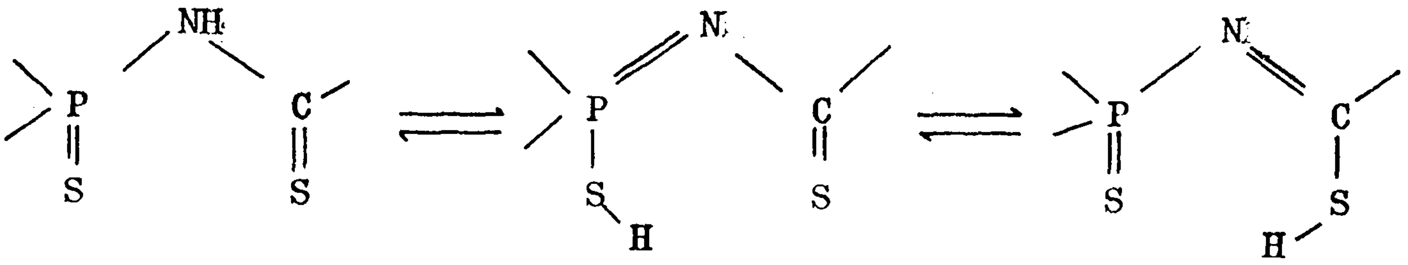


Figure 1.10

All the ligands are found to be bidentate and the type of structures of the complexes formed with the metal ions are shown in Figure 1.11, below. With Ni(II) and Pd(II) the complexes are square planar and with Co(II), although the co-ordination sites are the same, they are tetrahedral. As in the case of the phosphine sulphide, the lowering of the stretching frequency of the ν(P=S) band in the complexes by 20-70 cm^{-1} when compared to the free ligand vibration of this band, is indicative of the (P=S) co-ordination. However, no comments have been noted on the C=S stretching frequency[70] thus making it difficult to compare the chelating properties of this ligand with those of the thiocarbamic acids, but the

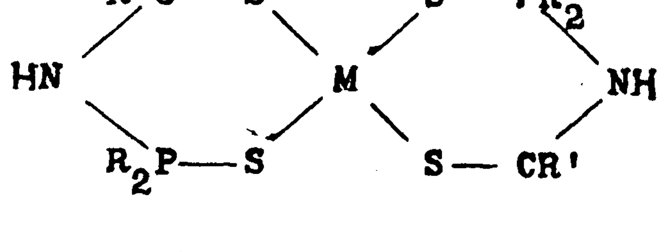


Figure 1.11

P=S data allow the comparison of these types of ligand with those formed by the O'O-dialkyl phosphorodithioic acids[71-75]. The dithioic acids form complexes of square planar stereochemistry with a number of metals. With the divalent metals such as Co(II), Ni(II), Cu(II) and Zn(II) the complexes are bis-chelate structure as shown in the Figure 1.12, below.

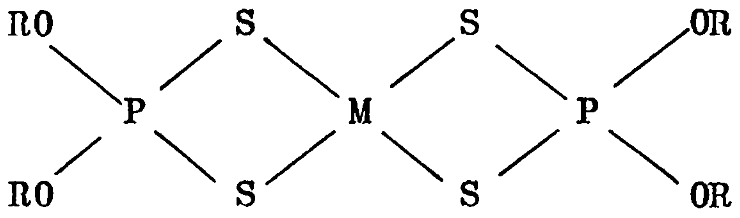
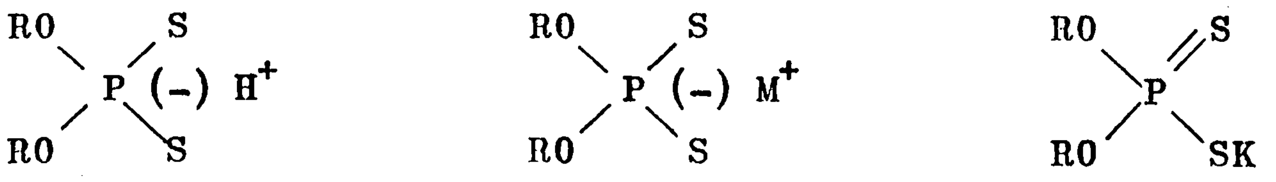


Figure 1.12

Although as indicated in the figure, the phosphoryl sulphur is involved in the co-ordination, there is no observable shift of the ν(P=S) absorption in the spectra of the complexes when compared to the ν(P=S) frequency found in the free ligand spectrum. Furthermore, with strongly electropositive metal like potassium or sodium, the salt formed showed a ν(P=S) absorption band 30 cm^{-1} higher than the observed in the free acid. It appears that the resonance structures of the dithioic acid group (Figure 1.13, below) remains unchanged in the complexes which is reflected by the unaltered ν(P=S) vibration bands.



acid 'covalent salt' potassium salt

Figure 1.13

In potassium salt the highly ionic nature of the metal breaks down the resonance structure which results a rise in the energy of the system, which is in turn reflected by the higher vibration freqency of the P=S band.

In the uncharged Sulphur ligands, the addition of a ligand atom obviously enhances the co-ordinating properties of the phosphoryl sulphide ligand. Uncharged bidentate ligands with two P=S groups behave differently from their oxygen analogs of the general formula $R_2P(O)CH_2P(O)PR_2$[61]. With Ni(II) and Co(II) ions tetrahedral paramagnetic complexes are generally obtained with the sulfur ligands. The ligand methylenebis-(diphenylphosphine) sulfide (sps) forms stable tetrahedral and pseudotetrahedral cobalt(II) and nickel(II) complexes. The presence of other ligands such as halide ions leads to the formation of complexes of the type $Ni(sps)X_2$ and $Co(sps)X_2$, which are essentially non-electrolytes in nitromethane and therefore formulated as the monomeric moieties $[M(sps)X_2]$. With weak ligands such as perchlorate ions, cobalt(II) and nickel(II) ion form complexes $[M(sps)]^{2+}(ClO_4)_2$.

The above survey strongly supports the feasibility of the project, the aims of which are as follows:

1. The study of the possibility of complex formation of ®Tinox with the appropriate metals and the identification of the chelation sites of the ®Tinox isomers if complexation occurs.
2. To investigate the conditions under which the breakdown products of ®Tinox in the formulation may complex with the chosen metals and together with the results obtained from the isomer study to evaluate the possibility of the development of a photometric method of analysis of the ®Tinox isomers directly.

To accomplish these aims, the metal salts of Ni(II), Co(II) and Fe(III) are selected for the complexation study; in addition, certain organic compounds are introduced into the experiment, some to facilitate the identification of the co-ordination sites of the ®Tinox isomers, others for the comparison of the co-ordinating properties of the breakdown products.

The ultimate aim of the ®Tinox isomers study will be the practical application of the metal to a ®Tinox formulation so as to stabilise the ®Tinox isomers via complex formation. However, the complex must be able to hydrolyse instantly to yield the free isomers when mixed with water before field application of the insecticide. For this reason and for ecological and economic reasons, heavy metals such as palladium and mercury are not included in the study although they are known to form stable complexes with the thioether group. Furthermore the phytotoxicity of these elements also rules out their possible use in field application. In fact, the phytotoxicity problem rules out the use of most metals with possible potential. The most suitable metal under this condition is obviously iron in its oxidation state of three (Fe^{3+}) because of its low phytotoxicity and non-toxic nature to mammals. However, due to the complexity of the spectra of Fe(III) compounds and the easy reduction of Fe(III) to Fe(II), interpretation of the results may be difficult, thus, other metals were used for the initial chelation study and Fe^{3+} was deferred to a later stage.

The metal ions chosen for the study are the cobalt(II) and nickel(II). The reasons for their choice are as follows.

Firstly, the co-ordinating properties of these two metals have been well studied and results obtained here may be compared with those reported in literature. Secondly, the electronic spectra of cobalt(II) and nickel(II) are well documented, which makes the interpretation of electronic spectra of the complexes prepared relatively easier and thirdly, there is no complication from oxidation or reduction of the metal ions on chelation as both nickel(II) and cobalt(II) ions are not subjected to oxidation and reduction under the experimental conditions in the present study.

As for the second aim of the project, the choice of metal is not governed by the phytotoxicity issue, but by the selectivity of the metal in complex formation with the different ligands (chemical compounds) in the formulation. This again makes the use of heavy metals non-feasible as metals like palladium and mercury would form complexes with all the components present in the formulation. In this case, nickel(II) and cobalt(II) are again chosen partly for reasons outlined above and also for their different affinities towards complex formation with thioether, thiophosphate, phosphate and thiols.

The ®Tinox isomers have more than one possible site of co-ordination, thus, to conduct a study on their chelating properties, it is necessary to pre-determine the chelating centre(s) in the molecules. To do this, a series of model compounds is to be prepared and their co-ordination properties looked into, so that the chelating centre(s) in the ®Tinox isomers may be identified. Together with the ®Tinox isomers the list of phosphoryl compounds prepared for the investigation is as follows:

methyl thiophosphate $(CH_3O)_3P{=}S$

ethyl thiophosphate $(C_2H_5O)_3P{=}S$

O,O-dimethyl (methylthioethyl) phosphorodithioate

$(CH_3O)_2P(S)SCH_2CH_2SCH_3$

®Tinox-thiolo isomer $(CH_3O)_2P(O)SCH_2CH_2SCH_3$

®Tinox-thiono isomer $(CH_3O)_2P(S)OCH_2CH_2SCH_3$

O,O-dimethyl(methylthioethyl) thiophosphonate

$(CH_3O)_2P(S)CH_2CH_2SCH_3$

Among the sulphur compounds found in the formulation of ®Tinox listed on page 4, two of the compounds have been studied. These are the dimethyl sulphide $(CH_3)_2S$ and 2,5-dithiahexane $CH_3SCH_2CH_2SCH_3$ [44]. The former only forms complexes with the typical class 'b' metal ions and no significant class 'a' metal complexes have been reported. The latter has been studied by M. Goodgame and co-worker[44] and no further experimental work is designed for this ligand.

The remaining sulphur ligands are the 3-thiabutanol $[CH_3SCH_2CH_2OH]$, 1-mercapto-3-thiabutane $[CH_3SCH_2CH_2SH]$ and di-(methylthioethyl) disulphide $[(CH_3SCH_2CH_2S)_2]$. Three other sulphur ligands were added in the study for the purpose of comparison. These are the 1-mercapto-2-methoxy-ethane $[CH_3OCH_2CH_2SH]$, 1-methoxy-3-thiabutane $[CH_3OCH_2CH_2SCH_3]$ and di-(2-methoxyethyl) disulphide $[(CH_3OCH_2CH_2S)_2]$.

Thus, apart from the technical interest, the two groups of compounds provide an opportunity to investigate the chelating behaviour of the sulphur and oxygen in three different forms, sulphur as thiol, thioether and thiophosphate and oxygen as hydroxyl, ether and phosphate. Also a convenient comparison between the co-ordinating properties of sulphur and oxygen in their analogous forms i.e. thiol with hydroxyl, thioether with ether and thiophosphate with phosphate may be made.

II

THEORY

Contents of Section II

2.(i) Crystal Field Splitting of 3d orbitals

In a free ion the d orbitals are degenerate. When the ion is placed into a molecular environment, this degeneracy will be lifted at least partially. The relative energies of the d orbitals and therefore the electronic spectrum, will depend upon the stereochemistry concerned.

The simplest method to determine these orbital energies is by the Crystal Field Theory (C.F.T.)[77-80].

In an octahedral system, the theory predicts the splitting of d orbitals into two sets t_{2g} and e_g. It can be shown in terms of the geometry of an octahedral system that the energy of the t_{2g} orbitals is 4Dq (Dq is an inseparate parameter determined empirically) less than that of the five degenerate d orbitals and the energy of the e_g orbital is 6Dq higher than the degenerate orbitals.

In an octahedral complex that contains one d electron that electron will reside in the d orbital of lowest energy. Thus the complex will be 4Dq more stable than the complex with five hypothetical d degenerate orbitals. Hence, placement of the d electron into the t_{2g} orbital, the complex is stabilised by 4Dq relative to the spherically perturbed situation. The 4Dq is called the crystal field stabilisation energy for the complex.

Extending the Crystal Field Theory to other type of stereochemistry the splitting of the d orbitals in these different geometries can be qualitatively evaluated. Figure 2.1 shows the crystal splittings of the d orbitals of a central ion in complexes having different geometries.

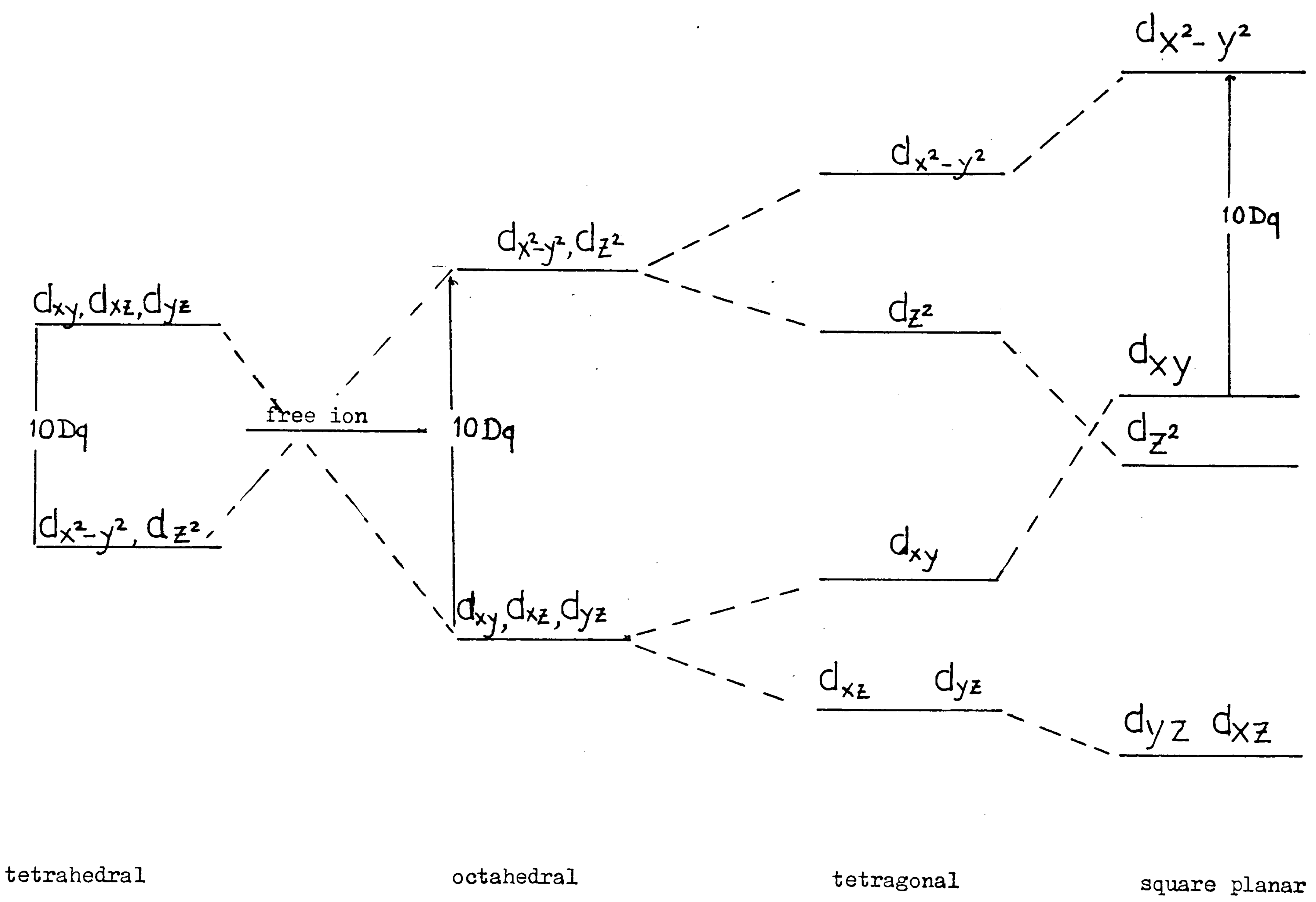


Figure 2.1. Crystal Field Splittings of the d orbitals of a central ion in complexes having different geometries.

2.(ii) Nickel(II) ion in an octahedral field

The nickel(II) $\underline{d}^8$ ion is characterized, within the approximation of Russel-Saunders[81] coupling, by a ^3F ground term followed at higher energy, by a ^3P term. The energy separating these terms is 15B where B is a parameter of interelectronic repulsion, introduced by Racah[82].

In an octahedral environment, the ^3F ion is split into $^3A_{2g}$, $^3T_{2g}$, and $^3T_{1g}(F)$ in order of increasing energy, whereas ^3P changes over into $^3T_{1g}$. Thus resulting three spin-allowed (parity-forbidden) transitions designated by:

$$^3T_{2g} \longleftarrow {}^3A_{2g} \qquad \nu_1$$
$$^3T_{1g}(F) \longleftarrow {}^3A_{2g} \qquad \nu_2$$
$$^3T_{1g}(P) \longleftarrow {}^3A_{2g} \qquad \nu_3$$

The energies of these transitions can be predicted from the C.F.T. The energy of the $^3A_{2g}$ term which derived from the $(t_{2g}^{\ 6}, e_g^{\ 2})$ configuration (according to the weak field appreach) is simply

$$6.(-4) + 2.(6) = -12\ Dq$$

The energy of $^3T_{2g}$ which also occurs once is derived from the configuration of $(t_{2g}^{\ 5}, e_g^{\ 3})$ is

$$5.(-4) + 3.(6) = -2\ Dq$$

The energy of the $^3T_{1g}$ term is derived by noting that in the limit of the weak field, the centre of gravity (barricentre) of the various terms obtained from a common spherically perturbed atomic term lies at zero relative to that term. In evaluating this the orbital degeneracy of each term must be taken into account, hence if 'x' is the energy of the term $^3T_{1g}$ then

$$3x + 3.(-2) + (-12) = 0$$
$$x = 6\ Dq$$

Thus, the energies for the three transitions are as follows

$$\nu_1 \quad E = 10\ Dq$$
$$\nu_2 \quad = 18Dq$$
$$\nu_3 \quad = 12Dq + 15B$$

On the energy correlation diagram these transitions are illustrated on the extreme left as shown in figure 2.2. (p.39). As the field becomes stronger, terms of the same symmetry (and spin) can mix together (configurational interaction). The $^3T_{1g}(F)$ term mixes with the $^3T_{1g}(P)$ term so that their energies are functions of both Dq and B. Thus, if the weak-field coupling scheme is applied, the energies of these states follow from:

$$E_g\ (^3A_{2g}) = -12Dq \qquad (1)$$
$$E_g\ (^3T_{2g}) = -2Dq \qquad (2)$$

$$\begin{array}{c|cc|} & ^3T_{1g}(F) & ^3T_{1g}(P) \\ ^3T_{1g}(F) & 6Dq - E & 4Dq \\ ^3T_{1g}(P) & 4Dq & 15B - E \end{array} = 0 \qquad (3)$$

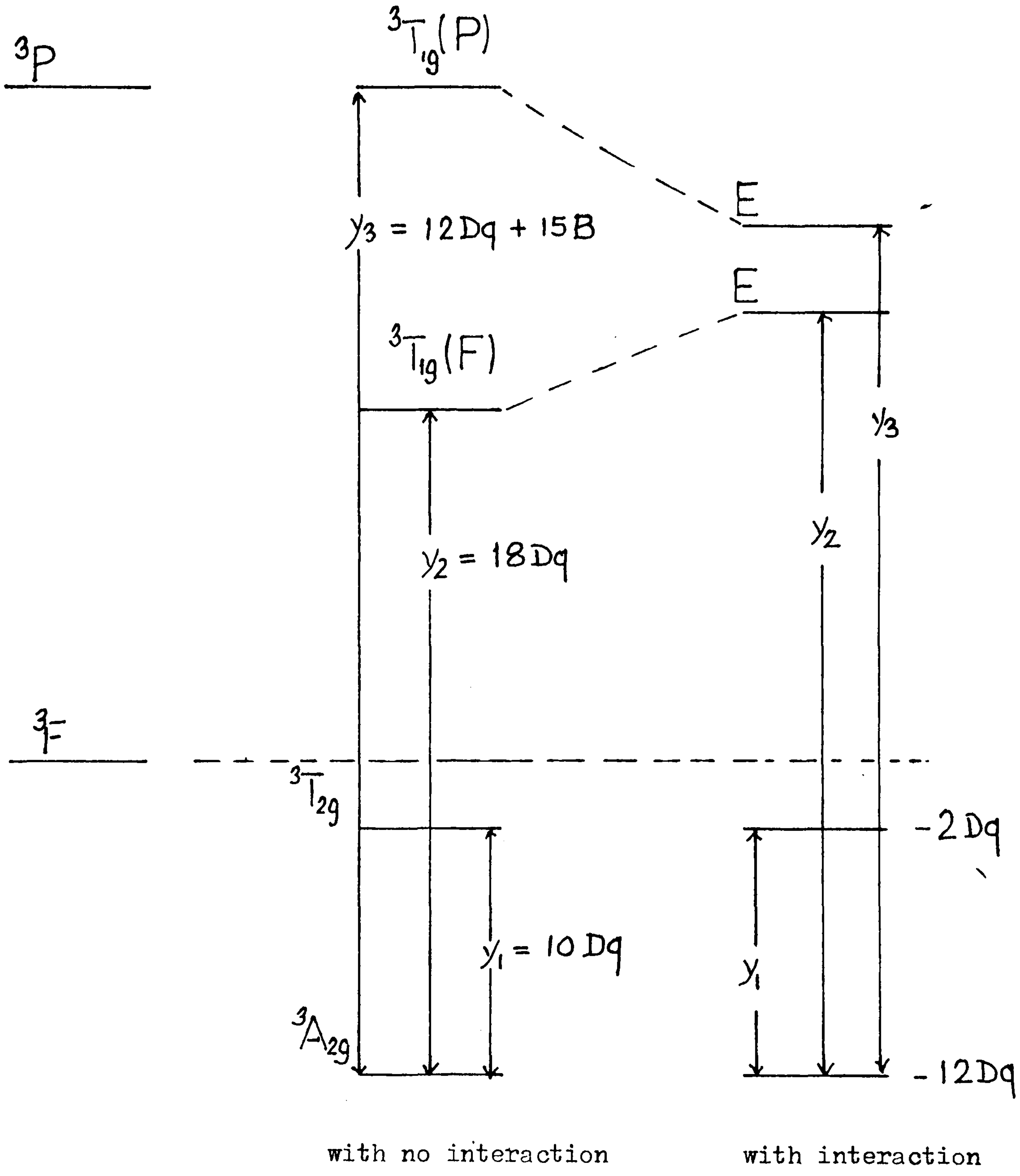


Figure 2.2. Energy correlation diagram of Ni(II) ion in an octahedral field

where equation (3) is equivalent to

$$E(^3T_{1g}) = 75B + 3Dq \pm \tfrac{1}{2}(225B^2 + 100Dq^2 - 180DqB)^{\frac{1}{2}} \quad (4)$$

The energy of each transition is represented as

$$\begin{aligned} \nu_1 &= 10Dq \\ \nu_2 &= \tfrac{1}{2}(15B + 30Dq) - \tfrac{1}{2}\left[(15B - 10Dq)^2 + 12B.10Dq\right]^{\frac{1}{2}} \\ \nu_3 &= \tfrac{1}{2}(15B + 30Dq) + \tfrac{1}{2}\left[(15B - 10Dq)^2 + 12B.10Dq\right]^{\frac{1}{2}} \end{aligned} \quad (5)$$

2.(iii) Nickel(II) ion in a tetragonal distorted environment

The splitting of the energy level in a tetragonal field is best considered by the withdrawing of the charges along the z axis. As the distance of the charges on the z axis increases the repulsion felt by the d_{z^2} and d_{xz} d_{yz} orbitals will lessen and lead to a decrease of their energies, with the former decreases more rapidly than the latter. The moving away of the charges on the z axis allows the charges on the xy plane to approach the central ion more closely thus d_{xy} and $d_{x^2-y^2}$ orbitals experience a greater repulsion from the ligands than they do in an octahedral structure and resulting an increase in their energy. Additional radial parameters Ds and Dt are required to describe the splitting terms.

The splitting of the ^3F ion (d^8) term in a tetragonal field as illustrated in the Figure 2.3. This diagram may be used as a basis for predicting the spin-allowed transitions expected. Although all the three energy levels in the O_h symmetry are expected to be split under the D_{4h} system, usually only the splitting of the lowest band is observed. This is explained by the fact that the two energy levels $^3T_{1g}(F)$ and $^3T_{1g}(P)$ split in a reverse sense[83], thus when configurational interaction occurs, the splittings tend to cancel out (it must be noted that Rowley and Drago[84,85] reported separation of the other energy states on their spectral analysis at liquid nitrogen temperature). They have only to be reduced to about 500 cm^{-1}, or less and they would not be resolved in the spectrum.

The two near infrared transitions observed in the spectra of the nickel(II) ion in tetragonal environment are assigned to the transition arising from the splitting of the $^3T_{2g}$ in octahedral symmetry on going to D_{4h} symmetry, to ^3E_g and $^3B_{2g}$, and have energies of $10Dq^E$ and $10Dq^E - 35Dt/4$ respectively[83]. Which transition is which may be adduced on the basis of the sign of Dt[83].

The sign of Dt follows theoretically from a consideration of relative field structure of the different ligands. In the D_{4h} system it is shown to be

$$Dq^E = 1/6\ \alpha_4^E$$
$$Dq^A = 1/6\ \alpha_4^A$$

where Dq^E and Dq^A are the in-plane and out-of-plane strengths respectively and α_4^E and α_4^E are the equatorial and axial fourth power radial integrals respectively. It is shown that

$$Dt(D_{4h}) = 4/7(Dq^E - Dq^A)$$

The determination of Dt can lead to the derivation of the in-plane and out-of-plane field strengths in tetragonal molecules. If the in-plane field strength is greater than the out-of-plane field strength then the Dt will be positive and ^3E_g level will lie lower than $^3B_{2g}$. In the absence of steric hindrance, the sign of Dt may generally be ascertained by consideration of the relative positions of the in-and out-of-plane ligands in the spectrochemical series. In the system where the in-plane ligand is stronger than the axial plane, the transitions are depicted in Figure 2.3, p.43 as ν_1 and ν_2 assignable to $^3E_{1g} \leftarrow {}^3B_{1g}$ and $^3B_{2g} \leftarrow {}^3B_{1g}$, respectively[83].

The energies in the d^8 system (neglecting configurational interaction) of the tetragonal field relative to the octahedral terms are zero are:

$^3A_{2g}$		–	$^3B_{1g}$ = +7Dt	
$^3T_{2g}$	$^3B_{2g}$	+	7Dt	separation (–35/4)Dt
	^3E_g	–	(7/4)Dt	
$^3T_{1g}$ F	$^3A_{2g}$	–	4Ds + 2Dt	separation 6Ds – (5/4)Dt
	$^3E_{2g}$	+	Ds + (3/4)Dt	
$^3T_{1g}$ P	$^3A_{2g}$	+	2Ds – 8Dt	separation –3Ds + 5Dt
	^3E_g	–	Ds – 3Dt	

When configurational interaction between the two T_{1g} levels is taken into account the splitting in these is 4.9Ds – 0.5Dt and –1.9Ds + 4.35Dt for the F and P terms, respectively.

The above treatment applies to <u>trans</u> complexes of the type ML_4X_2 (Figure 2.4, p.43). In the <u>cis</u> complexes of ML_4X_2 the splitting of the octahedral terms is half of that of the <u>trans</u> complex and the level order will be inverted. Thus the T_{2g} term in the <u>cis</u> complex seldom splits whereas the

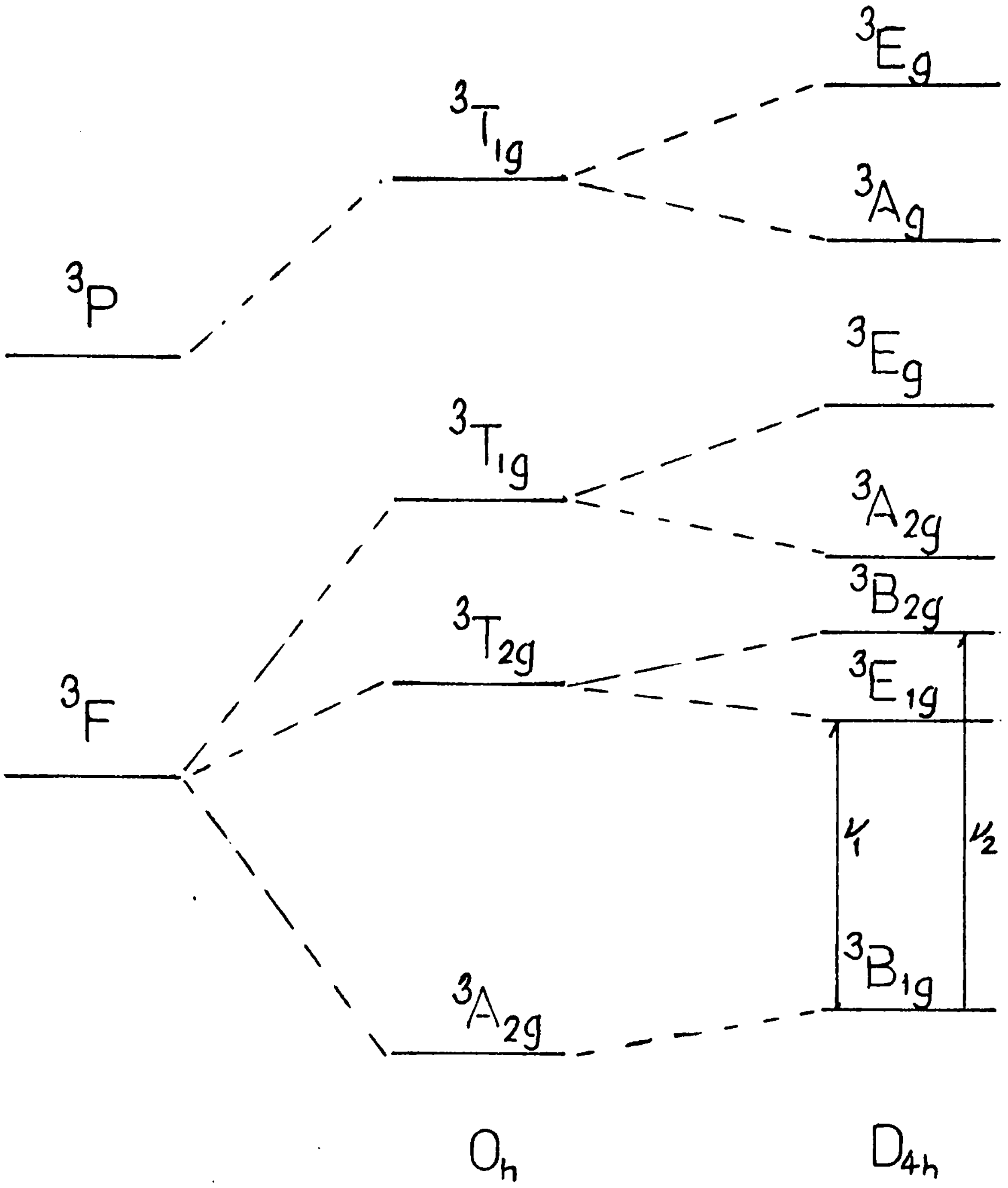
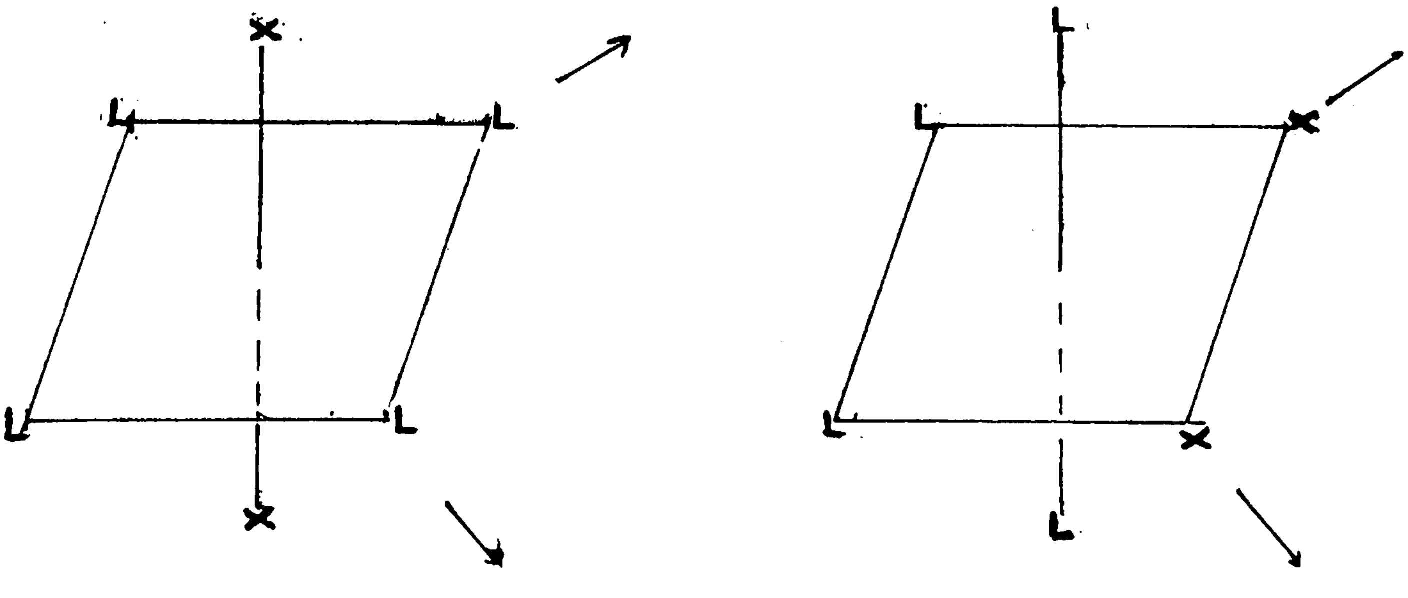


Figure 2.3. Splitting of the free ion terms for Ni(II) in octahedral (O_h) and tetragonal (D_{4h}) environments



<u>trans</u> ML_4X_2 <u>cis</u> ML_4X_2

Figure 2.4

splitting of the T_{1g} term is often observed.

In the high spin nickel(II) complexes a splitting of the ν_1 absorption band can usually be regarded as indicative of a trans configuration, although the absence of ν_1 splitting, does not necessarily indicate a cis configuration.

2.(iv) Nickel(II) ion in a square planar stereochemistry

Square planar systems may be regarded as the extreme case of tetragonal distortion with very weak or no charge along the z axis, resulting the lowering of the z orbital as illustrated in the energy correlation diagram in Figure 2.1,p. 36[86].

In the case of nickel(II) diamagnetic square planar complexes, the energy level diagram is shown in Figure 2.5, below.

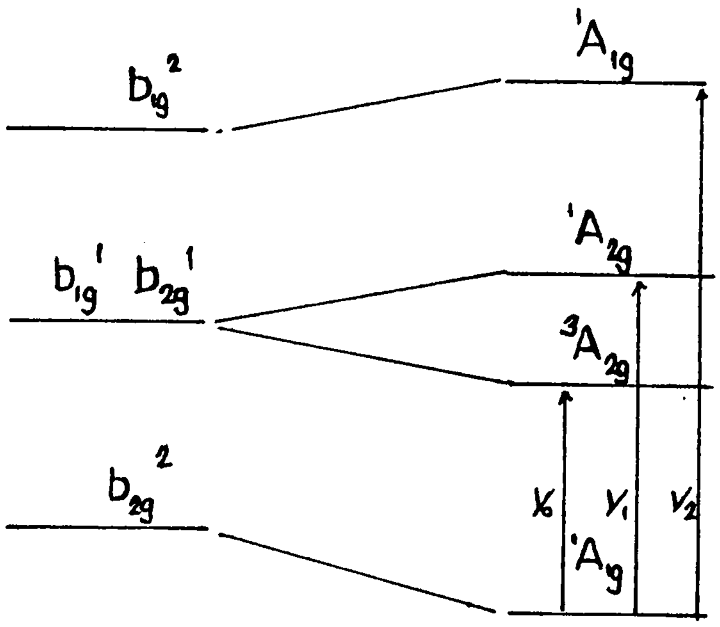


Figure 2.5

As ν_0 is a singlet-triplet transition, which is spin-forbidden, this is normally not observed in the electronic spectra, Thus the diagram predicts that the diamagnetic square planar Ni(II) complexes to show one (ν_2) crystal field band ($\varepsilon > 10^2$). This is what generally observed except in the case of the complexes with sulphur ligands which generally exhibit an additional well defined band to lower energies than ν_2, this is referred to as ν_1 .

The lowest energy band (if the assumption in the assignment of the transition is correct) ${}^1A_{2g} \leftarrow {}^1A_{1g}$, arises as a consequence of a transition from the d_{xy} orbital to the $d_{x^2-y^2}$ orbital, whose one electron separation is $10Dq^E$, can be used for crystal field strength comparison.

2.(v) Nickel(II) ion in a tetrahedral environment

The C.F.T. predicts that in tetrahedral environment the d orbitals are split in the reverse sense to the octahedral environment with t_2 at higher energy than the e orbitals as shown in Figure 2.1. If the energy separation is designated by 10Dq' then

$$E_{(e)} = E\,(d_{x-y}, d_{z^2}) = -6Dq'$$

$$E_{(t)} = E\,(d_{xz}, d_{xy}, dyz) = +4Dq'$$

For nickel(II) ion in tetrahedral environment, the C.F.T. stabilisation energy is 8Dq', which is relatively low.

The ${}^3F$ ion in tetrahedral field is split inverse of the octahedral field, with ${}^3T_1$ as the ground state. The expected transitions in increasing energy are

$${}^3T_2\,(F) \leftarrow {}^3T_1(F) = \nu_1$$

$$^{3}A_{2}\,(F) \longleftarrow {}^{3}T_{1}(F) = \nu_2$$
$$^{3}T_{1}\,(P) \longleftarrow {}^{3}T_{1}(F) = \nu_3 \qquad (6)$$

the energies of the three transitions taking configuration interaction into consideration are given as

$$\nu_1 = \tfrac{1}{2}(10Dq - 15B) + \tfrac{1}{2}\left[(10Dq + 15B)^2 - 12B.10Dq\right]^{\frac{1}{2}}$$
$$\nu_3 = \left[(10Dq + 15B)^2 - 12B.10Dq\right]^{\frac{1}{2}} \qquad (7)$$
$$\nu_2 = \tfrac{1}{2}(30Dq - 15B) + \tfrac{1}{2}\left[(10Dq + 15B)^2 - 12B.10Dq\right]^{\frac{1}{2}}$$

The ν_2 transition may occur at higher energy than the ν_3, if the crystal field strength is sufficiently large ($12Dq' > 15B$). This rarely occurs with tetrahedral nickel as Dq' is normally very low.

2.(vi) Cobalt(II) ion in tetrahedral field

In a tetrahedral system, the free ion term ^4F and ^4P of the cobalt(II) ion split into $^4T_1$, $^4T_2$, and $^4A_2$ and $^4T_1$(P) states, respectively. Due to the inversion of terms between octahedral and tetrahedral systems and the relationship between d^n and d^{5+n} ligand field system, if one ignores multiplicity, the energy expressions of d^8 octahedral system (p.38) and d^7 tetrahedral system become identical. Therefore, equation 5 (p.40) is valid for the energy calculation for the electronic transitions of d^7, high spin tetrahedral system. The energy diagram of this system is shown in Figure 2.6,p.48.

2.(vii) Cobalt(II) ion in square planar field

The electronic spectra of the cobalt(II) low spin square planar complexes have only being elucidated by several detailed analyses recently using esr technique[87-89]. Although there is still doubts on the exact energy levels of the orbitals, it is generally assumed that the ground state of cobalt(II) is $\left[(xz)^2(yz)^2(yx)^2(z^2)^1\right]$ (with the assumption that the $d_{x^2-y^2}$ orbital which is directed at the ligand donor atoms is energetically unfavourable for electron occupation). The energy levels of the four occupied orbitals depend both on the symmetry of the complex and the nature of the donor atoms of the ligands. Generally the d_{z^2} is highest in energy and remains unpaired in the ground state as shown in Figure 2.7. The observed absorptions may be interpreted in terms of the transitions between electronic states shown in Figure 2.8, p. 49.

$$\nu_1 = {}^2E_g \leftarrow {}^2A_g$$

$$\nu_2 = {}^2B_g \leftarrow {}^2A_g$$

$$\nu_3 = {}^2E'_g \leftarrow {}^2A_g$$

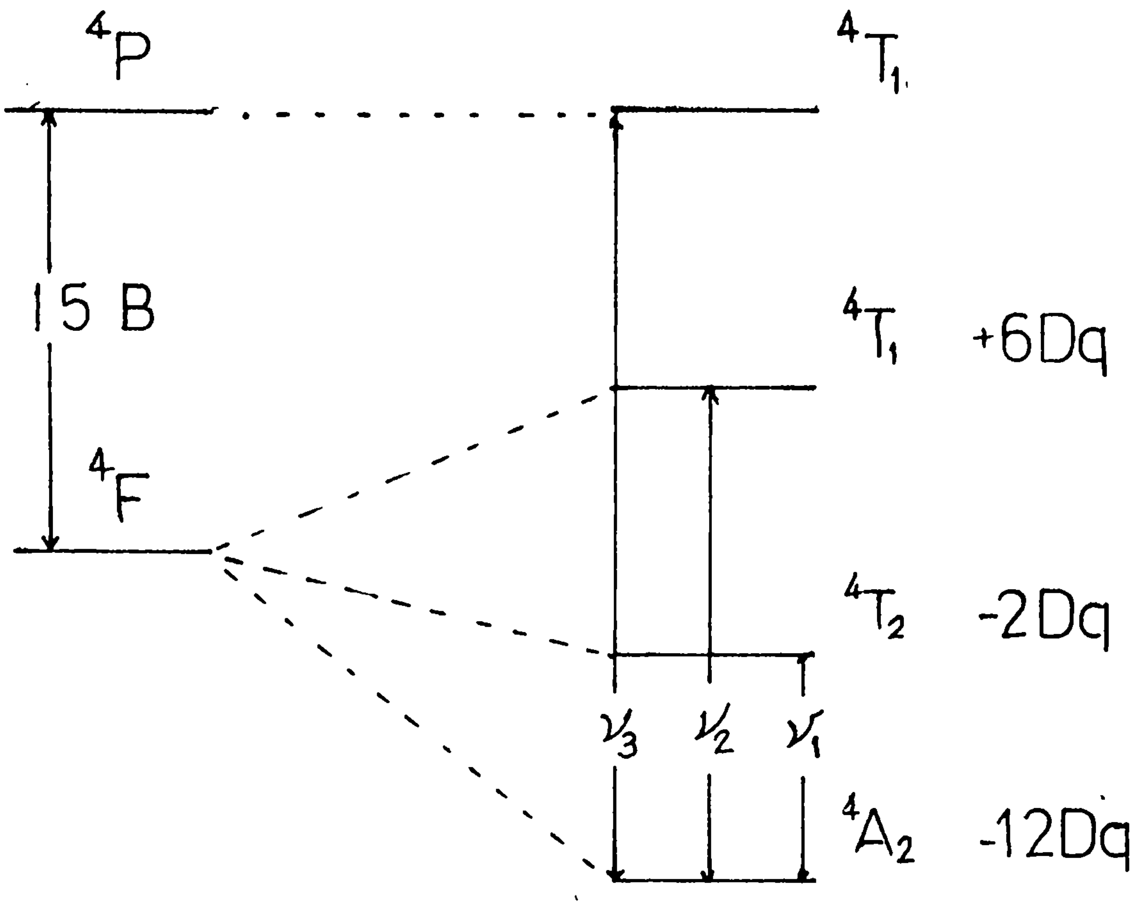


Figure 2. 6 Correlation diagram for Co(II) ion in tetrahedral field

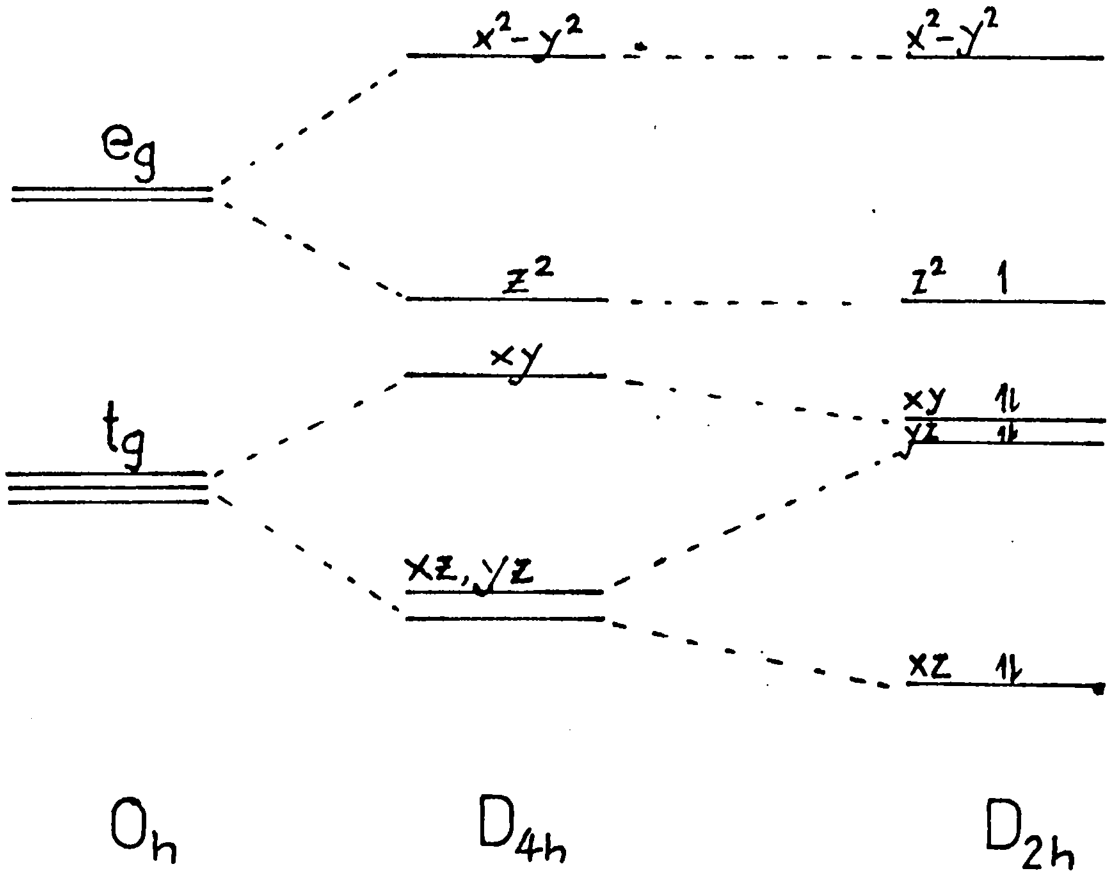


Figure 2.7 Ground state configuration of Co(II) low spin complexe

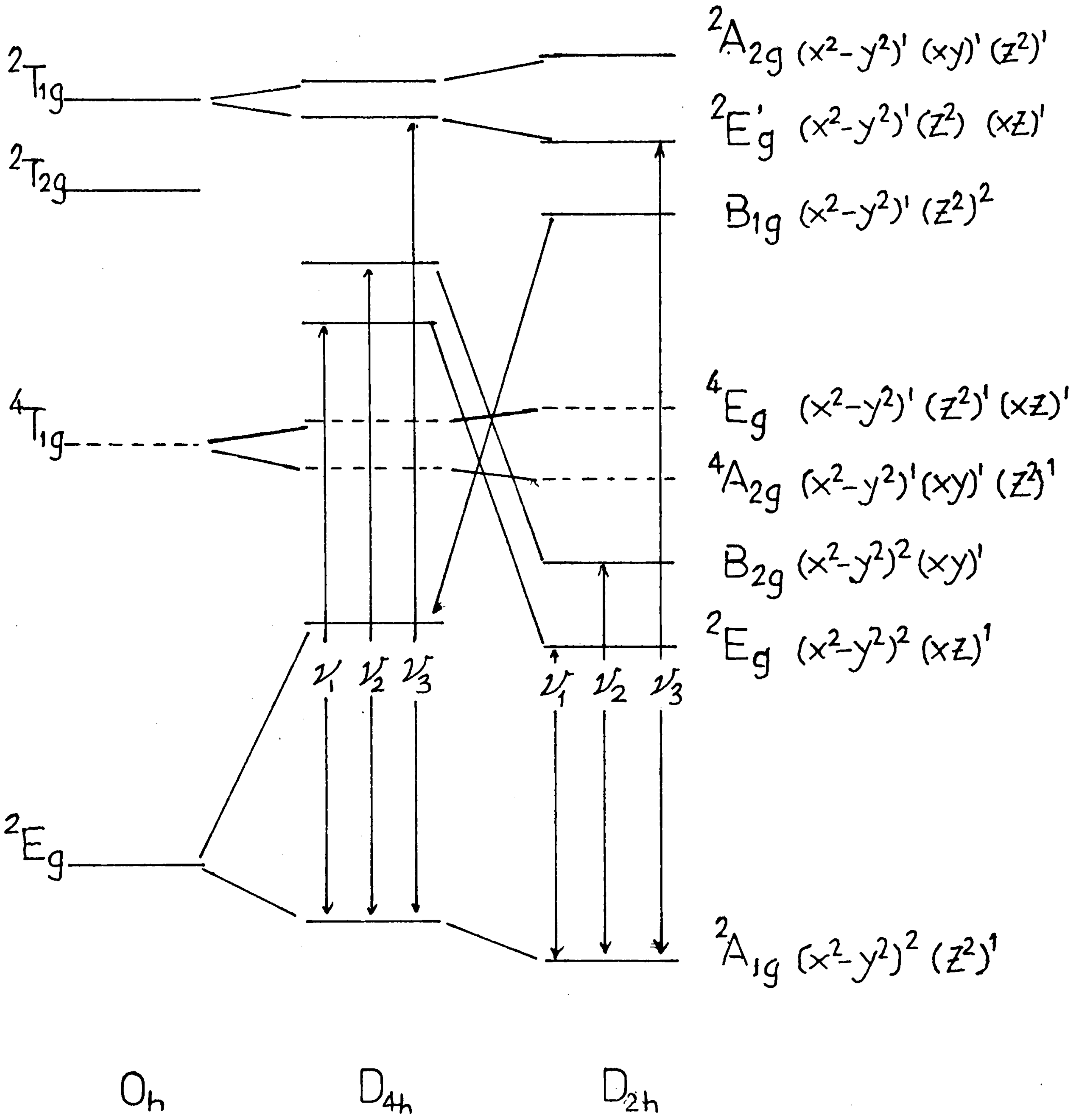


Figure 2.8 Energy levels of low spin Co(II) complex

Figure 2.9 electronic spectra of Ni(II) ion in various stereochemistries

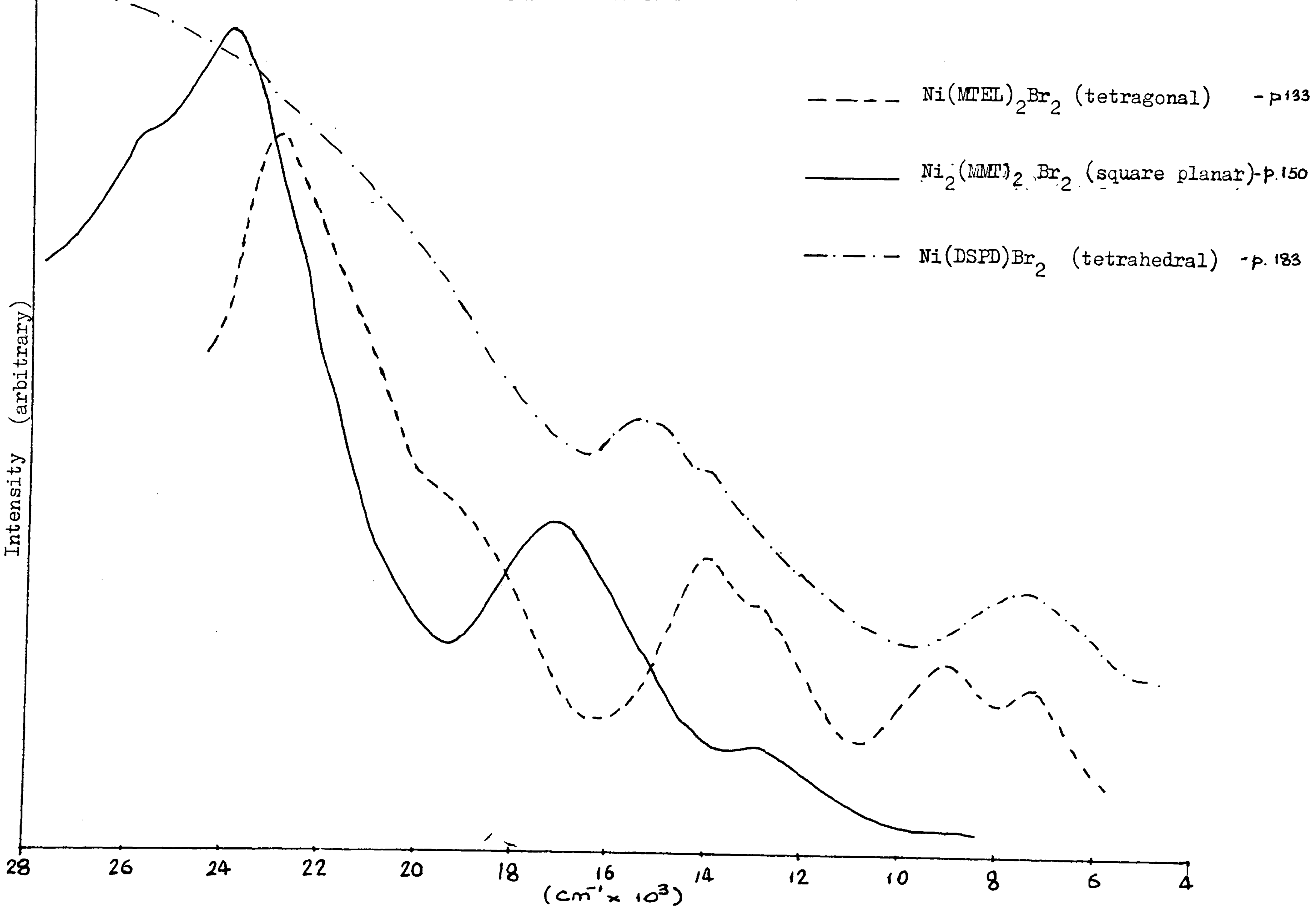
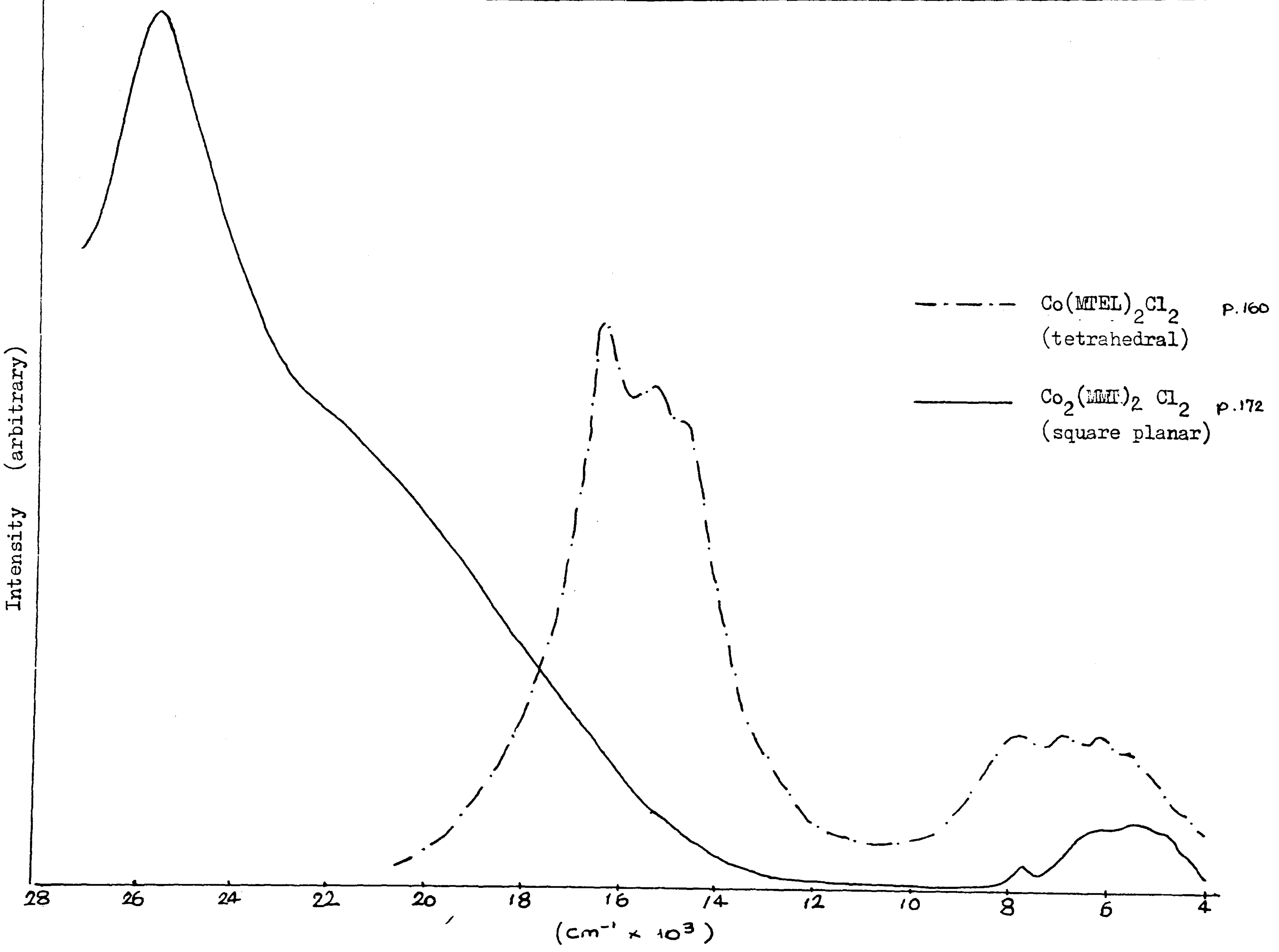


Figure 2.10 electronic spectra showing Co(II) ion in various stereochemistries



2.(viii) The Racah Parameter B and the Nephelauxetic Series.

It is generally observed that the interelectronic parameter B (and to a lesser extent C) obtained for the metal ion in a complex is lower than the free ion value. The observation is explained as the nephelauxetic effect[90]. In the free 3d metal ion, the interelectronic repulsion integrals are approximately proportional to the average reciprocal radius $\left[r^{-1}\right]_{3d}$ of the partly filled 3d shell[90]. The decrease in B is therefore attributed to an expanded radial distribution of d electrons in the complex i.e.

$$\left[r^{-1}\right]_{3d}^{\text{complex}} < \left[r^{-1}\right]_{3d}^{\text{free electron}}$$

Two different origins of the nephelauxetic effects have been advanced (i) the central-field covalency is due to screening the nuclear charge of the central ion by electrons of the ligands; (ii) the symmetry restricted covalency is caused by delocalization of metal d electrons onto the ligand (the delocalization is symmetry dependent on e_g electrons for σ, t_{2g} for π-bonding). However, no quantum mechanical theory has yet been developed which would provide a quantitative basis for the nephelauxetic effect.

If indeed the assumptions are correct then the lowering of the B value in the metal ion on complexation would reflect on the covalency of the co-ordination bond, One may reasonably argue that the greater the reduction in B, as represented by the ratio:

$$\frac{\text{B in complex}}{\text{B in free ion}} = \frac{B}{B_0} = \beta_{35}$$

the greater the covalency in the metal ligand bond, and the smaller the effective charge experienced by the d electrons.

The numerical value of the interelectronic repulsion parameter may be determined from the spectrum of an actual transition metal compound, using the energy transition equation expressions appropriate to the calculation.

In the octahedral and tetrahedral system, all the electronic parameters may be evaluated employing the equation from the crystal field approximation, To solve for the Racah parameter in a tetragonal nickel complex, it is necessary to know the Dt and Ds values (the additional parameters for the splitting of the electronic states). Ds is related to the splitting of the $^3T_{1g}(F)$ band which is normally not observed in weakly tetragonally distorted system, such as those studied in the present work. Thus all the calculation on the tetragonal system are treated as the octahedral system.

This approximation is always borne in mind in the interpretation of the results obtained which are only used as supplementary data and no direct conclusion is drawn from these data.

The validity on the conclusion drawn, however does not rely heavily on the exact value of the results. This is because the conclusions are normally arrived by comparison with chelation systems which are analogous to the one studied e.g. the tetragonal complexes obtained by the ligand 3-thiabutanol with nickel (II) halides are only compared with complexes which are known to have the same structure with the same type of halide ion as in the case of Ni(MTEL)$_2$Cl$_2$[†] with Ni(2,5-dithiahexane)$_2$Cl$_2$ where the co-ordination of the halide ions is the same.

2.(vx) Magnetic Behaviour.

Diamagnetism and paramagnetism are properties of individual atoms or molecules. These properties are quite different to the ferromagnetism which is of force much greater (perhaps 10^6 times) than paramagnetism. The present discussion will be limited to diamagnetic and paramagnetic behaviour of transitional complexes.

The presence of the incomplete _d_ shell in the transitional metals means that in accordance to Hund's rule, there will be unpaired electrons e.g. with nickel(II), there will be three paired and two unpaired electrons. Materials that contain unpaired electrons are attracted to a magnet and are said to be paramagnetic. In instances where Hund's rule is not obeyed and the unpaired electrons in the free ion become paired in the complex, a low spin complex is obtained as opposed to the high spin or paramagnetic complexes.

The magnetic properties of transition metal complexes may be explained by C.F.T.. To cause electrons to pair, sufficient energy is required to overcome the repulsion interaction of two electrons occupying the same orbital. In the presence of crystal field splitting, the d electrons will tend to occupy the lowest energy orbitals, so as to avoid as much as possible interaction with the ligands. If the energy thus gained is large enough to overcome the loss in stability due to electron pairing the electrons couple and

[†] MTEL = 3-Thiabutanol

the result is a low spin complex. Thus, complexes with large crystal field splitting energy will generally be low spin.

2.(x) Far Infrared

Far infrared spectroscopy (450 - 80 cm^{-1}) becomes increasingly important as a technique for studying metal-ligand bonding in inorganic and co-ordination compounds. Improvement in instrumentation and simple cells have made direct observation of stretching vibrations down to the low frequency region of 50cm^{-1} possible. In the present study, the region of most interest is between 500 to 100 cm^{-1} because absorption bands associated with metal-ligand bonding stretching vibrations are generally in this range.

The stretching frequency of a particular metal-ligand mode is dependent on the stereochemistry of the complex.[91] Due to the fact that a variety of stereochemistries is feasible, the stretching frequency observed can varies considerable from one compound to another e.g. ν(Ni-Cl) is 190 - 230 cm^{-1}, 260 - 330 cm^{-1} and 340 - 400 cm^{-1} for octahedral, tetrahedral and square planar stereochemistries, respectively.

The procedure used for analysing far-infrared spectra in the presence study is by comparison of ligand and complex spectra. The interaction of vibration modes makes it unrealistic to regard any band in the spectrum as derived from a particular type of vibration such as metal-sulphur or metal-oxygen. Thus, in the statement of ν(M-Cl), it should be infered to the band arises mainly, but not necessarily totally from such a normal co-ordinate.

To analyse the bands observed in the spectra of the complexes a number of vibration modes reported in the literature concerning metal-halogen[92-8], metal-sulphur[99-104] and metal-oxygen[91,105] have been collected and most of the conclusions drawn for the results of the complexes studied are derived by comparison with these reported data.

Much more is known about metal-halogen frequencies than other metal-ligand vibrations, because of the high intensity of these bands and they may also be identified as such by the wavelength shift that occurs when one halogen is substituted for another in complexes of similar structure. Moreover these shifts have been found with ratio M-Cl/M-Br ~ 0.77[97] and M-Cl/M-I ~ 0.65 in most compounds. This general trend is also observed in the present study.

III

EXPERIMENTAL AND RESULTS

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FIGURE (IR) PAGE NO.

FIGURE (FIR)

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PAGE NO.

3.A THE REAGENTS

3.B THE COMPLEXES

3.C PHYSICAL MEASUREMENTS

3.A Preparation of Compounds

The ligands employed in the present study were prepared in this laboratory using published procedures for known compounds and modified methods for the new compounds. Carefully purified specimens of commercially available materials were also used in some cases.

Literature survey indicated that most of the required compounds which could not be obtained commercially, have been synthesised before and various preparative methods were noted. Most of these were tried in the laboratory in a small scale; the method used for the preparation of the compounds in larger quantities were selected on the basis of (1.) simplicity of the reaction scheme, thus reducing impurities formed by side reaction; (2.) purity of the final product, even on the expense of the yield; (3.) ease of extraction and purification of the final product.

All the products have been characterised by spectroscopic means e.g. infrared spectra, nuclear magnetic resonance and mass spectra. The purity of the compounds was ascertained by GLC.

The identity of a known compound was confirmed by comparing its physical constants with values given in the literature and also, whenever possible, by comparing infrared spectra.

3.A1 3-Thiabutanol [$CH_3SCH_2CH_2OH$]

Methyl sulphate (94.5 ml) was added to a stirred solution of 2-mercapto-ethanol (78g; 1 mol) in aqueous sodium hydroxide (300 ml 2M solution). During the addition the temperature of the reaction mixture was not allowed to rise above 30^o. Addition was complete in two hours. After standing overnight, the reaction mixture was extracted with chloroform (2 x 50 ml.) and the extract was washed with water, dried over magnesium sulphate and the solvent was removed. The residue was distilled and the fraction boiling at 66-70°/20mm. was collected. On re-distillation, this fraction gave 3-thiabutanol (51g; 55% yield), b.p. 69-71°/20mm. (E. Booth, V. Burnop and Jones[106], b.p. 68-70°/20mm.) (IR 1).

3.A2 1-Chloro-3-thiabutane $[CH_3SCH_2CH_2Cl]$

A solution of 3-thiabutanol (46.5g; 0.5 mole) in dried chloroform (150g.) was placed in a 500 ml. Claisen flask fitted with a thermometer set for distillation and dropping funnel. A calcium chloride guard tube was attached to the side arm of the flask. A solution of thionyl chloride (83.3g; 0.7 mole) in dried chloroform (200g.) was then introduced dropwise with stirring. Addition was complete in an hour. Hydrogen chloride and sulfur dioxide were liberated. The reaction vigour was moderated by cooling (ice bath) as necessary. After the addition, the reaction mixture separated into two layers and it was allowed to stand at room temperature for a further one and a half hours. The solvent was then distilled off and the residue fractionated at reduced pressure. The product 1-chloro-3-thiabutane (51.2g; 61.5% yield) boiled over at 55-56°/30mm. (W.R. Kirner[107] b.p. 55-56°/30mm.). The purity of the product was checked with GLC and no redistillation was required.

3.A3 1-Mercapto-3-thiabutane $[CH_3SCH_2CH_2SH]$

Thiourea (38g; 0.5 mole) was added in four portions to a solution of 1-chloro-3-thiabutane (55g; 0.5 mole) in ethyl alcohol (100 ml.); the resulting mixture was stirred at reflux for three hours. The reaction mixture was cooled to room temperature. The air in the reaction vessel was subsequently replaced by nitrogen and aqueous sodium hydroxide (2M solution; 150 ml.) was added and the reaction mixture was refluxed for two hours. On cooling, the thiol formed a separate layer and was removed. The aqueous layer was extracted with ether (4 x 50 ml.) and the combined ethereal extracts and the thiol layer were together washed successively with dilute hydrochloric acid and with water. The organic layer was then dried over magnesium sulphate and the solvent was distilled off. The residue was distilled and the fraction boiling in the range 77-82°/32mm. was collected and was refractionated yielding 35g. (54% yield) of 1-mercapto-3-thiabutane b.p. 78-80°/32mm. (Miroslav[108] b.p. 79-80°/30-35mm.). The purity of the product was checked with GLC.(IR 2).

3.A4 1-Mercapto-2-methoxy-ethane $[CH_3OCH_2CH_2SH]$

This was prepared by the alkaline decomposition of the appropriate isothiouronium salt using the method as described for 1-mercapto-3-thiabutane. The following quantities of reactants were used: 1-chloro-2-methoxy-ethane (47g; 0.5 mole), thiourea (38g; 0.5 mole), and sodium hydroxide (2M solution; 150 ml.).

The product was distilled and the fraction boiling in the range 78-92°/40mm. was collected and was fractionated yielding 15g. (14.5% yield), b.p. 80-82°/40mm. of the product which was identified as the right compound by mass spectroscopy and proton magnetic resonance spectroscopy. Analysis gave C 38.7%, H 9%; C_3H_8OS requires C 39%, H 8.7% (IR 3, PMR 1).

3.A5 1-Methoxy-3-thiabutane $\left[CH_3OCH_2CH_2SCH_3\right]$

Sodium metal (5g.) was dissolved in methyl alcohol (100 ml.). To this solution, a solution of 1-chloro-3-thiabutane (23.0g; 0.25 mole) in methyl alcohol (50 ml.) was added dropwise. The reaction mixture was refluxed for four hours and it was then cooled and poured into water (300 ml.) in a conical flask. The resulting organic layer was separated and aqueous layer was extracted with ether (3 x 50 ml.). The combined ethereal extracts and the oil were together washed successively with dilute sulphuric acid and with water. After drying over anhydrous magnesium sulphate, the solvent was distilled off and the residue was fractionated. The fraction which boiled over the range 76-80°/30mm. was collected and re-distilled. The product 8g. (35% yield) boiled at 78°/30mm. was identified as the right compound by its mass spectrum and p.m.r. spectrum. Analysis gave C 47.2%, H 9.9%; $C_4H_{10}OS$ requires C 48.0%, H 10.0% (IR 4, PMR 2).

3.A6 Di-(2-methylthioethyl) disulphide $\left[(CH_3SCH_2CH_2S)_2\right]$

To a stirred and cooled solution of 1-mercapto-3-thiabutane (27g; 0.25 mole) in water (60 ml.), 3% H_2O_2 was added dropwise. The reaction was tested for completion at intervals and it was shown to be complete when one drop of the reaction mixture acidified with hydrochloric acid did not decolourise aqueous potassium tri-iodide. The reaction mixture was then treated with dilute hydrochloric acid till it was acid to methyl orange and the solvent was subsequently removed completely leaving the crude dihydrochloric crystal of the disulphide which was recrystallised from alcohol. The purified material was dissolved in water and this solution was neutralized with sodium bicarbonate and the disulfide separated as an oil. The aqueous layer was extracted with ether (2 x 50 ml.). The ethereal solution was combined with the disulphide and was dried over magnesium sulphate. The solvent was removed and the residue which was an oil boiled at 125°/30mm. (K. Christopher[109] b.p. 124-125/30mm.) (IR 5).

3.A7 Di-(2-methoxyethyl) disulphide $\left[(CH_3OCH_2CH_2S)_2\right]$

This was prepared by the oxidation of the compound 1-mercapto-2-methoxyethane by H_2O_2 as described in the preparation of di-(2-methylthioethyl) disulphide. The following quantities of reactants were used: 1-mercapto-2-methoxyethane (23g; 0.25 mole), H_2O_2 (50 ml. of 3% solution).

The product was identified by mass spectroscopy and proton magnetic resonance spectroscopy. The compound boiled at 112°/25mm. and analysis gave C 39.7%, H 7.7%; $C_6H_{14}O_2S_2$ requires C 39.5%, H 7.69% (IR 6, PMR 3).

3.A8 0,0-Dimethyl phosphorodithioic acid $\left[(CH_3O)_2PS_2H\right]$

Methyl alcohol (64g; 2 mole) was stirred vigorously at room temperature and phosphorus pentasulfide (111g; 0.5 mole) was added as rapidly as the concomitant foaming and exothermic reaction permitted. After addition was complete, the reaction mixture was heated on the steam bath for ninety minutes. It was cooled and treated with charcoal (25g.) and filter aid (25g.)

and filtered. The crude product (150g; 94% yield) was purified by the following method.

Crude 0,0-dimethyl phosphorodithioic acid (150g; 0.85 mole) was added dropwise to a solution of sodium carbonate (63g; 0.6 mole) in water (600 ml.) under nitrogen. After addition was complete, the product was agitated for thirty minutes and then it was extracted by ether (2 x 50 ml.) to remove neutral material. The aqueous layer containing sodium 0,0-dimethyl phosphorodithioate was made strongly acidic with concentrated hydrochloric acid and the mixture was extracted with ether (4 x 100 ml.). The ethereal layer was dried over magnesium sulphate, and the solvent was distilled off. Fractionation of the residual liquid gave one main fraction (117g; 78% yield), b.p. 65-67°/0.8mm. (W.E. Bacon[110] b.p. 65-67°/0.8mm.), (IR 7).

3.A9 0,0-Dimethyl methyl phosphorodithioate

$\left[(CH_3O)_2P(S)SCH_3\right]$

0,0-Dimethyl phosphorodithioic acid (39g; 0.25 mole) was dissolved in benzene (150 ml.) and the acid was neutralized by pyridine (27g; 0.25 mole) added slowly under cooling. Iodomethane (35g; 0.25 mole) was then added dropwise. Addition was complete in half an hour. The reaction mixture was refluxed for two hours. On cooling a yellow precipitate deposited, which was filtered off. The benzene solution was washed with water (2 x 50 ml.) and was dried over magnesium sulphate. The benzene was distilled off and the residue was fractionated and the main portion boiling at 110°/1mm. (14g; 33% yield), (G.M. Kosolapoff[111] b.p. 110°/1mm.) (IR 8).

3.A10 0,0-Dimethyl (methylthioethyl) phosphorodithioate

$[(CH_3O)_2P(S)SCH_2CH_2SCH_3]$

This compound was prepared by the same method as the methyl ester of the dithiophosphoric acid. The following quantities of reactants were used: 0'0-dimethyl phosphorodithioic acid (39g; 0.25 mole), 1-chloro-3-thiabutane (27g; 0.25 mole) and pyridine (15g; 0.25 mole). The product was fractionated and the fraction (20g; 38% yield) boiling at 121-122°/1.0mm. was collected and identified by its infrared spectrum (G. Schrader[112] b.p. 121-122°/1.0mm.), (IR 9).

3.A11 Dimethyl chlorothiophosphonate $[(CH_3O)_2P(S)Cl]$

A solution of 12.3 ml. of thionyl chloride (0.15 mole) in 50 ml. of dry carbon tetrachloride was added gradually with good stirring at appromately 0° to a suspension of potassium 0,0-dimethyl dithiophosphate (19.6g; 0.1 mole) in 50 ml. of dry carbon tetrachloride. After stirring overnight the mixture was poured into a 2N aqueous sodium carbonate solution. The carbon tetrachloride layer was separated; washed with with aqueous sodium bicarbonate solution, twice with water and dried over anhydrous sodium sulphate and the carbon tetrachloride removed in vacuo. The residue was substantially pure dimethyl chlorothiophosphonate and on distillation, gave 10.8g. of pure material b.p. 38-39°/2mm. The yield was 67.5%, (G. Schrader b.p. 38-39°/2mm.).

3.A12 0,0-Dimethyl 0-(2-methylthioethyl) phosphorothionate

$[(CH_3O)_2P(S)OCH_2CH_2SCH_3]$

Finely pulverized metallic sodium (12g.) were suspended in 50 ml. of dry benzene. Into this suspension 3-thiabutanol (50g; 0.54 mole) was dropped and the temperature was maintained at 40° to 50° for half an hour. After this period the sodium was dissolved. The mixture was then cooled to 20° and dimethyl chlorothiophosphonate (87g; 0.54 mole) was added drop by drop at temperature 10° to 20°. This temperature was kept with stirring for further two hours. Water (50 ml.) were added to dissolve the salt and the aqueous layer was subsequently removed and the benzene layer was fractionated. The product O'O-dimethyl O-(2-methylthioethyl) phosphorothionate (50g; 45.7% yield) distilled over at 115°/2mm. (G. Schrader[8] b.p. 115°/2mm.)

3.A13 Preparation of Pure Thiolo-Tinox

$$\left[(CH_3O)_2P(O)SCH_2CH_2SCH_3\right]$$

Technical® Tinox (6 ml.) was added to a 500 ml. beaker and treated with 60 ml. of diethyl ether. Any precipitate formed was filtered off using a sintered glass filter porosity 4. The filtrate was collected in a distillation flask and the ether was removed on a rotary evaporator. The residue was treated with 100 ml. of chlorobenzene in 5 x 20 ml. portions. Each 20 ml. portion was removed by evaporation under vacuum. This evaporation was done quantitatively using a vacuum of 4-6 mm. and a water bath temperature of 80°. When the distillation was complete the residue was dissolved in n-hexane (300 ml.) and the solution was transfered to a separating funnel. The solution was extracted with 15 x 30 ml. portions of water. Each extraction was thoroughly shaken for two minutes before separating. The aqueous extract was collected in another separation funnel and was extracted with 3 x 40 ml. of n-hexane. The hexane solution was discarded.

The aqueous layer was extracted with 10 x 40 ml. portions of chloroform, which was collected together in a beaker and dried by sodium sulphate. The chloroform was removed by distillation and the product was the purified thiolo-Tinox.

3.A14 Dimethyl thiophosphonate $\left[(CH_3O)_2PSH\right]$

Di-methyl phosphonate (19g; 0.18 mole) and phosphorus pentasulfide (7.5g; 0.035 mole) was refluxed for 20 minutes at the temperature of 90 to 100°. The reaction was continued gently and phosphorus pentasulfide was dissolved to pale yellow solution. Before the end of reaction, it was necessary to heat the mixture for 20 minutes additionally and to keep the reaction temperature at 100 to 110°. When nearly all the phosphorus pentasulfide was dissolved, the mixture turned turbid rapidly. Heating was stopped immediately and the mixture was allowed to cool. The unreacted materials were filtered off and the filtrate was washed with water and dried over sodium sulphate. The product was fractionated and the fraction boiling at 60-64°/7mm. was collected. This was re-distilled and the final product di-methyl thiophosphonate (4.5g; 20% yield) boiled at 60-61°/7mm. (T. Yamaski^{113} b.p. 60-61/7mm.).

3.A15 O,O-Dimethyl (methylthioethyl) thiophosphonate $\left[(CH_3O)_2P(S)CH_2CH_2SCH_3\right]$

Finely pulverized metallic sodium (1.4g;) was suspended in 20 ml. of dry benzene. Into this solution dimethyl thiophosphonate (6.3g; 0.5 mole) was dropped and the temperature was maintained at 40° to 50° for half an hour After this period the sodium was dissolved. To this mixture 1-chloro-3-thiabutane (5.5g; 0.5 mole) was added dropwise. The resulting solution was refluxed for 2 hours. This was cooled and 25 ml. of water was added to the mixture. The reaction mixture was extracted with 2 x 25 ml. of diethyl ether. The ethereal extract was washed with water and subsequently dried over magnesium sulphate. The solvent was then distilled off and the residue fractionated. The fraction boiling at 91-92°/4mm. was collected and identified as the required product (12g; 12% yield). Analysis gave C 29.6%, H 6.8%; $C_5H_{13}O_2PS_2$ requires C 30%. H 6.5% (IR 10).

3A.16 Butanol

Butanol was dried according to the method of Jones and Christian[114]

Butanol (2 l.) was refluxed overnight over freshly ignited 12-20 mesh calcium oxide (50 g.) and then filtered. Magnesium turnings (15 g.) were added to the filtered butanol. This was brought to the boil and a little iodine was added. The mixture was refluxed overnight.

The resultant butanol was distilled through a fractionating column (length 75 cm., packed with porcelain Lessing rings). The main fraction boiling at 117-118° was collected.

3.A17 Dichloromethane

The dichloromethane employed for the preparation of the phosphate complexes was Hopkin and William's spectroscopic grade. It was used without further treatment.

3.A18 2,2-Dimethoxypropane

This material was obtained from Koch-Light Laboratory Ltd., and was used as a dehydrating agent by a modification of the procedure described by Starke[115], without further treatment.

3.A19 Nickel(II) Halides

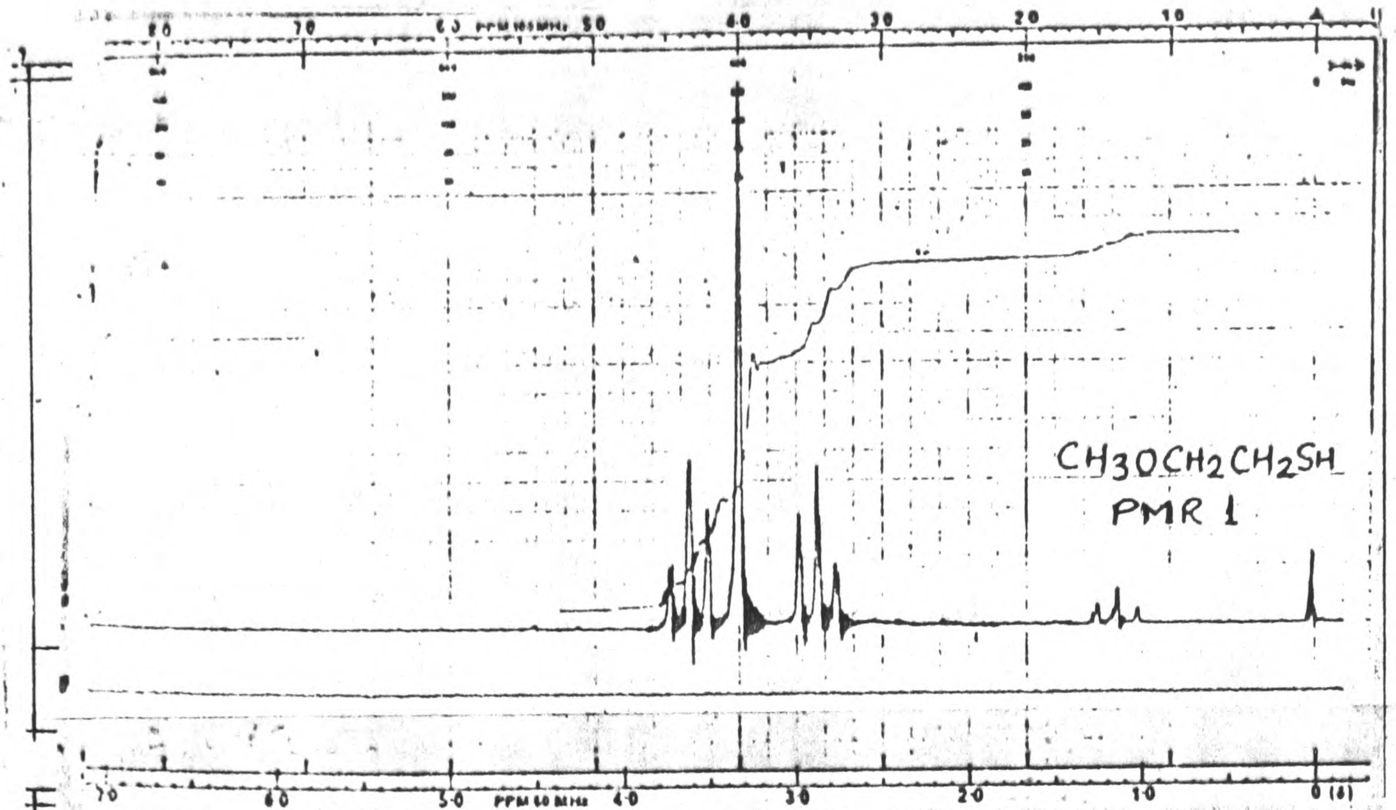
The following hydrated nickel(II) halides were used in the preparation of the complexes. These are supplied by Hopkin and Williams (Analar Grade)

Nickel (II) chloride hexahydrate	$NiCl_2.6H_2O$
Nickel (II) bromide hexahydrate	$NiBr_2.6H_2O$
Nickel (II) iodide hexahydrate	$NiI_2.6H_2O$

3.A20 Cobalt(II) Halides

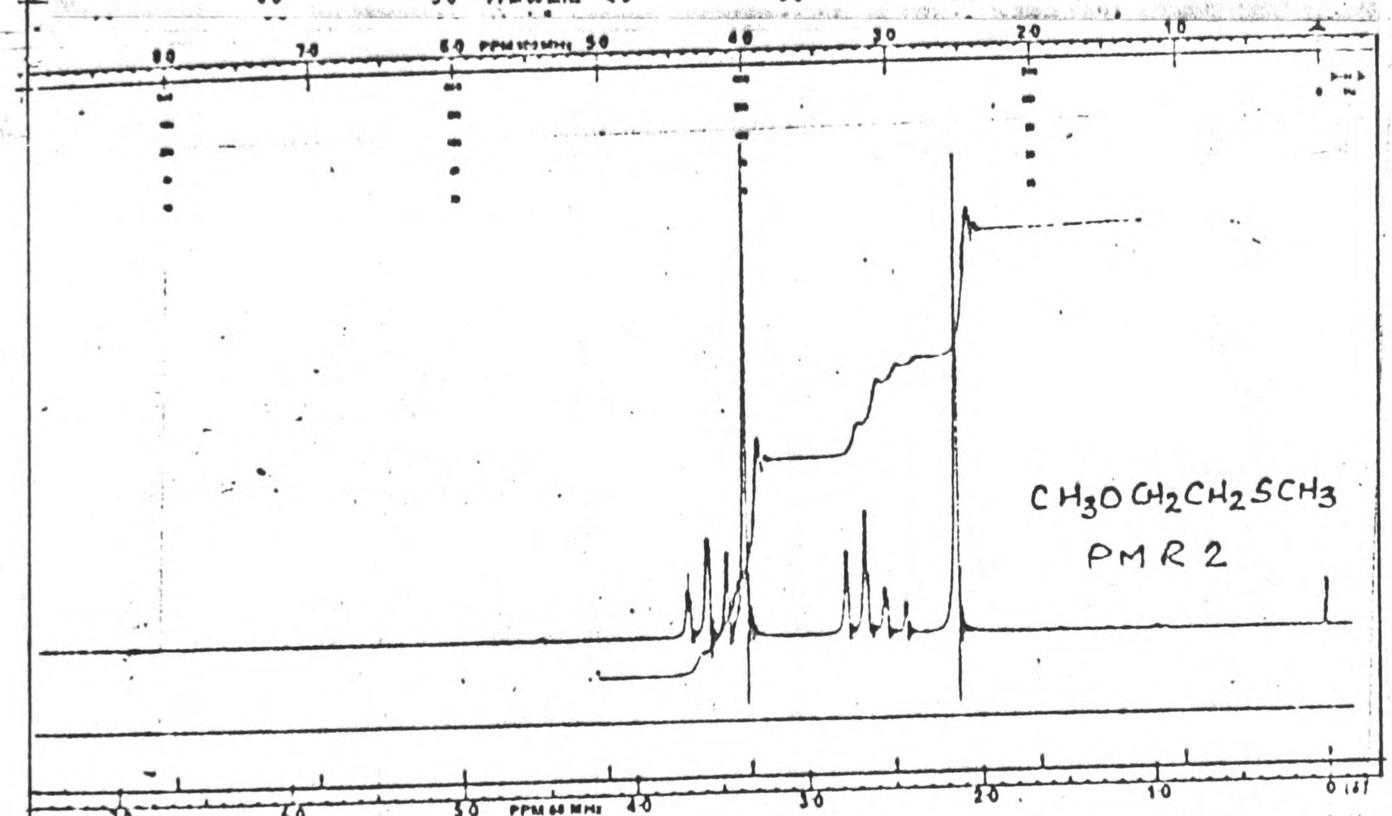
The following hydrated cobalt(II) halides were used in the preparation of the complexes. These are supplied by Hopkin and Williams (Analar Grade):

Cobalt (II) chloride hexahydrate	$CoCl_2.6H_2O$
Cobalt (II) bromide (hydrated)	$CoBr_2.(H_2O)$
Cobalt (II) iodide dihydrate	$CoI_2.2H_2O$



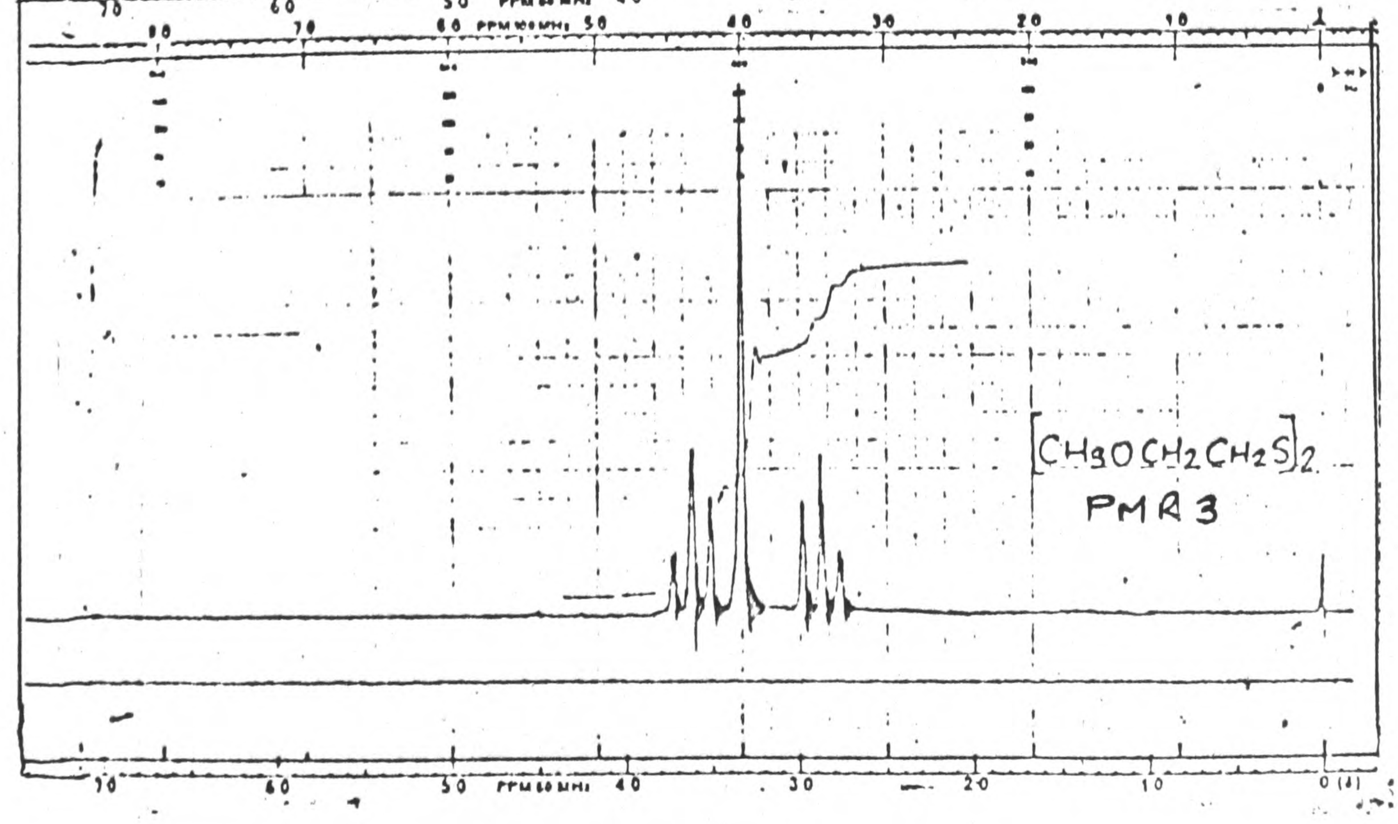
$CH_3OCH_2CH_2SH$

PMR 1



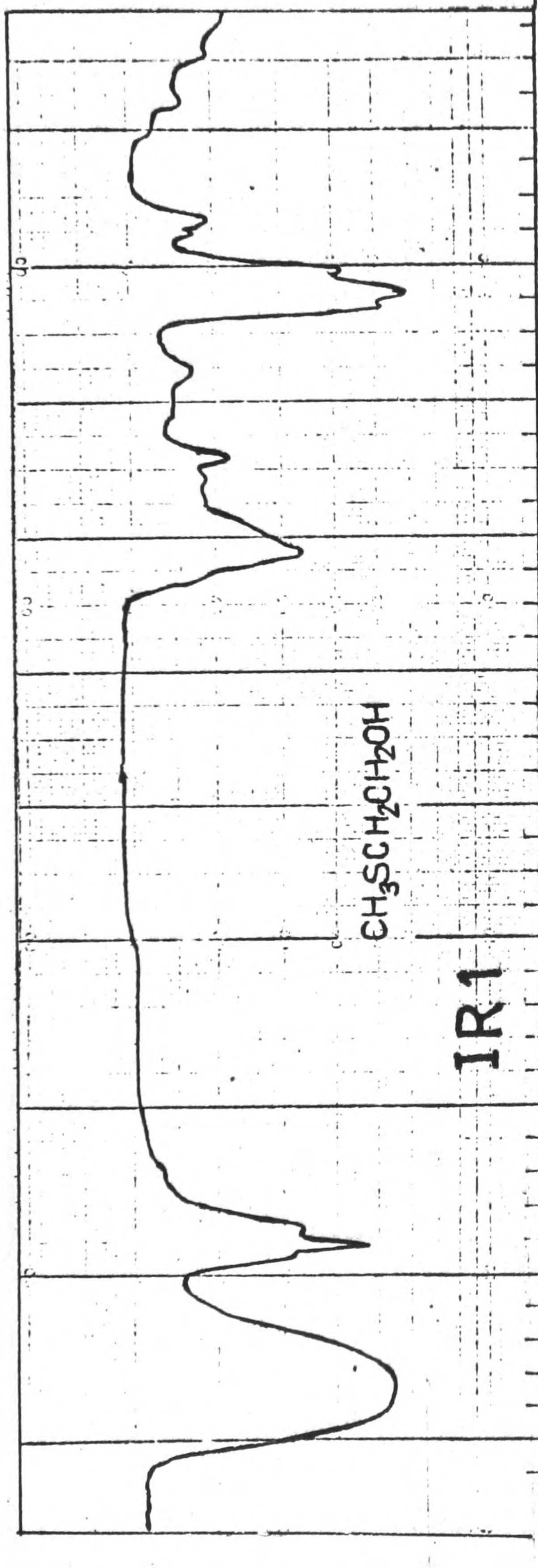
$CH_3OCH_2CH_2SCH_3$

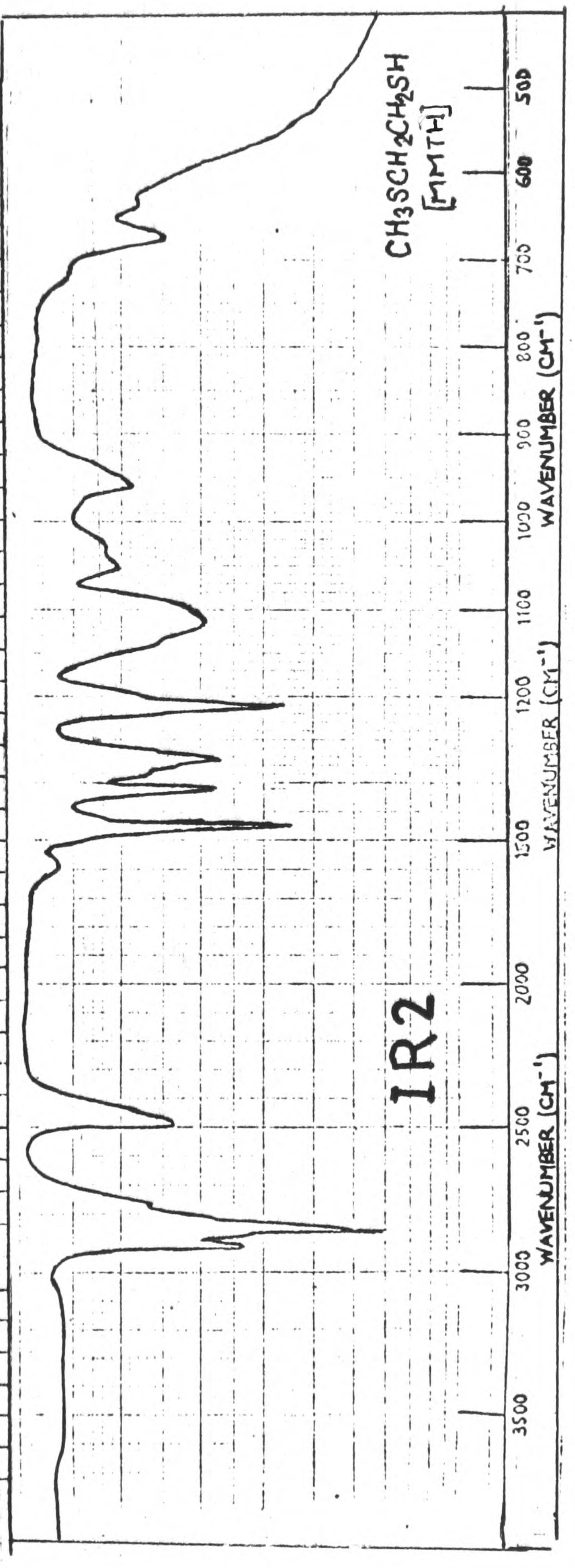
PMR 2

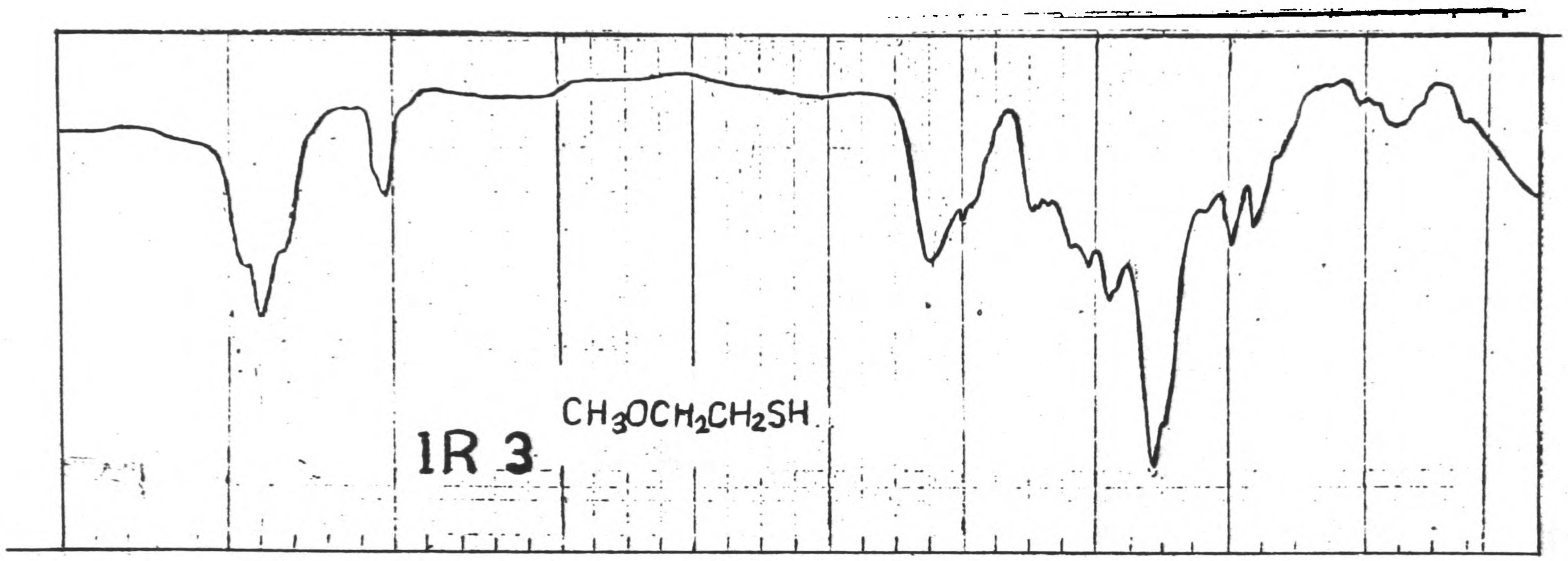


$[CH_3OCH_2CH_2S]_2$

PMR 3

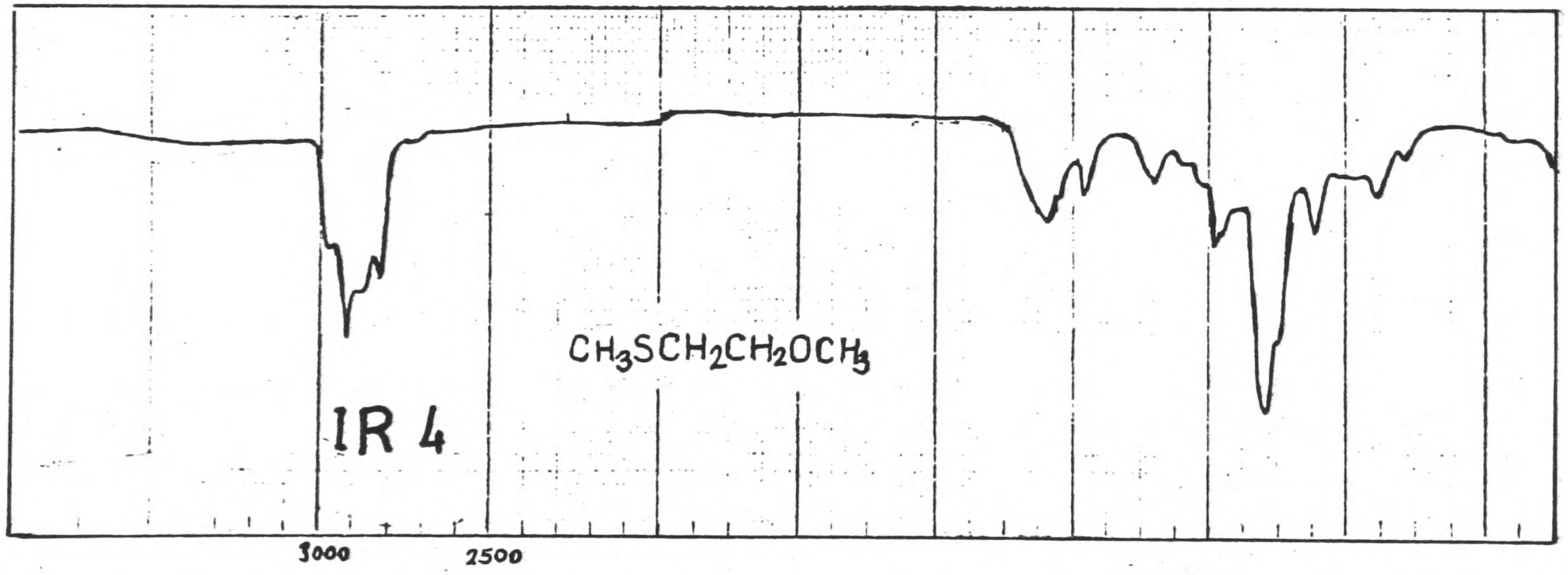

IR1
$CH_3SCH_2CH_2OH$


IR2
$CH_3SCH_2CH_2SH$
[MMTH]
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM^{-1})



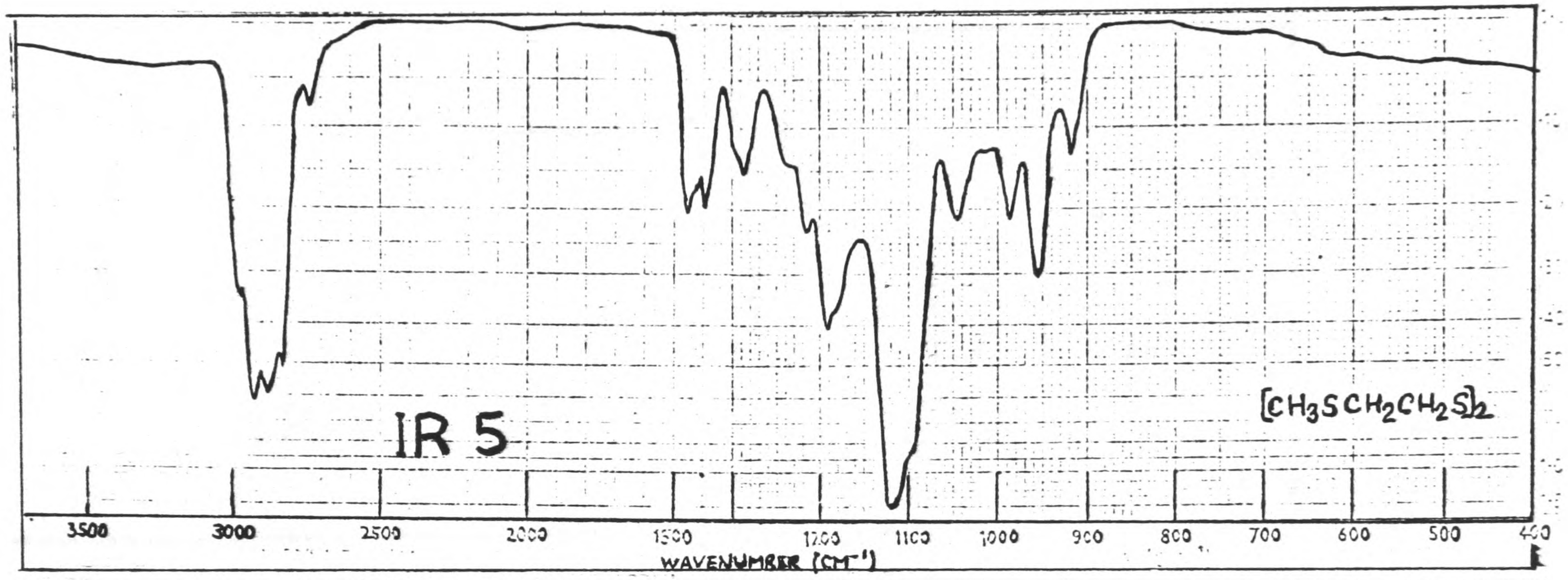
IR 3

$CH_3OCH_2CH_2SH$



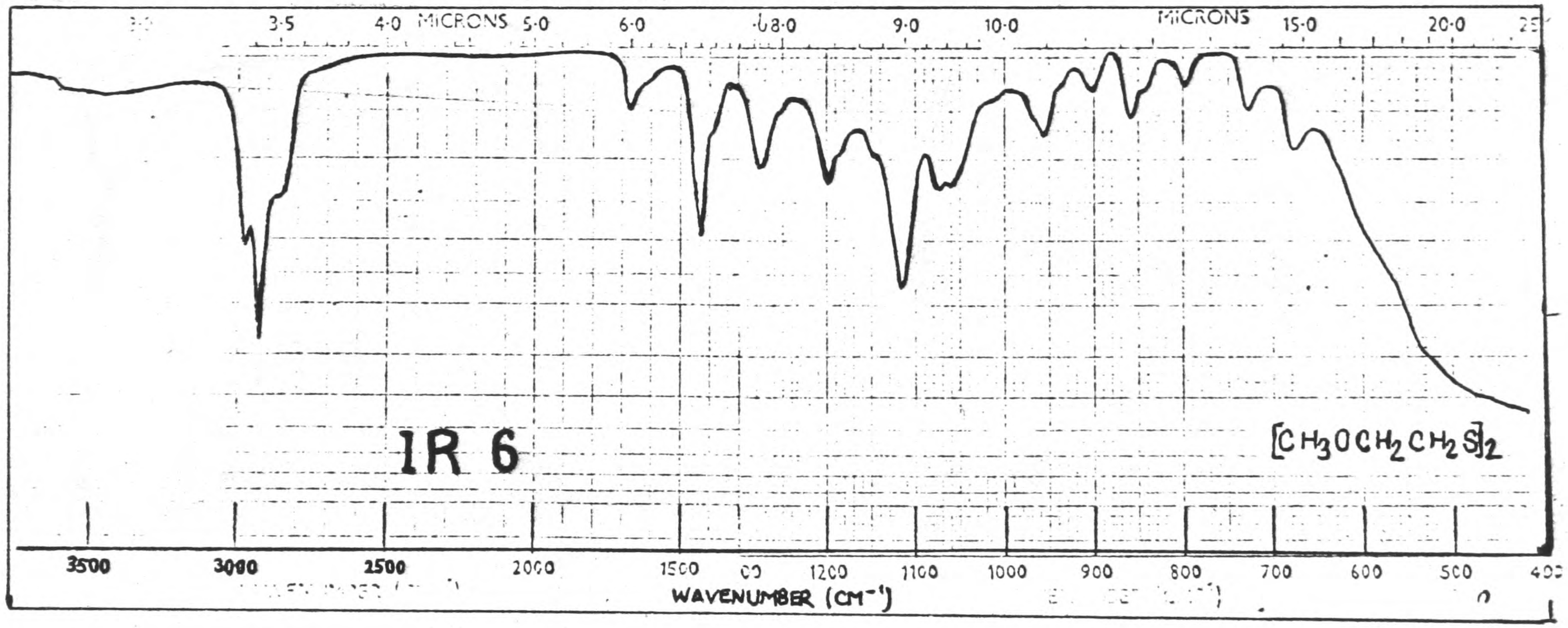
IR 4

$CH_3SCH_2CH_2OCH_3$



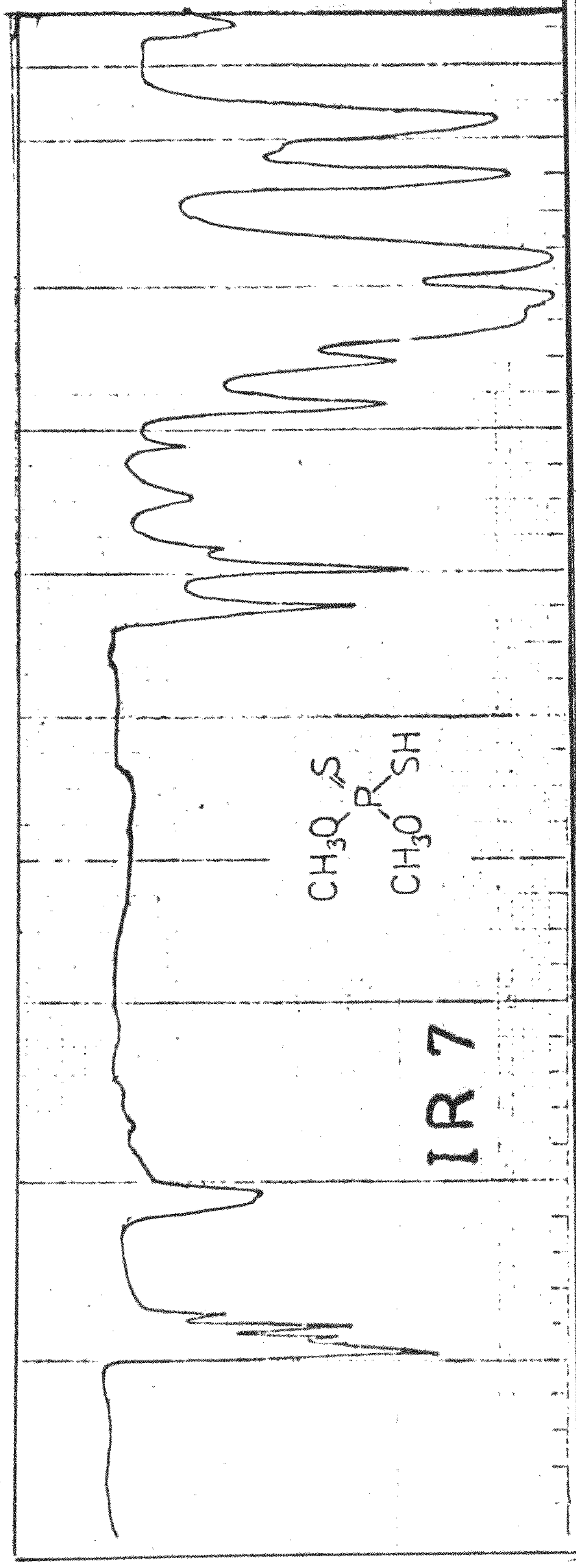
IR 5

[CH3SCH2CH2S]2
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER (CM⁻¹)

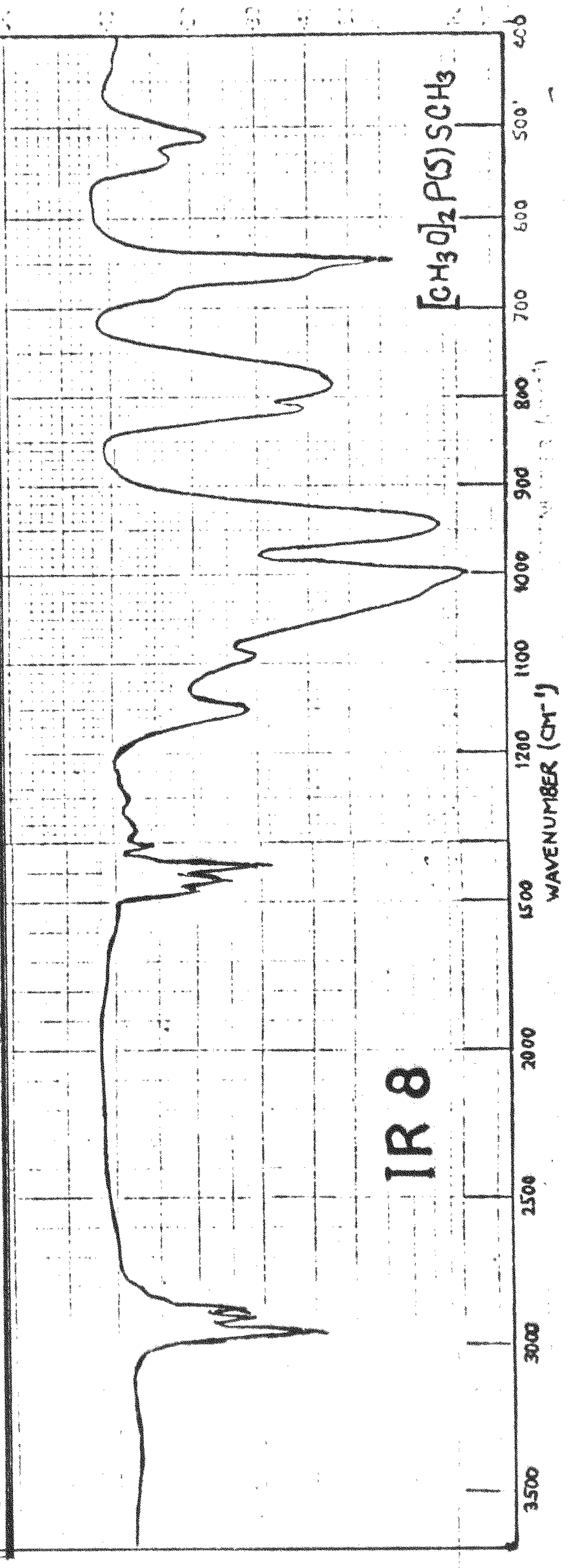


IR 6

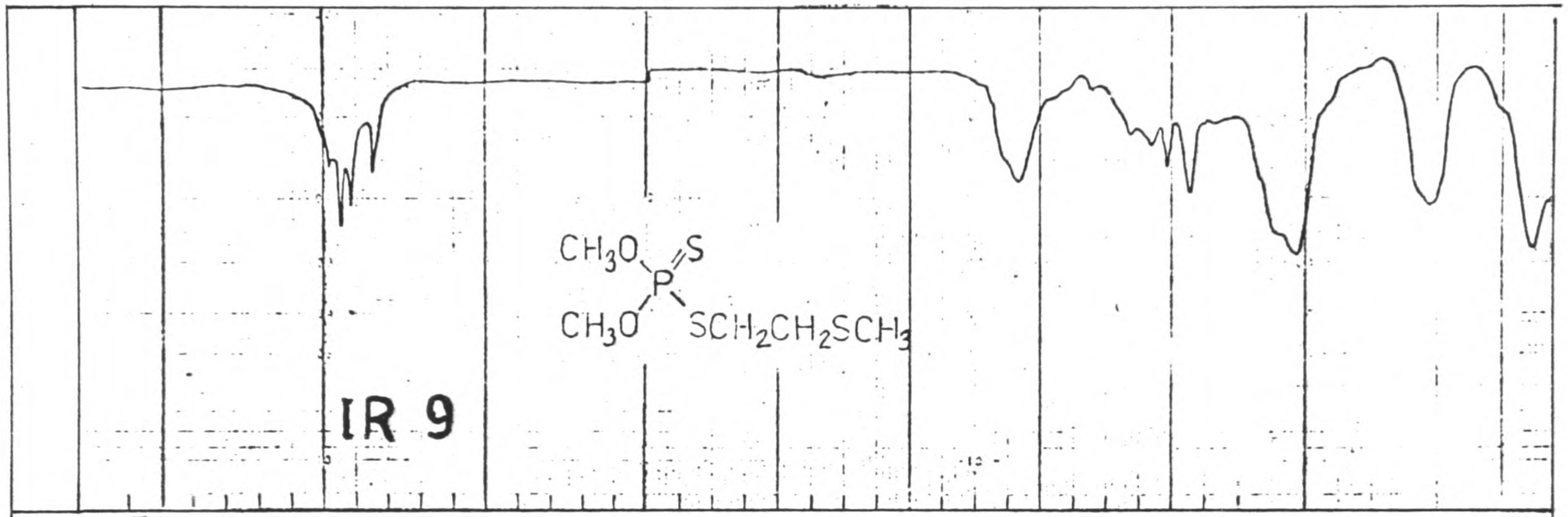
[CH3OCH2CH2S]2
3·5
4·0
MICRONS
5·0
6·0
8·0
9·0
10·0
MICRONS
15·0
20·0
25
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER (CM⁻¹)

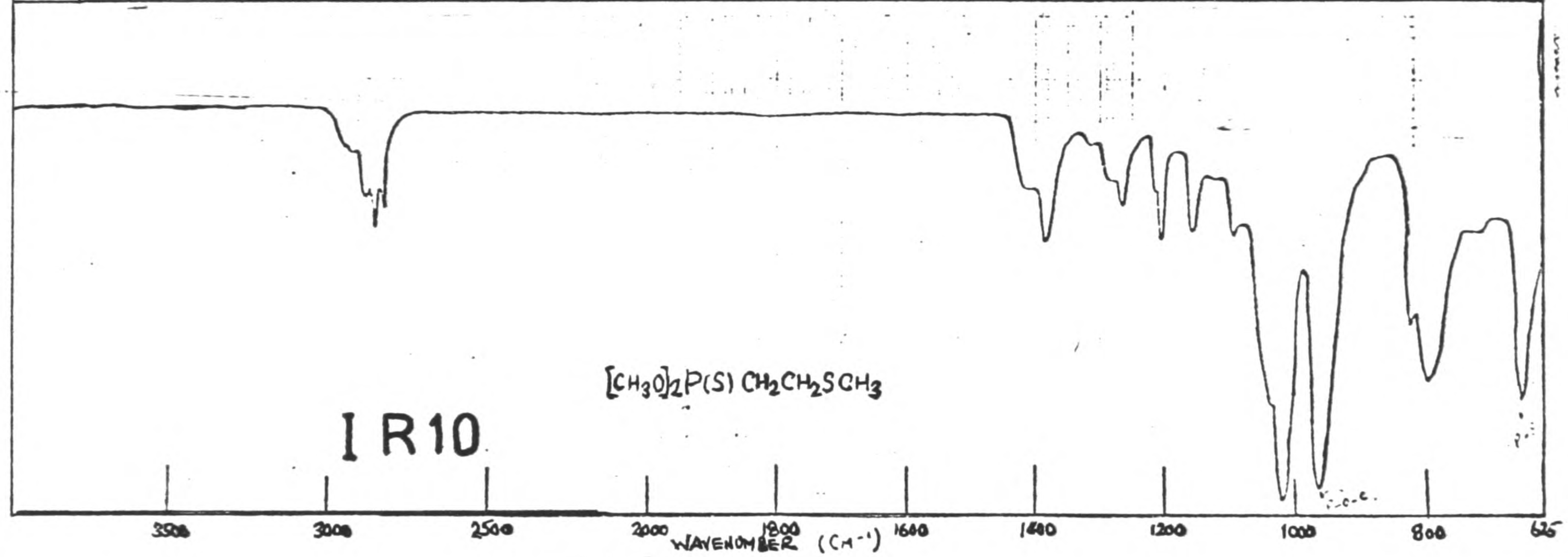

CH$_3$O S P CH$_3$O SH

IR 7


[CH$_3$O]$_2$ P(S) SCH$_3$
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER (CM^{-1})

IR 8


IR 9
CH3O
CH3O
P
S
SCH2CH2SCH3


I R10
[CH3O]2P(S) CH2CH2SCH3
3500
3000
2500
2000
1800
WAVENUMBER (CM-1)
1600
1400
1200
1000
800
625

3.B (1) Preparation of Complexes

The compounds reported in this thesis were prepared by the general methods outlined below. Three methods a, b and c were used. Method a is applicable to all the sulphur-ligands except for the mercapto-sulphur ligand complexes which were prepared by method b. Due to the weak co-ordinating strength of the phosphoryl-oxo and phosphoryl-thioxo ligands, alcoholic solvents could not be used for the preparation and a modified method using dichloromethane as solvent was employed for the preparation of these complexes as detailed in method c

Method a

The metal salt (0.01 mol.) was refluxed with 2,2dimethoxypropane (30ml) on an oil bath for thirty minutes. The product was evaporated to dryness under reduced pressure. The resulting anhydrous metal salt was dissolved in butanol (50 ml.) and the solution was refluxed. The ligand (0.03 mol.) was added dropwise to the refluxing solution of metal salt; usually a colour change is observed during the addition of the ligand. When the addition was complete the solution was refluxed for a further fifteen minutes and was then reduced to about half of its volume under reduced pressure. Crystallisation of the required product usually occurred during the distillation. The resulting mixture was allowed to stand for twelve hours and the crystals were filtered and dried in vacuo.

Method b

Hydrated metal salt (0.01 mol) was dissolved in ethanol (50 ml) and the ligand (0.03 mol.) was added dropwise. The brown (or deep coloured) compound which precipitated was filtered off, washed with ethanol and dried in vacuo.

Method (c)

The anhydrous metal salt (0.01 mol.) prepared as described in method a was dissolved in minimum volume of dichloromethane and was heated to 50^{0} on the oil bath. Excess ligand (0.06 mol.) was then added with stirring for 2-3 hours at 50^{0}, and was allowed to cool slowly to room temperature under stirring. The mixture, in general, became very viscous. Precipitation was effected by the addition of a small amount (ca.25 ml.) of dried pet. ether. The amount of precipitate increased considerably when the mixture was left in the freezer overnight. The separated solid complex was filtered in a dry box in an atmosphere of nitrogen. The crystals were washed with dried pet. ether to get rid off excess solvent. No suitable solvent could be found for the recrystallisation of the complex and the product was used for analysis without any purification.

3. B (2) Analytical Results

The complexes were analysed for the metal and for the halides according to published methods referred to in the following section. Samples of the complexes were submitted for the determination of the carbon, hydrogen and when appropriate for phosphorus as well.

3. B (3) Analytical Methods

(i) G.L.C.

Analytical gas liquid chromatography was carried using a Pye 104 gas chromatograph with a hydrogen flame ionisation detector. The column used was :

5 ft.; 10% S.E. 30 on Chromosorb W

(ii) T.L.C.

Thin layer chromatography was carried out using silica gel (GF_{254}) for layer 0.25mm thick.

(iii) Analysis for halides

Before analysis of the inorganic elements, an accurately weighed sample (about 0.1 g) of the complex was treated with a mixture of concentrated sulphuric (8 ml.), nitric acid (6 ml.) and perchloric acid (1 ml.) to destroy all organic materials present. The resultant mixture was evaporated cautiously to a very small volume on a hot plate. This usually resulted in the complete destruction of all organic material.

The residue was dissolved in water and chloride and bromide were determined volumetrically by complete precipitation of the halide ions with excess silver nitrate solution. The excess silver nitrate solution was titrated by standard potassium thiocyante solution[116a].

Due to the easily oxidised nature of iodide the above method could not be used and the iodide was determined gravimetrically by precipitation of its silver salt from a solution of the complex acidified with nitric acid[116b].

(iv) Analysis for metals cobalt and nickel

The cobalt and nickel contents were determined using the same method. The metal ion was precipitated as a complex of pyridine and ammonium thiocyanate. The excess thiocyanate used was determined by standard silver nitrate solution[116c].

(v) Microanalysis for carbon and hydrogen

The microanalysis of these elements was carried out at the analytical laboratory of the School of Chemistry of Thames Polytechnic.

Table 3.1

Colours and Analyses of Ni(II) and Co(II) halide complexes with 3-thiabutanol (MTEL)

Compounds	Colour	Analysis Result %[#]			
		M	C	H	X
Ni(MTEL)$_2$Cl$_2$	Green	17.8(18.7)	22.0(23.0)	4.95(5.14)	22.0(22.7)
Ni(MTEL)$_2$Br$_2$	Green	14.0(14.5)	17.8(17.9)	4.03(4.0)	40.0(39.9)
Ni(MTEL)$_2$I$_2$	Brown	12.0(11.6)	14.3(14.5)	3.20(3.2)	52.0(51.1)
Co(MTEL)$_2$Cl$_2$	Purple	18.0(18.0)	22.9(23.0)	5.0 (5.14)	23.0(22.7)
Co(MTEL)$_2$Br$_2$	Purple	13.9(14.5)	17.8(17.8)	4.12(4.0)	41.0(39.0)
Co(MTEL)$_2$I$_2$	Dark brown	12.2(11.6)	14.2(14.5)	3.1 (3.2)	52.0(51.0)

[#] For this and subsequent tables - calculated values in brackets

Table 3.2

Colours and Analyses of Ni(II) and Co(II) halide complexes with 1-methoxy-3-thiabutane (MTOE)

Compound	Colour	Analysis Result			
		M	C	H	X
$Ni(MTOE)_2Cl_2$	Green	16.2(17.1)	27.6(28.1)	6.1 (5.8)	21.2(20.7)
$Ni(MTOE)_2Br_2$	Green	13.8(13.6)	22.8(22.5)	4.3 (4.1)	38.0(36.8)
$Ni(MTOE)_2I_2$	Dark brown	11.0(11.1)	18.2(18.3)	3.75(3.8)	48.0(48.4)
$Co(MTOE)_2Cl_2$	Purple	16.8(17.1)	27.9(28.1)	5.9 (5.8)	20.9(20.7)
$Co(MTOE)_2Br_2$	Purple	13.7(13.6)	22.3(22.5)	4.6 (4.2)	37.0(36.8)
$Co(MTOE)_2I_2$	Purple	12.0(11.1)	18.2(18.3)	3.8 (3.8)	48.2(48.4)

Table 3.3

Colours and Analyses of Ni(II) halide complexes with di-(2-methylthioethyl) disulphide (MTD)

Compound	Colour	Analysis Result			
		M	C	H	X
Ni(MTD)Cl_2	Green	15.2(17.0)	22.4(20.9)	4.3 (4.0)	18.5(20.6)
Ni(MTD)Br_2	Green	13.6(13.5)	16.6(16.6)	3.2 (3.2)	37.1(36.9)
Ni(MTD)I_2	Dark green	11.0(11.1)	13.4(13.6)	2.5 (2.6)	48.1(48.2)

Table 3.4

Colour and Analyses of Ni(II) and Co(II) halide complexes with 1-mercapto-3-thiabutane (MMTH)

Compound	Colour	Analysis Result			
		M	C	H	X
$Ni_2(MMT)_2Cl_2$	Orange	28.5(29.1)	18.2(17.9)	3.3 (3.4)	18.2(17.5)
$Ni_2(MMT)_2Br_2$	Brown	33.7(23.8)	14.7(14.6)	2.9 (2.86)	31.6(32.2)
$Ni_2(MMT)_2I_2$	Brown	20.1(19.9)	12.6(12.3)	2.2 (2.29)	42.9(43.2)
$Co_2(MMT)_2Cl_2$	Dark blue	27.8(29.0)	18.2(17.9)	3.8 (3.4)	18.1(17.8)
$Co_2(MMT)_2Br_2$	Dark blue	23.2(23.8)	14.9(14.6)	3.0 (2.8)	31.2(32.4)
$Co_2(MMT)_2I_2$	Dark blue	20.6(19.8)	12.9(12.2)	2.1 (2.3)	42.6(43.2)

Table 3.5

Colours and Analyses of Ni(II) and Co(II) halide complexes with 1-mercapto-2-methoxy-ethane (MMEH)

Compound	Colour	Analysis Result			
		M	C	H	X
$Ni_2(MME)_2Cl_2$	Brown	18.9(18.8)	23.2(23.1)	4.4 (4.4)	22.7(22.7)
$Ni_2(MME)_2Br_2$	Brown	14.7(14.6)	17.6(17.9)	3.5 (3.5)	40.0(39.9)
$Ni_2(MME)_2I_2$	Brown	11.4(11.9)	14.6(14.5)	2.8 (2.8)	50.2(51.3)
$Co_2(MME)_2Cl_2$	Dark Brown	18.6(18.8)	23.0(23.1)	4.5 (4.4)	22.5(22.7)
$Co_2(MME)_2Br_2$	Dark Brown	14.3(14.6)	17.7(17.9)	3.6 (3.5)	40.5(39.9)
$Co_2(MME)_2I_2$	Dark Brown	11.4(11.9)	14.2(14.5)	2.9 (2.8)	52.5(51.3)

Table 3.6

Colours and Analyses of Ni(II) and Co(II) halides complexes with O'O-dimethyl S-(2-methylthioethyl) phosphorothiolate (DSPD)

Compound	Colour	Analysis Result			
		M	C	H	X
Ni(DSPD)Cl_2	Dark green	17.2(16.8)	16.6(17.3)	3.7 (3.7)	20.2(20.5)
Ni(DSPD)Br_2	Dark green	13.2(13.5)	13.5(13.8)	3.0 (2.9)	35.2(36.8)
Ni(DSPD)I_2	Dark green	11.4(11.0)	11.2(11.4)	2.5 (2.4)	45.2(47.9)
Co(DSPD)Cl_2	Dark blue	16.2(16.8)	16.7(17.3)	3.6 (3.7)	20.2(20.5)
Co(DSPD)Br_2	Dark blue	13.2(13.5)	12.9(13.8)	2.7 (2.9)	35.2(36.8)

3.C Physical Measurements

(1) Electronic Spectra

The electronic spectra of the solution of the compounds were measured in the range 300-2500nm (33.3-4.0kK) on a Unicam SP700 Spectrophotometer.

The diffuse reflectance spectra of the solid compounds were measured on the same apparatus using a Unicam SP735 Diffuse Reflectance Attachment; magnesium carbonate was used as the reference material.

(2) Spectral Calculations

Calculation of the crystal field parameters is confined to octahedral and tetrahedral complexes, where the relationship of the energy levels and the observed transitions are empirically established. No such calculation was possible with the square planar complexes.

The data obtained from the electronic spectra of the complexes are used to calculate the crystal field parameters according to the expressions obtained from the C.F.T. analysis. In complexes where three transitions are observed in their spectra, the calculation is simply substitution of the appropriate spectral results into the equations concerned. In cases where only two bands are observed, with the highest energy transition obscured by the ligand absorption in the UV region or the lowest band covered by the overtone vibration of the ligand in the near infrared region one of the numerical procedures for estimation reviewed by E.Konig[90] was employed. A few worked examples are shown and attached to the appropriate spectral results.

(2a) Octahedral Nickel Complexes where three bands are observed e.g. $Ni(MTEL)_2Cl_2$

Table 3.7, p. 93

Band observed: 24000, 14000, 8650 cm^{-1}

(the value of the last band is taken on the centre of gravity of the band ignoring splitting)

Equation (5),p. 40 has the consequence that an extremely simple relation may be obtained from the sum of $\nu_2 + \nu_3$. Thus the equation

$$10\,Dq = \nu_1$$

$$B = (\nu_3 + \nu_2 - 3\nu_1) / 15$$

$$B = (14000+24000-3.8650) / 15$$

$$B = 803.4 \qquad B_o = 1041$$

$$\beta_{35} = 803.4/1041$$

$$= \underline{0.77}$$

(2b) Tetrahedral Cobalt Complex where last band is not observed, e.g. Co$(MTEL)_2Cl_2$.

Table 3.7, p. 93

Bands observed 15500, 6750 cm^{-1}

As ν_1 is not observed, it is necessary to calculate the parameters using only these two bands. The equations resulting from ν_2 and ν_3 of equation (5), p. 40 are

$$10Dq = (1/34)\left[9(\nu_2 + \nu_3) \pm \left\{81(\nu_2^2 + \nu_3^2) - 178\nu_2\nu_3\right\}^{\frac{1}{2}}\right]$$

$$B = (\nu_2 + \nu_3 - 30Dq)/15$$

$$10Dq = (1/34)\left[9(22250) \pm \left\{10^8.81(.45 + 2.4) - (1.04 x 178)10^8\right\}^{\frac{1}{2}}\right]$$

$$= (1/34)\left[200200 \pm \left\{10^8(230.85) - (185.12)10^8\right\}^{\frac{1}{2}}\right]$$

$$= (1/34) \times (132750) \text{ or } (1/34) \times (267750)$$

$$= 3904 \text{ or } 7875$$

It is obvious that 7875 cm^{-1} can not be the correct ligand field splitting energy, thus

$$B = (22250 - 11820)/15$$

$$= 10430/15 = 695$$

$$\beta_{35} = \underline{0.71}$$

(2c) Tetrahedral Nickel where the last band is not observed e.g. Ni(DSPD)Cl_2.

Table 3.12, p. 99

Band observed 14500, 7300 cm^{-1}.

Fitting the second and third bands, employing the expressions of ν_2 and ν_3 in equation (7), p. 46, one obtains

$$10Dq = (1/3)(2\nu_2 - \nu_3) + 5B$$

$$B = (1/510)\left[7(\nu_3 - 2\nu_2) \pm 3\left\{81\nu_3^2 - 16\nu_3^2(\nu_2 - \nu_3)\right\}^{\frac{1}{2}}\right]$$

$$B = 782$$

$$10Dq = 4020$$

$$\beta_{35} = 782/1041$$

$$= \underline{0.75}$$

Table 3.7

Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) halides complexes with 3-thiabutanol (MTEL)

Compound	μ_{eff}(B.M.)*	Λ'	ν (cm^{-1} x 10^3)**
Ni(MTEL)$_2$Cl$_2$	3.3	-	22.7, 19.1(sh), 14.3, 8.5, 6.0
Ni(MTEL)$_2$Br$_2$	3.25	-	23.2, 19.2(sh), 14.1, 12.3, 8.75, 7.0
Ni(MTEL)$_2$I$_2$	3.1	-	21.5, 13.9, 8.3, 6.0
Co(MTEL)$_2$Cl$_2$	4.2	290	17.0, 14.5, 7.0, 5.4
Co(MTEL)$_2$Br$_2$	4.23	260	16.7, 15.3, 7.0, 5.5
Co(MTEL)$_2$I$_2$	4.3	280	17.0, 15.7, 15.2, 6.8, 5.3

For this and subsequent tables on electronic spectra:

* at room temperature; Λ' $ohm^{-1} cm^{-2} mole^{-1}$, 1 x 10^{-3}M in nitromethane, $(Et_4N)^+Br^-$ has a value of 110 at 1 x 10^{-3}M;

** Diffuse reflectance spectra against $MgCO_3$, sh=shoulder.

Table 3.8

Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) halides complexes with 1-methoxy-3-thiabutane (MTOE)

Compound	μ_{eff}(B.M.)*	Λ'	ν (cm^{-1} x 10^3)**
$Ni(MTOE)_2Cl_2$	3.4	12.1	23.9, 15.1, 12.9(sh), 8.6, 7.95
$Ni(MTOE)_2Br_2$	3.4	13.5	22.8, 14.6, 12.4(sh), 8.6, 7.9
$Ni(MTOE)_2I_2$	3.5	15.0	*** 14.6, 12.9(sh), 8.5, 7.75
$Co(MTOE)_2Cl_2$	4.5	280	17.9, 15.2, 14.3, 7.9, 5.7
$Co(MTOE)_2Br_2$	4.55	275	17.4, 14.9, 13.4, 7.3, 5.4
$Co(MTOE)_2I_2$	4.43	260	16.9, 14.9, 14.2, 6.9, 5.4

*** Band obscured by intense charge transfer band

Table 3.8b

Electronic Spectra of Ni(II) and Co(II) halide complexes with 1-methoxy-3-thiabutane (MTOE) in nitromethane

Compound	ν (cm^{-1} x 10^3)
$Ni(MTOE)_2Cl_2$	23.9(6.1), 15.1(3.2), 9.1,7.9
$Ni(MTOE)_2Br_2$	22.8(11), 14.8(4.2), 9.1, 7.9
$Ni(MTOE)_2I_2$	*** 14.9(5.1), 9.2, 7.6
$Co(MTOE)_2Cl_2$	18.0(250), 15.4, 14.5, 8.1, 6.
$Co(MTOE)_2Br_2$	17.8(200), 15.1, 13.7, 7.6, 5.8
$Co(MTOE)_2I_2$	17.1(220), 15.2, 13.9, 7.2, 5.6

Table 3.9

Electronic Spectra and Magnetic Moments of Ni(II) halide complexes with di-(2-methylthioethyl) disulphide (MTD)

Compound	μ_{eff}(B.M.)*	Λ'	ν (cm^{-1} x 10^3)**
Ni(MTD)Cl_2	3.35	-	24.5, 19.5(sh), 15.5, 11.0, 9.1
Ni(MTD)Br_2	3.4	-	24.3, 20.1(sh), 15.7, 11.0, 8.9
Ni(MTD)I_2	3.4	-	*** 15.8, 11.0, 88.6

Table 3.10

Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) halide complexes with 1-mercapto-3-thiabutane (MMTH)

Compound	μ_{eff}(B.M.)*	Λ'	ν ($cm^{-1} \times 10^3$)*****
$Ni_2(MMT)_2Cl_2$	0	20.1	26.0(1452), 23.9(1800), 17.85(550), 13.0sh
$Ni_2(MMT)_2Br_2$	0	17.2	26.0(1490), 23.8(1928), 17.8(600), 13.1sh
$Ni_2(MMT)_2I_2$	0	16.1	26.0(1660), 23.8(2000), 17.8(450),13.2sh
$Co_2(MMT)_2Cl_2$	2.2	-	26.3(989.5), 22.2sh, 7.2(8), 4.4(21)
$Co_2(MMT)_2Br_2$	2.2	-	26.3(1162), 21.7sh, 7.1(7), 4.4(25)
$Co_2(MMT)_2I_2$	2.36	-	26.3(1300), 21.2sh, 7.1(5), 4.5(20)

***** Spectra are taken in ca. 1 x 10^{-3}M concentration solution in nitromethane

Extinction coefficient in parenthesis

Table 3.11

Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) halide complexes with 1-mercapto-2-methoxy-ethane (MMEH)

Compound	μ_{eff}(B.M.)*	Λ'	ν (cm^{-1} x 10^3)*****
$Ni_2(MME)_2Cl_2$	0	-	27.0(2000), 22.3sh, 17.5(200), 12.5(24)
$Ni_2(MME)_2Br_2$	0	-	27.2(2100), 22.0sh, 17.5(250), 13.0(26)
$Ni_2(MME)_2I_2$	0	-	27.1(2000), 22.4sh, 17.4(280), 13.2(30)
$Co_2(MME)_2Cl_2$	2.1	-	26.4(1200), 20.0, 7.4, 4.6(31)
$Co_2(MME)_2Br_2$	2.2	-	26.3(1300), 19.8, 7.2, 4.6(25)
$Co_2(MME)_2I_2$	2.15	-	26.4(1200), 7.3, 4.5(20)

Table 3.12

Electronic Spectra and Magnetic Moments of Ni(II) and Co(II) halide complexes with O'O-dimethyl S-(2-methylthioethyl) phosphorothiolate (DSPD)

Compound	μ_{eff}(B.M.)*	Λ'	ν (cm^{-1} x 10^3)**
$Ni(DSPD)Cl_2$	3.45	20	14.5, 11.5sh, 7.3, 5.0sh
$Ni(DSPD)Br_2$	3.47	15	14.4, 11.6sh, 7.3, 5.2sh
$Ni(DSPD)I_2$	3.5	29	14.9, 7.3
$Co(DSPD)Cl_2$	4.62	8	15.8, 14.9, 13.5, 7.2, 6.2, 5.1
$Co(DSPD)Br_2$	4.71	11	16.1, 14.7, 13.8, 7.5, 6.4, 5.2

(3) Infrared Spectra

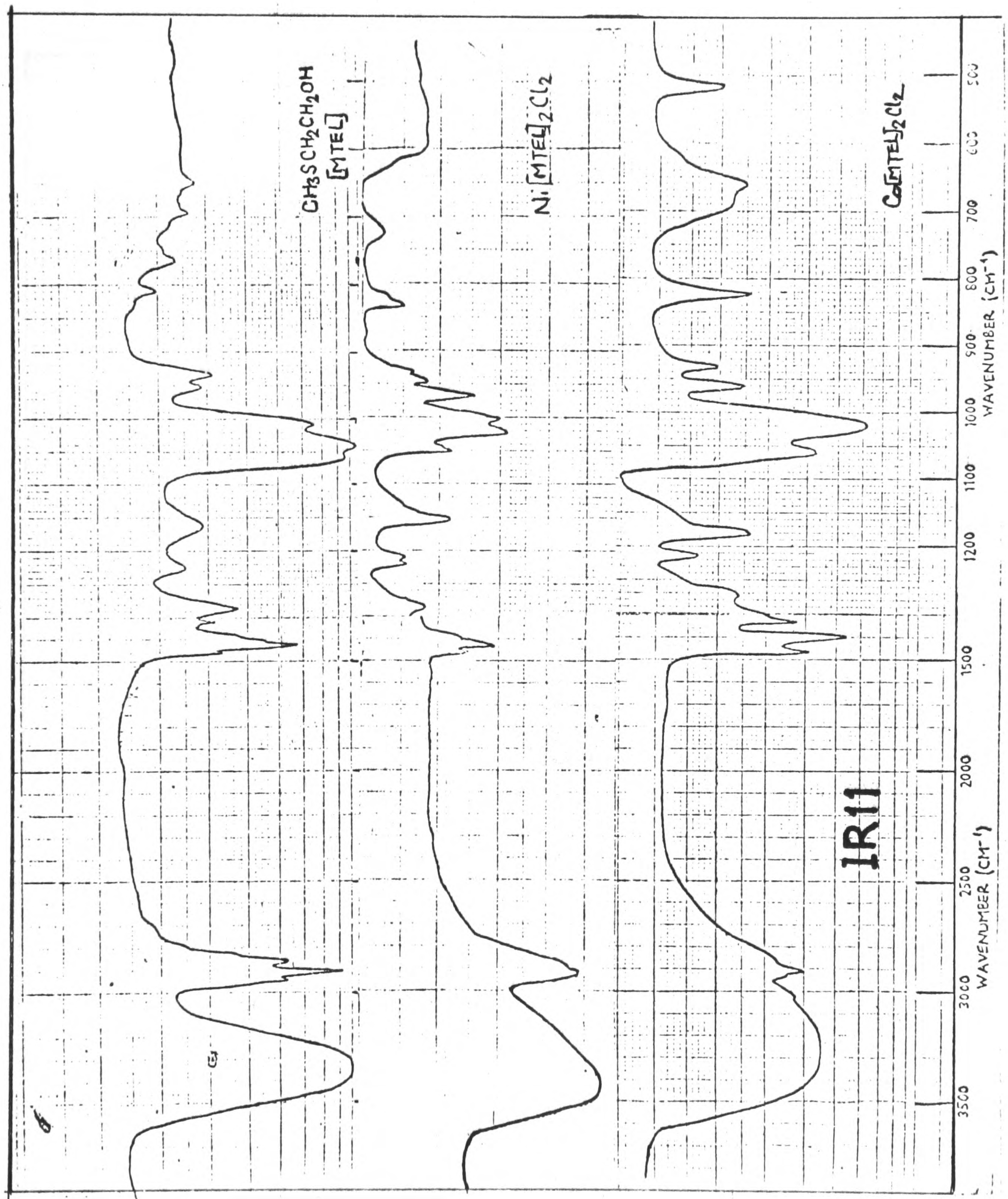
The infrared spectra in the range 4000–400 cm^{-1} were measured on a Perkin Elmer P.E. 337 Grating Spectrophotometer. For solid state spectra nujol or bromoform mulls were used between potassium bromide discs.

Spectra in the region 450–80 cm^{-1} were recorded on nujol mulls held between 'Rigidex' plates or pressed discs in polythene on a Research and Industrial Instrument Company F.S. 720 Interferometer; the requisite calculations were carried out on an Elliot 4100 Computer.

Tables and Figures

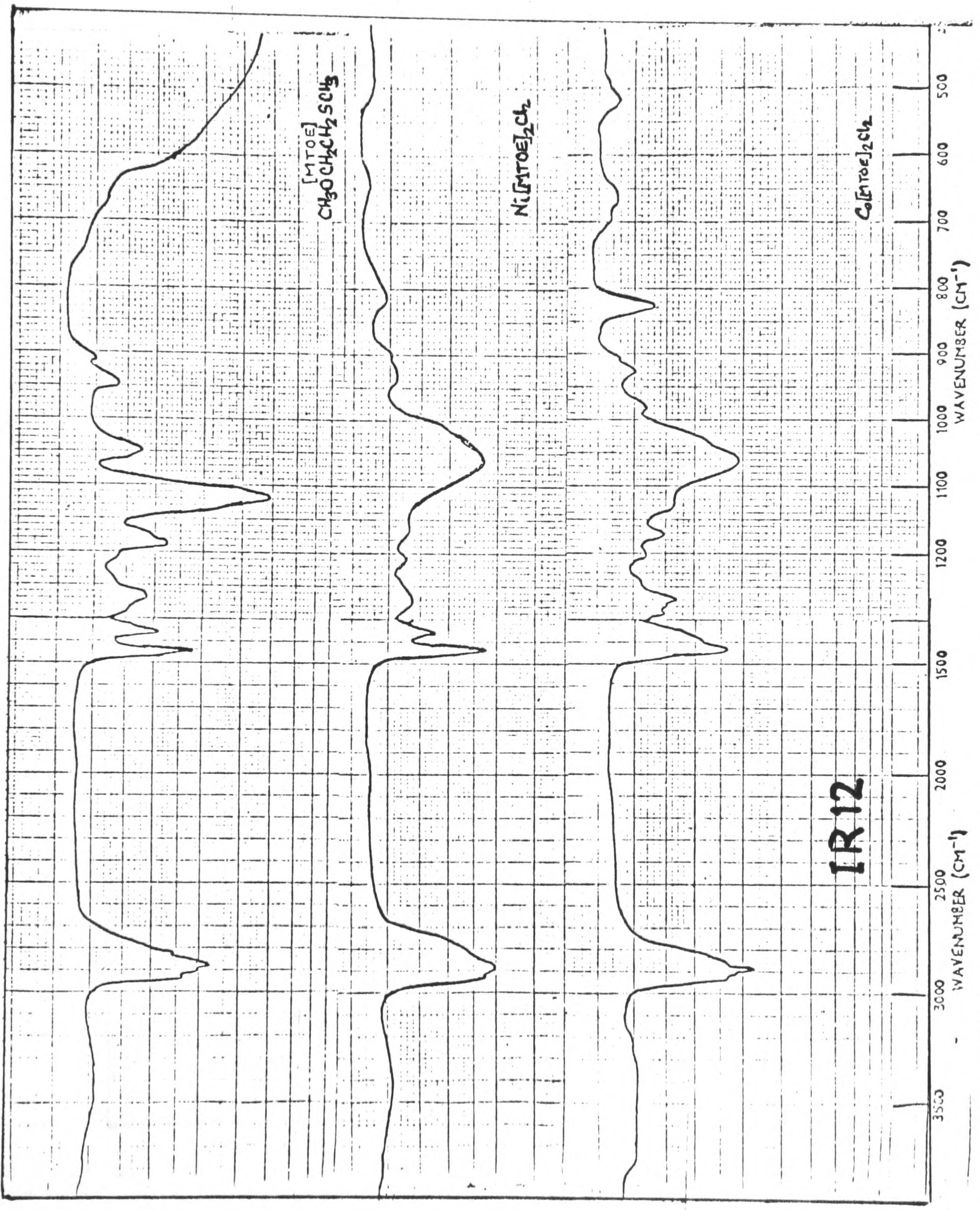
The following tables and figures record the infrared and far infrared spectra of the complexes prepared in this work.

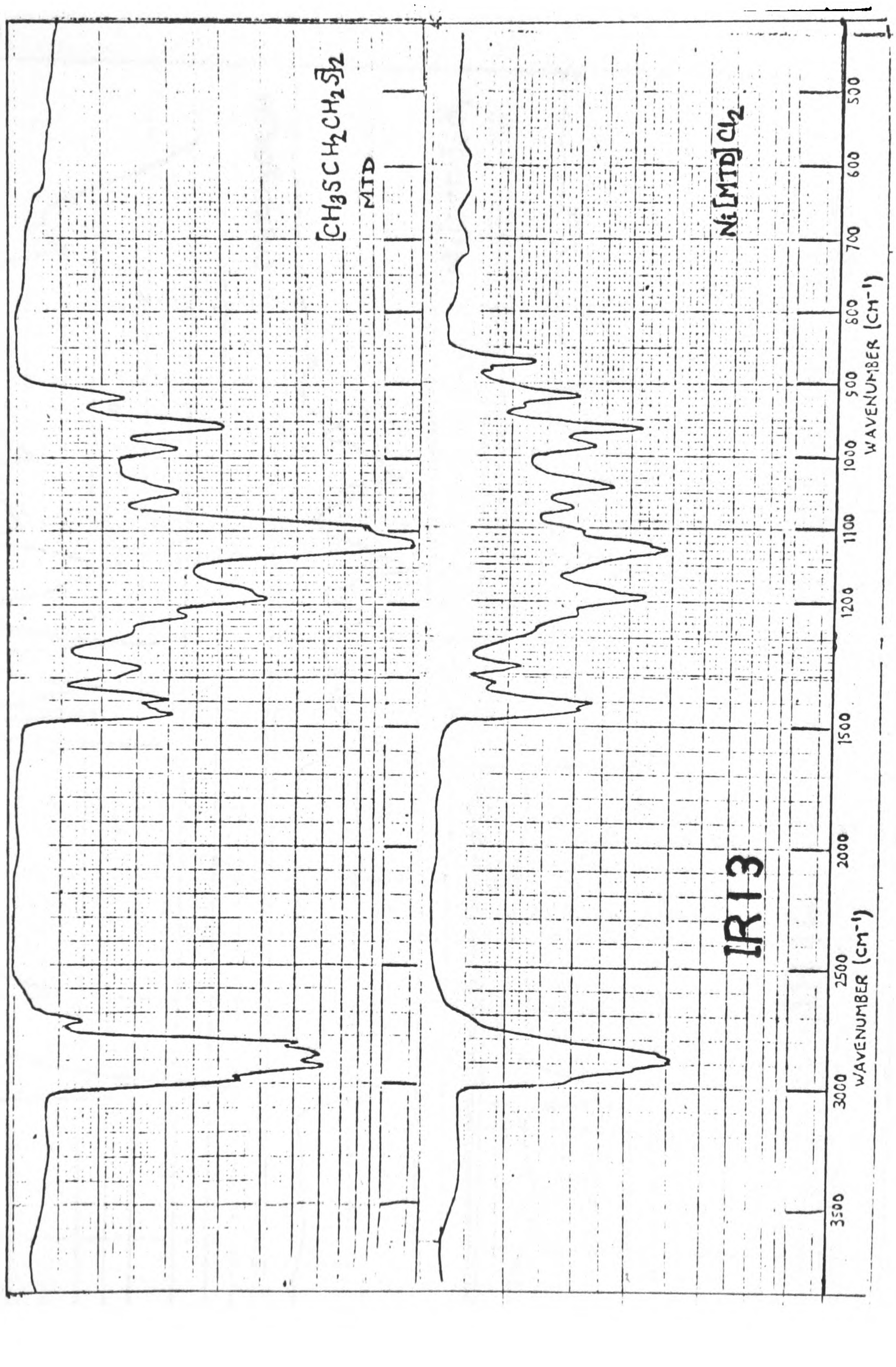
For the tables, the small letters after the wavenumber of the band refer to the intensity of the peak, i.e. v=very, m=medium, w=weak, s=strong, sh=shoulder and b=broad.



IR11

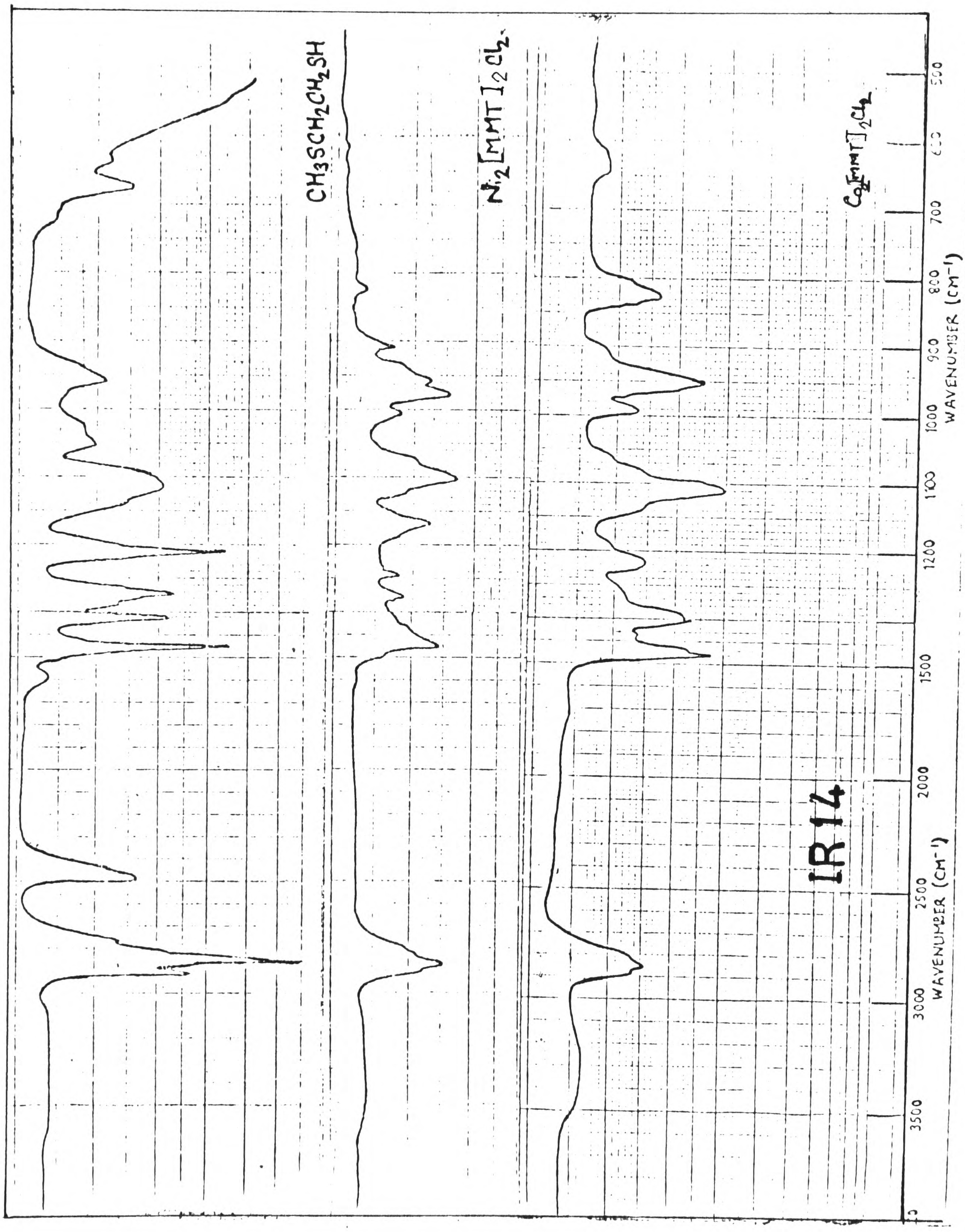
$CH_3SCH_2CH_2OH$
[MTEL]
Ni[MTEL]$_2$Cl$_2$
Co[MTEL]$_2$Cl$_2$
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM^{-1})
WAVENUMBER (CM^{-1})


[MTOE]
CH3OCH2CH2SCH3
Ni[MTOE]2Cl2
Co[MTOE]2Cl2
IR12
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM⁻¹)



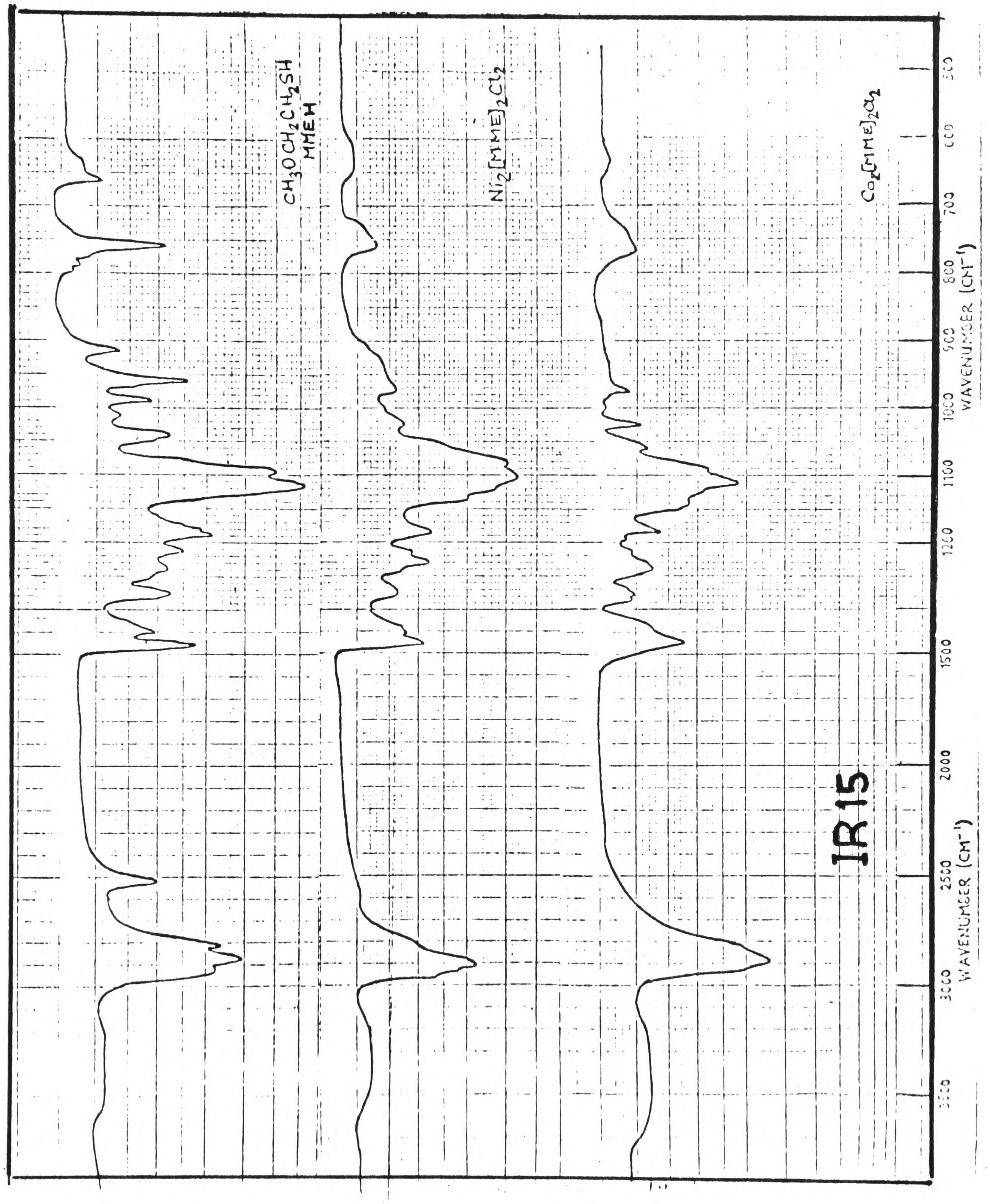
IR13

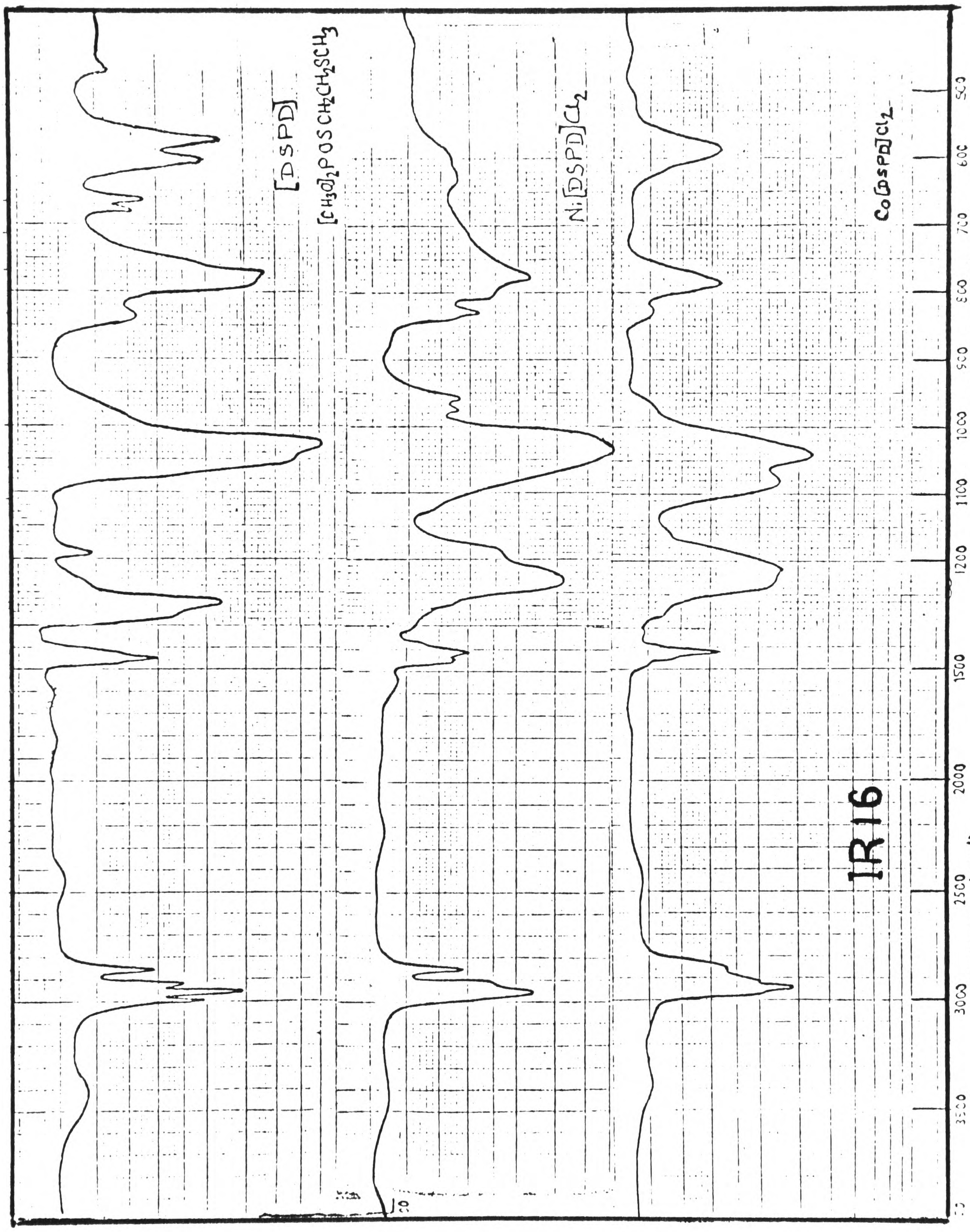
[CH$_3$SCH$_2$CH$_2$S]$_2$
MTD
Ni[MTD]Cl$_2$
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM^{-1})
WAVENUMBER (CM^{-1})

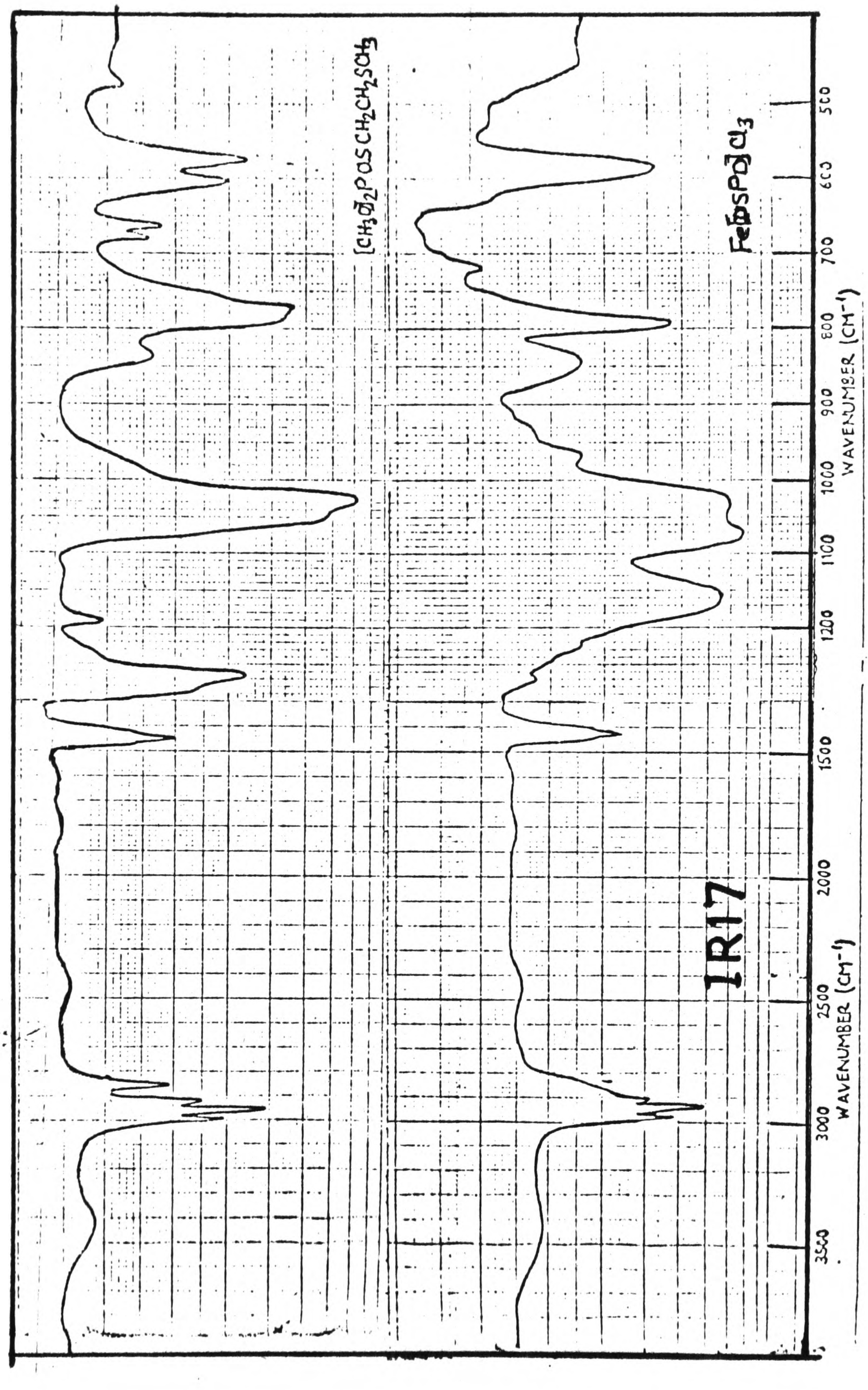


IR14

CH3SCH2CH2SH
Ni2[MMT]2Cl2
Co2[MMT]2Cl2
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)


CH3OCH2CH2SH
MMEH
Ni2[MME]2Cl2
Co2[MME]2Cl2
IR15
3500
3000
2500
WAVENUMBER (CM⁻¹)
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM⁻¹)


IR16
[DSPD]
[CH3O]2POSCH2CH2SCH3
Ni[DSPD]Cl2
Co[DSPD]Cl2
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500
WAVENUMBER (CM-1)



IR17

[CH$_3$O]$_2$POSCH$_2$CH$_2$SCH$_3$
Fe[DSPD]Cl$_3$
WAVENUMBER (CM^{-1})
3500
3000
2500
2000
1500
1200
1100
1000
900
800
700
600
500

Table 3.13

Assignments of Far Infrared Spectra of Ni(II) and Co(II) halide complexes with 3-thiabutanol (MTEL)

(cm^{-1})

Compound	Ligand vibrations	ν(M-X)	ν(M-O)	ν(M-S)
MTEL	446w, 402w, 384w, 332w			
Ni(MTEL)$_2$Cl$_2$	450w	260vs	420m, 370w	342w,350m
Ni(MTEL)$_2$Br$_2$	450w, 342w	198vs	435m, 387w	345w, 320w
Ni(MTEL)$_2$I$_2$	448w, 339w	150vs	450m, 390w	350w, 326w
Co(MTEL)$_2$Cl$_2$	455w	-	446m, 410w	360m, 340w, 318w
Co(MTEL)$_2$Br$_2$	445w, 340w	-	450m, 394w	354w, 338m
Co(MTEL)$_2$I$_2$	449w, 340w	-	437s, 415w	361m, 342w

Table 3.14

Assignments of Far Infrared Spectra of Ni(II) and Co(II) halide complexes with 1-methoxy-3-thiabutane (MTOE) (cm^{-1})

Compound	Ligand vibration	ν(M-X)	ν(M-O)	ν(M-S)
MTOE	450w, 402w, 310w		-	
$Ni(MTOE)_2Cl_2$	448w	280vs	424m, 387w	320m, 315w
$Ni(MTOE)_2Br_2$	448w	220vs	410m, 372w	312m
$Ni(MTOE)_2I_2$	449w	155vs	415m, 369m	315m,
$Co(MTOE)_2Cl_2$	450w, 438s, 186m		390w	284m
$Co(MTOE)_2Br_2$	450w, 435s, 191m		376m,	229w
$Co(MTOE)_2I_2$	448w, 437s, 198m		380w, 300m	249w

Table 3.15

Assignments of Far Infrared Spectra of Ni(II) halide complexes with di-(2-methylthioethyl) disulphide (MTD) (cm^{-1})

Compound	Ligand Vibration	ν(M-X)	ν(M-S)
MTD	446w, 435m, 386w, 294s		
Ni(MTD)Cl_2	442w, 410w, 287s	265s, 235sh	340m, 335w
Ni(MTD)Br_2	448w, 415m, 290s	210s, 183m	350m
Ni(MTD)I_2	450w, 420m, 286s	157s, 145w	356m

Table 3.16

Assignments of Far Infrared Spectra of Ni(II) and Co(II) halide complexes with 1-mercapto-3-thiabutane (MMTH) (cm^{-1})

Compound	Ligand vibration	ν(M-X)	ν(M-S)
MMTE	430s, 408m, 365bm, 224w		
$Ni_2(MMT)_2 Cl_2$	450m, 438m, 406w	372s, 360m, 191w	326ms
$Ni_2(MMT)_2 Br_2$	447m, 426m, 406w	342s, 160w	322ms
$Ni_2(MMT)_2 I_2$	443m, 422m, 420w, 412w	281w, 272s, 100wb	360ms
$Co_2(MMT)_2 Cl_2$	432m, 422w, 390m	370s	336m
$Co_2(MMT)_2 Br_2$	429m, 420w, 382m	342s	330m
$Co_2(MMT)_2 I_2$	426m, 420w, 392m	290s	340m

Table 3.17

Assignment of Far Infrared Spectra of Ni(II) and Co(II) halides complexes with 1-mercapto-2-methoxy-ethane(MMEH)

(cm^{-1})

Compound	ν (M-X)	ν (M-O)	ν(M-S)
$Ni_2(MME)_2Cl_2$	370s	415w, 435m	340w, 342m
$Ni_2(MME)_2Br_2$	340s	434m	354w, 348m
$Ni_2(MME)_2I_2$	290s	440m	341m, 339w
$Co_2(MME)_2Cl_2$	380s	428m	364m
$Co_2(MME)_2Br_2$	345s	430m	361m
$Co_2(MME)_2I_2$	300s	425m	359m

Table 3.18

Assignment of Infrared Spectra of Ni(II) and Co(II) halide complexes with O'O-dimethyl S-(2-methylthioethyl) phosphorothiolate (DSPD)
(cm^{-1})

Compound	ν(P=O)	ν(M-O)	ν(M-L)	ν(M-X)	Others
DSPD	1250				450s, 418s, 385w, 320s, 260w
Ni(DSPD)Cl_2	1220	432m, 428m	445s, 424s	320s	394w, 245w
Ni(DSPD)Br_2	1220	434m	441s, 414s	270s	367m, 320s, 256w
Ni(DSPD)I_2	1220	435m	441s, 416s	240s	392w, 364w, 320s
Co(DSPD)Cl_2	1220	430m	448s, 417s	315s	385m, 344m, 280w
Co(DSPD)Br_2	1220	435m	444s, 418s	260s	390m, 360m, 286w

Far Infrared Spectra in the Range 450 - 80 cm^{-1}

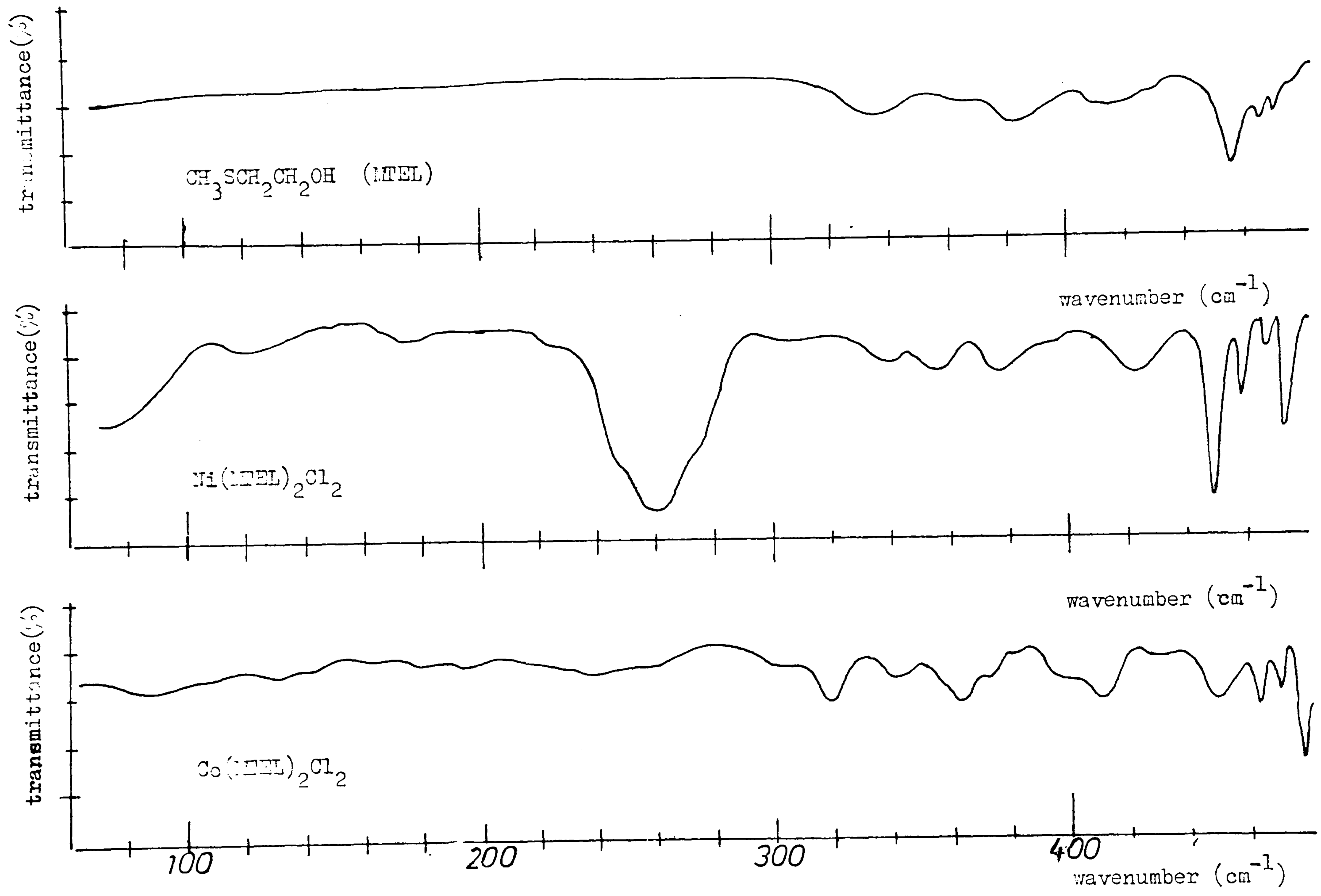


Figure fir 1

Far Infrared Spectra in the Range 450 - 80 cm^{-1}

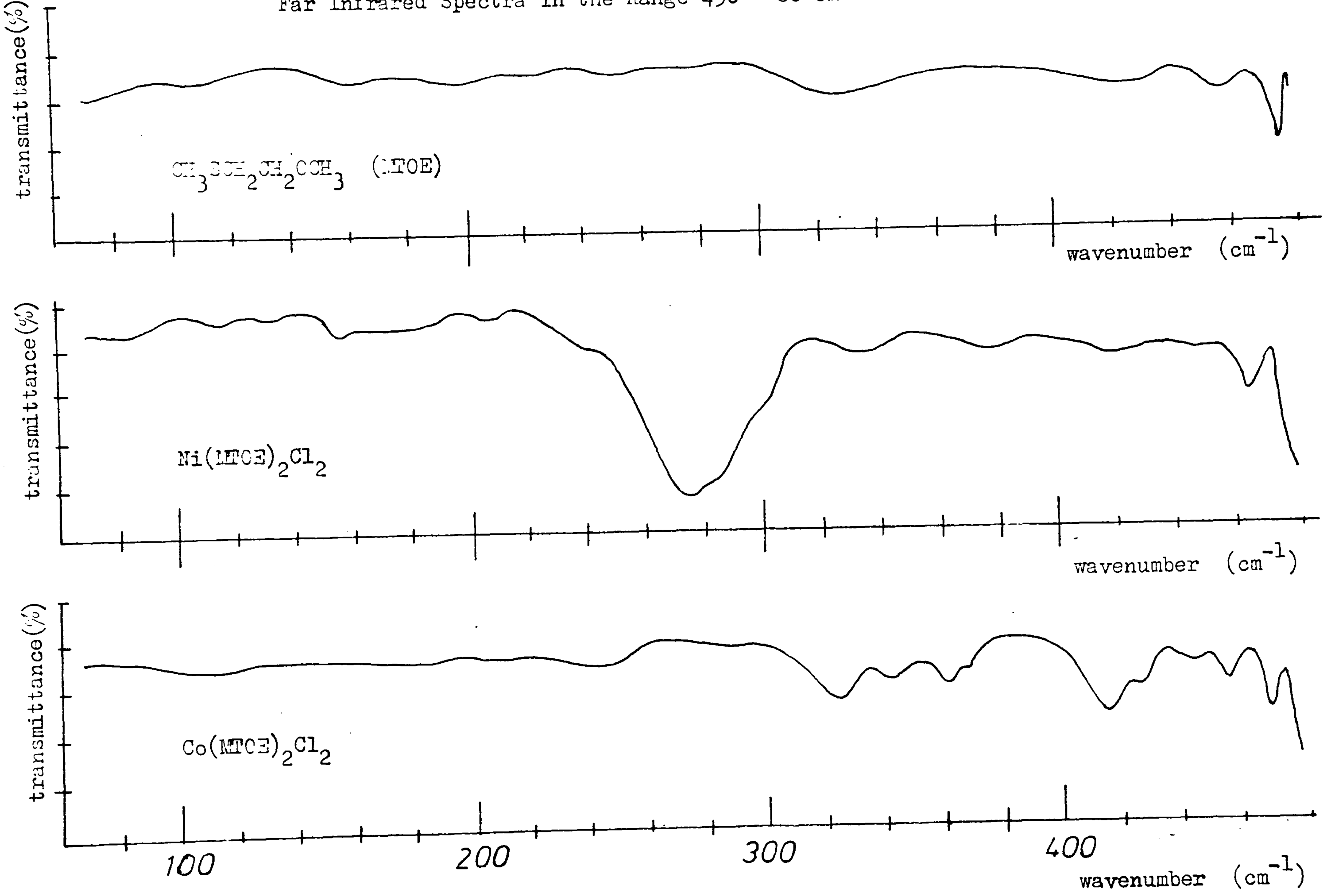


Figure fir 2

Far Infrared Spectra in the Range 450 - 80 cm^{-1}

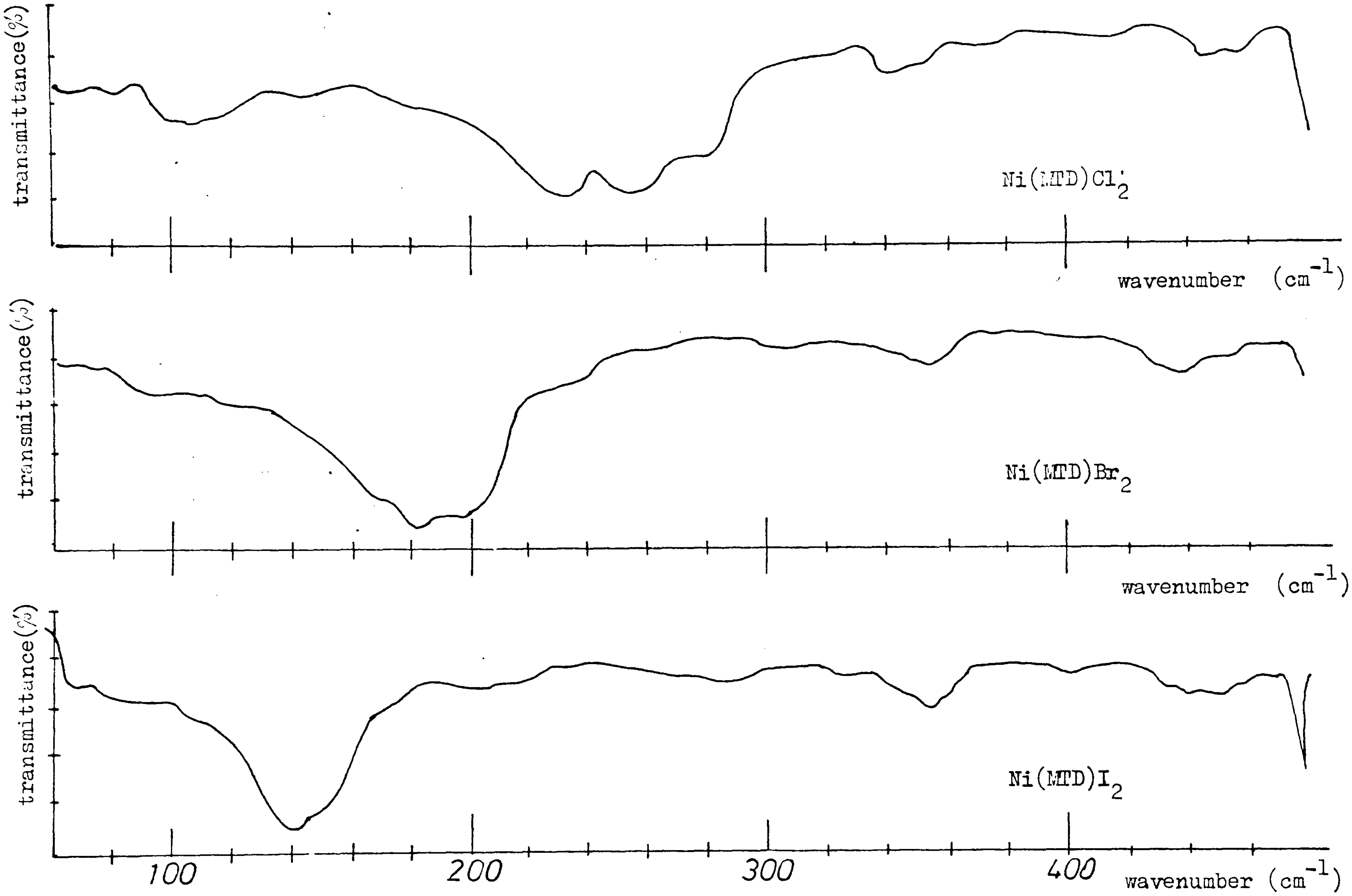


Figure fir 3

Far Infrared Spectra in the Range 450 - 80 cm^{-1} (------ Ligand spectra)

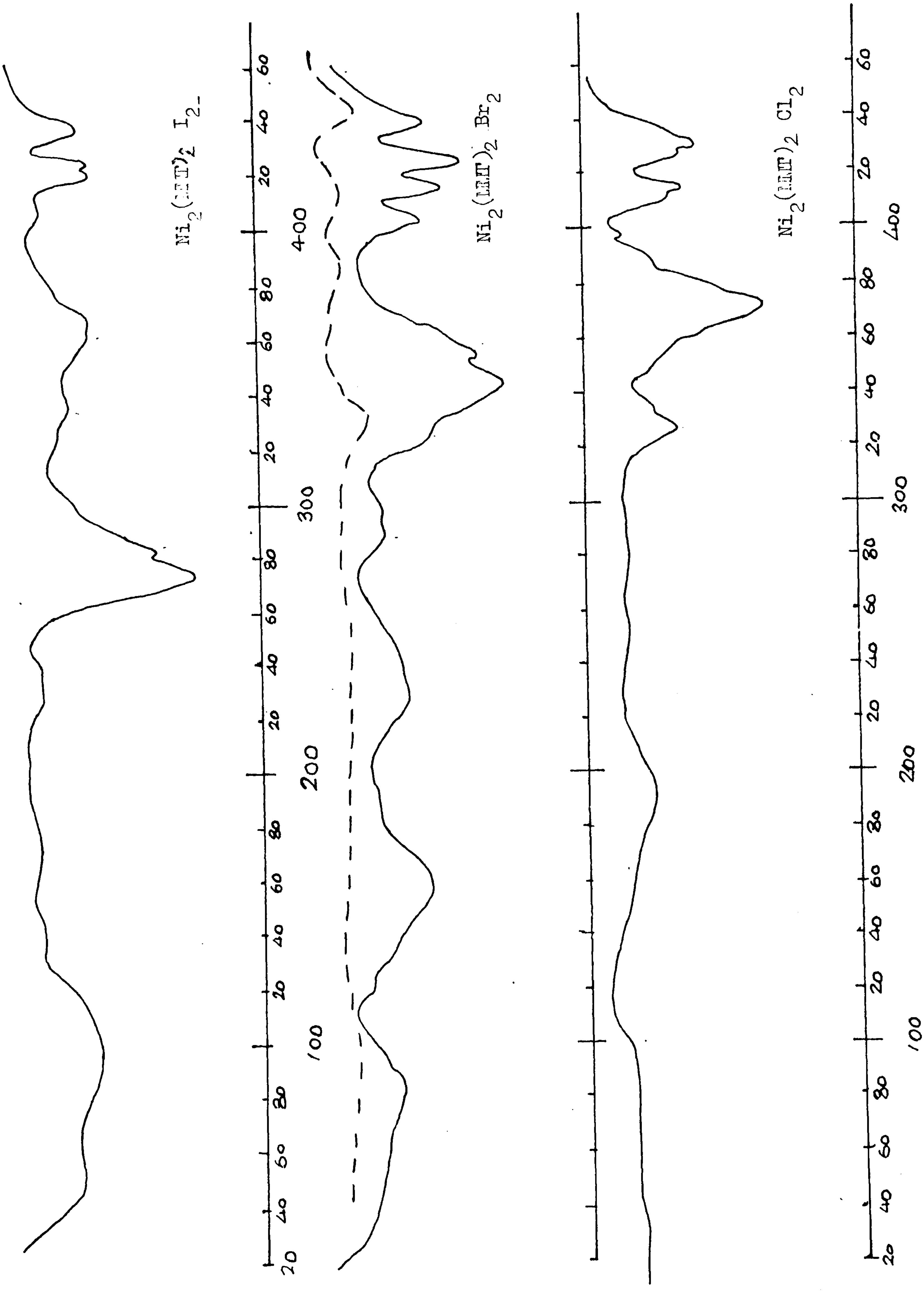


Figure fir 4

Far Infrared Spectra in the Range 450 - 80 cm^{-1}

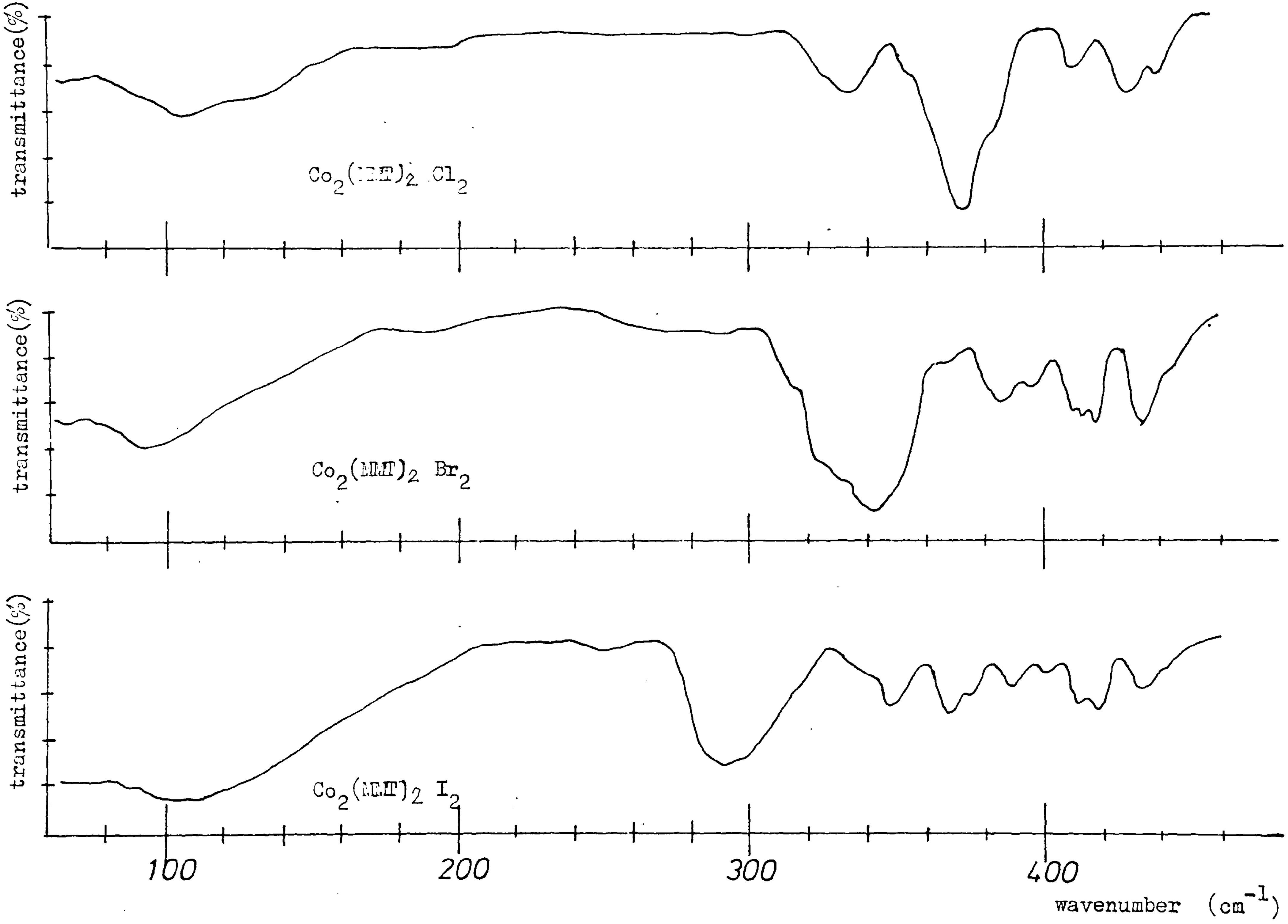


Figure fir 5

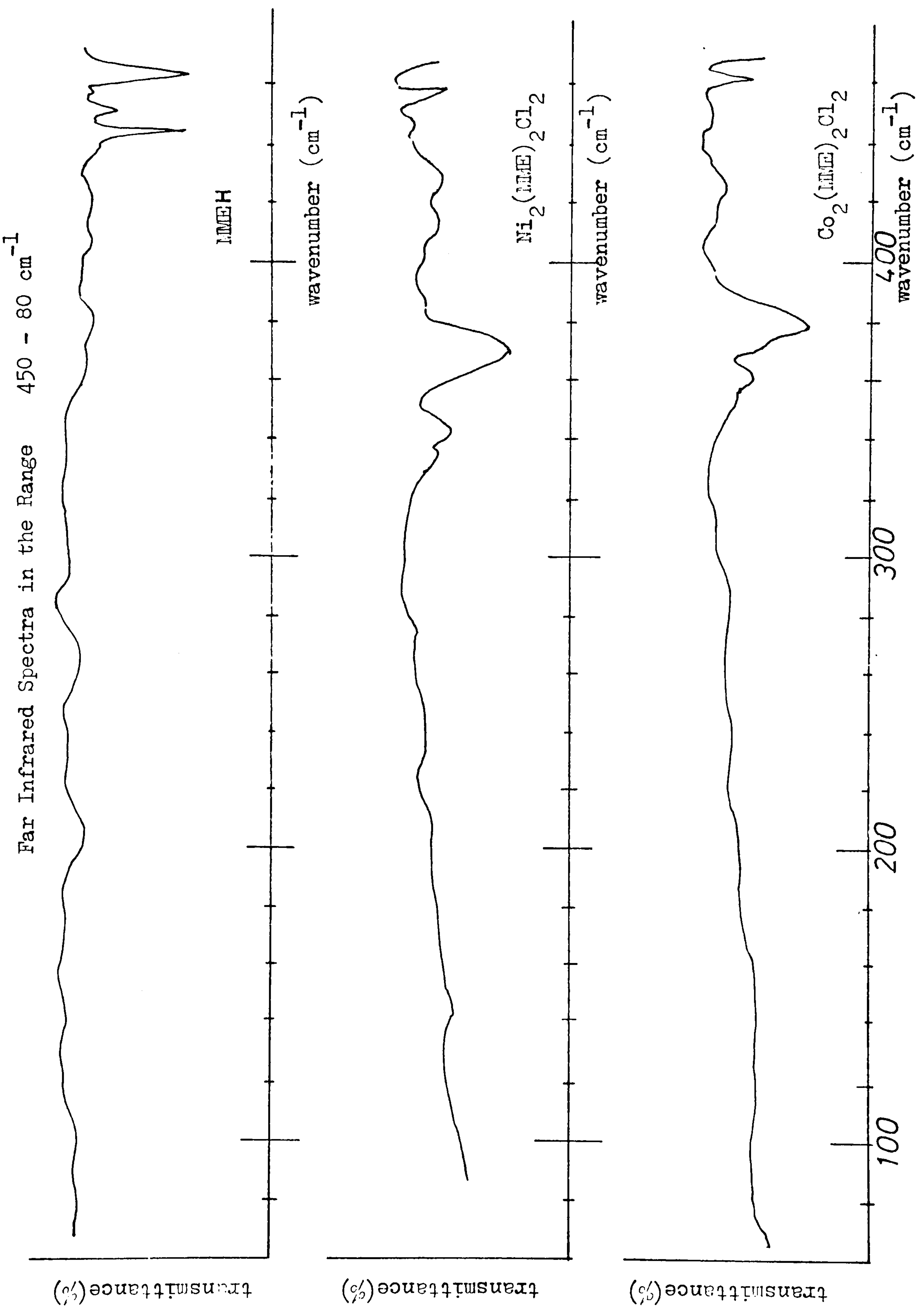

Far Infrared Spectra in the Range 450 - 80 cm^{-1}
MMEH
$Ni_2(MME)_2Cl_2$
$Co_2(MME)_2Cl_2$
wavenumber (cm^{-1})
wavenumber (cm^{-1})
wavenumber (cm^{-1})
400
300
200
100
transmittance(%)
transmittance(%)
transmittance(%)

Figure fir 6

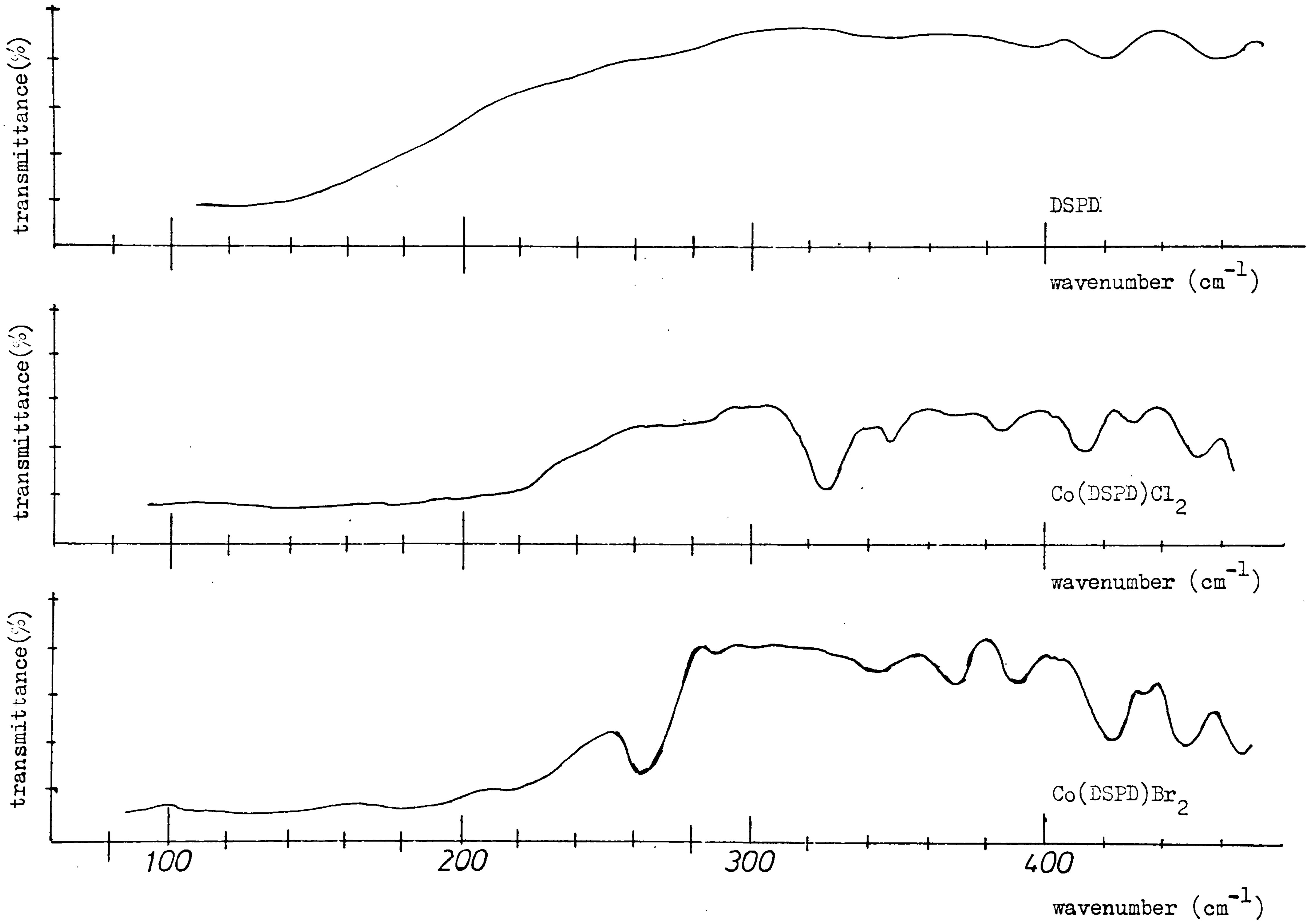

transmittance(%)
DSPD
wavenumber (cm^{-1})
transmittance(%)
Co(DSPD)Cl$_2$
wavenumber (cm^{-1})
transmittance(%)
Co(DSPD)Br$_2$
100
200
300
400
wavenumber (cm^{-1})

Figure fir 7

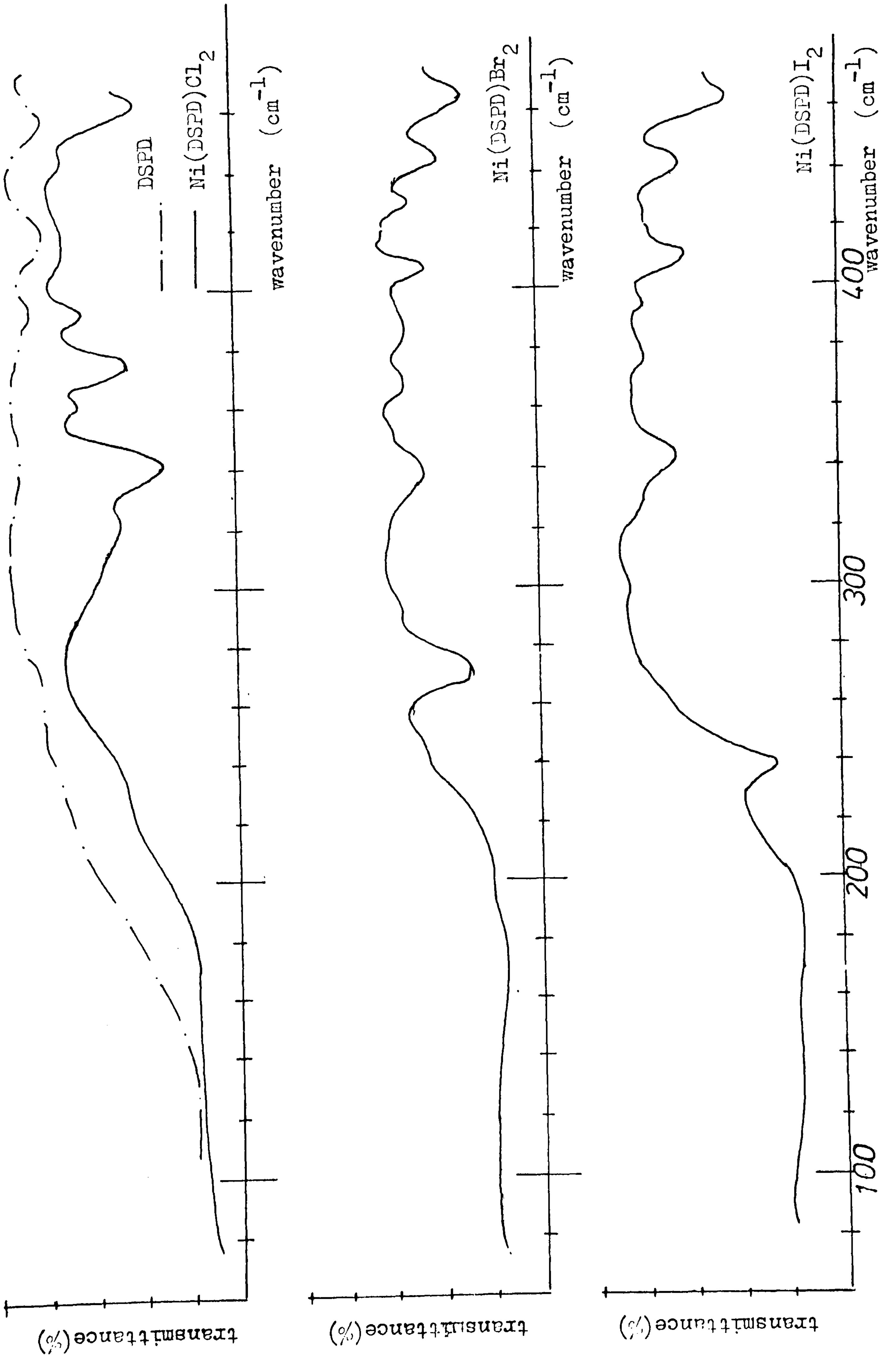

DSPD
Ni(DSPD)Cl$_2$
wavenumber (cm^{-1})
transmittance (%)
Ni(DSPD)Br$_2$
wavenumber (cm^{-1})
transmittance (%)
Ni(DSPD)I$_2$
wavenumber (cm^{-1})
transmittance (%)
400
300
200
100

Figure fir 8

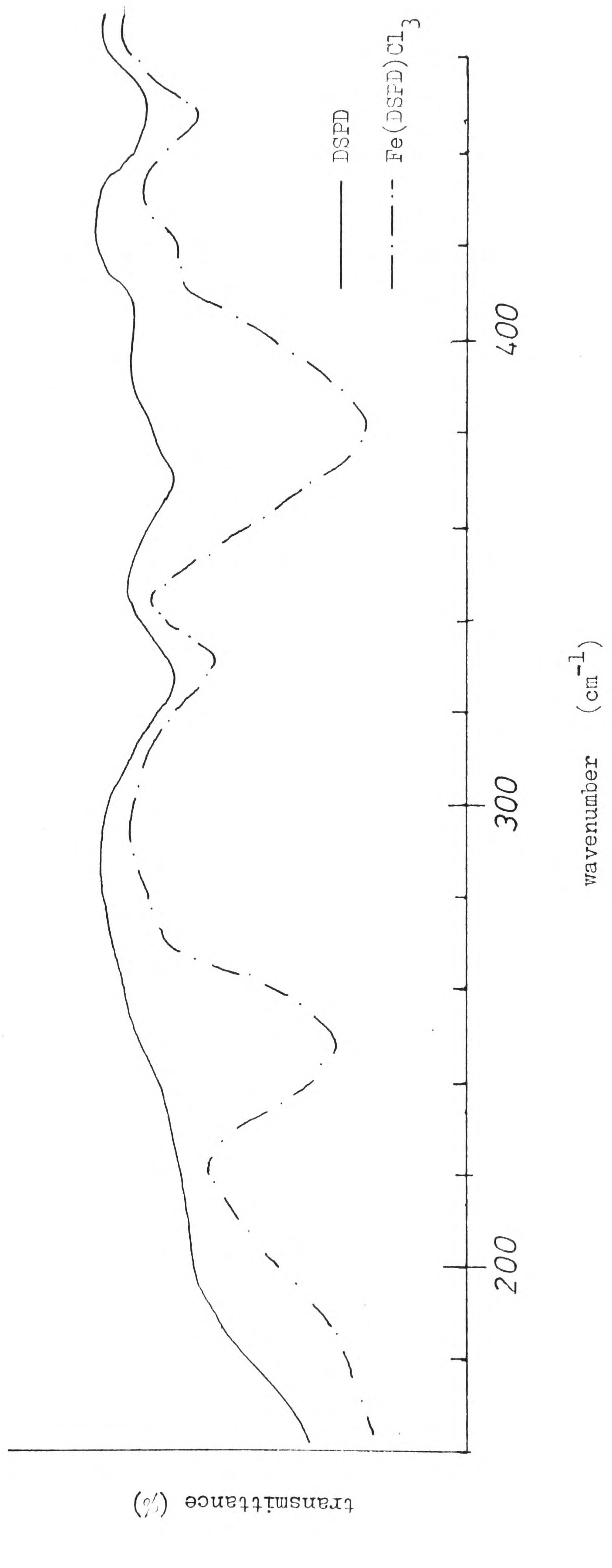


Figure fir 9

Table 3.19a

Colour and Analyses of Fe(III) chloride complexes with DSPD and Tinox

Compound	Colour	Analysis Result			
		M	C	H	X
Fe(DSPD)Cl_3	Pale Brown	15.8(15.2)	16.1(16.3)	3.48(3.53)	30.0(28.9)
Fe(Tinox)Cl_3	Pale Brown	15.6(15.2)	16.2(16.3)	3.52(3.53)	29.1(28.9)

Table 3.19b

Assignment of Far Infrared spectrum of ferric chloride complex with DSPD (cm^{-1})

Compound	Ligand Vibration	ν(M-X)	ν(M-L)
DSPD	450s, 418m,385m,320s,260w		
Fe(DSPD)Cl_3	450s,420m,325s	380	240

(4) Conductance Measurement

Conductance experiment provides useful information about the number of ions present in solutions of different complexes[117]. The greater the number of ions in a solution, the higher is the electrical conductivity of the solution. Therefore, a comparison of the conductivities of solutions containing the same concentrations of co-ordination compounds permits an estimate of the number of ions in each complex compound.

To obtain accurate information, the solvent used must not interact with the complex. In the present work nitromethane was normally employed for the experiment. The nitromethane used has been dried by molecular sieve and distilled, the fration boiling between 102-3^{o} was collected. The purified solvent had a specific conductance of 4.0×10^{-6} mhos. Solutions used for the experiment had a concentration of complex about 10^{-3}M.

The measurements were made using Mullard Conductivity Bridge (E 7556/3) and a conductance cell having dip-type platinum electrodes. The cell constant was determined with a standard solution of potassium chloride.

(5) Molecular Weight Determinations by Ebullioscopic Method

The ebullioscopic constant k_b of a solvent is the amount by which the boiling point of a molal solution would be raised.

The property is used in determination of the molecular weight of an unknown compound. In the experiment, it is not necessary to work directly with a molal solution of the particular compound. The dissolution of a non-volatile solute in a solvent reduces the vapour pressure. If the solution behaves in an ideal manner, obeying Raoult's law

$$p = x_1 p_1^o = (1-x_2)p_1^o$$

$$\text{or} \quad x = (p_1^o - p_1)/p^o = p/p^o$$

where the subscripts 1 and 2 refer to the solvent and the solute respectively i.e. the relative lowering of the vapour pressure is directly proportional to the mole fraction of the solute.

In the experiment, a known amount (w) of the compound is dissolved in an organic solvent (W) which does not interact~~ion~~ with the compound. The boiling elevation in the resulting solution was measured by a Beckmann thermometer which is sensitive to a difference of 0.002^o.

Calculation: Mg (the molecular weight of the compound) of solute would raise the boiling point of 1000g of the organic solvent by k^o (ebullioscopic constant). Hence, from the measured elevation ΔT when w g. of the compound have been dissolved in W g. of the solvent, the molecular weight M of the solute may be evaluated

$$M = (k/\ T)x(W/w)x1000$$

Due to the low k_b constant of most organic solvents, for an accurate determination of the molecular weight of the compound, it is necessary for the compound to have a relatively high solubility (concentration of 0.1 M, is usually required for reliable result). Furthermore, it is unlikely that there is absolutely no interaction between the solute and solvent molecules, thus the experiment seldom yields the exact formula weight However, it is the indication of the result obtained which is important. The result would indicate whether the compound is dimeric or monomeric or polymeric.

(6) Magnetic Susceptibility Measurements

Magnetic susceptibilities of the solid complexes were determined on a Newport Instruments Single Temperature Guoy Balance employing a water-cooled 'Newport' $1\frac{1}{2}$ inch electromagnet. A current of 1.1 amps per coil gave a field strength of ca. 5000 oersteds.

The gram susceptibility of the complex (Xg.) was calculate using the relationship

$$X_g = \frac{Kv + Bw}{W}$$

where k = volume of specimen

w = force exerted on specimen by field (corrected for the diamagnetism of the glass tube)

W = weight of specimen

B = a constant which depend on the dimensions of the specimen and on the magnetic field strength.

The constant B was determined by calibration of the apparatus using mercury tetrathiocyanocobaltate . The value of X obtained is the gram susceptibility of the substance, from which the molar susceptibility X_M, is obtained by multiplying this by the molecular weight. Allowance is made for the diamagnetism of the ligands,

$$X_A = X_M - X_L$$

where X_A is the susceptibility of the metal ion, X_L is the susceptibility of the ligands.

If the metal ion is paramagnetic X_A will be positive and the effective magnetic moment is given by

$$\mu_{eff} = 2.84(X_A T)^{\frac{1}{2}} \text{ Bohr magnetons}$$

where T is the temperature in degree absolute.

FERRIC THIOCYANATE EXPERIMENT

The effect of varying the concentration of the thiolo isomer solution in the extraction of ferric ion from a solution of ferric thiocyanate of known concentration was investigated by the experiment outlined below.

The ferric thiocyanate solution was prepared by adding sodium thiocyanate to a solution of 1M ferric sulphate solution. The thiocyanate to iron ratio was 3 to 1. This ratio was chosen so that the amount of iron extracted would be at optimum[128]. A fixed volume of this solution (15 ml.) was extracted with a series of thiolo solutions (20 ml. of 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M solutions in xylene).

The solutions were added in turn to a separating funnel and the mixture was shaken for one minute and was allowed to separate and the aqueous phase which was the denser of the two was drawn off. The absorbance of the organic layer was determined immediately in 1 cm. UV glass cell, to prevent error caused by colour fading on long standing (at 560 mμ). A solution of xylene was treated similarly with the ferric thiocyanate solution and was used as reference.

The results of the experiment are tabulated in Table 3.20, p.129 and the graph of absorbance against concentration of thiolo was plotted and is shown in Figure 3.1, p.128.

The linearity of the graph indicates that the amount of ferric thiocyanate extracted is directly proportional to the concentration of the thiolo solution.

Concentration	0.0 5M	0.1M	0.2M	0.3M	0.4M	0.5M
Absorbance	-	·13	·22	·35	·42	·55

Table 3.20

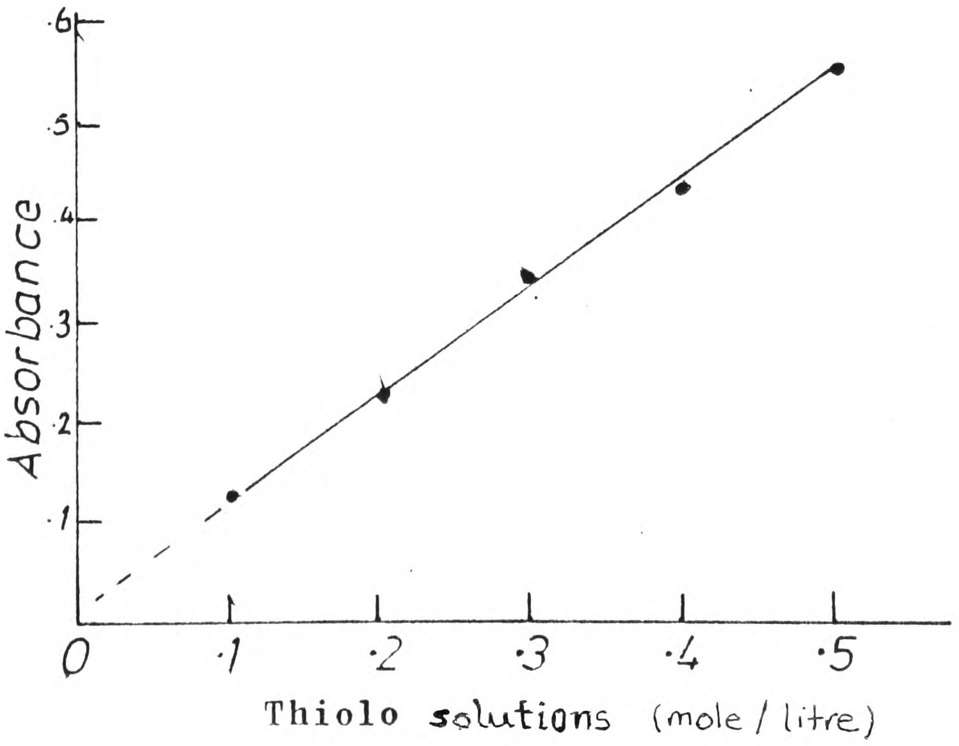


Figure 3. 1

IV

DISCUSSION

CONTENTS

4.1 Nickel(II) chlorides complexes of 3-thiabutanol $CH_3SCH_2CH_2OH$ MTEL

High spin $Ni(MTEL)_2X_2$ complexes are obtained by the reaction of nickel(II) halides with the ligand in ethanol under anhydrous condition. The complexes obtained are hygroscopic and decompose on prolonged exposure to the atmosphere. Elemental analysis (Table 3.1, p.84) gives a stoichiometric formula of $Ni(MTEL)_2X_2$ and molecular weight determination in chloroform indicates that the complexes are in monomeric form with molecular weight corresponding to the stoichiometric formula. Magnetic susceptibilities measured at room temperature using a Guoy balance (μ_{eff}= 3.1-3.3 B.M.) listed in Table 3.1, p.84 are typical for nickel(II) ion in an octahedral environment. Conductance measurement obtained for 10^{-3}M solution in nitromethane showed that the complexes are essentially non-electrolytes[117], which is indicative of the absence of ionic halides.

Electronic Spectra: The diffuse reflectance spectra of the complexes (Table 3.6, p.94; Figure 4.1, p.134) are typical of nickel ion in co-ordination number six with three well defined electronic transitions between the triplet states of the O_h system (p.37). Since the ligand fields in these compounds are not regular octahedron, the expected splitting of the orbital triplet levels is observed (p.40). As the complexes retain the same stereochemistry in nitromethane, the discussion of the electronic transitions will be based on the more detailed spectra in solution (Figure 4.2, p.134). The latter are very similar to the solid diffuse reflectance spectra. The three absorption maxima are found in the range 8300-8800, 13000-14500 and 21000 -25500 cm^{-1} corresponding to the three spin allowed transitions

Figure 4.1 Diffuse reflectance electronic spectra of $Ni(MTEL)_2X_2$

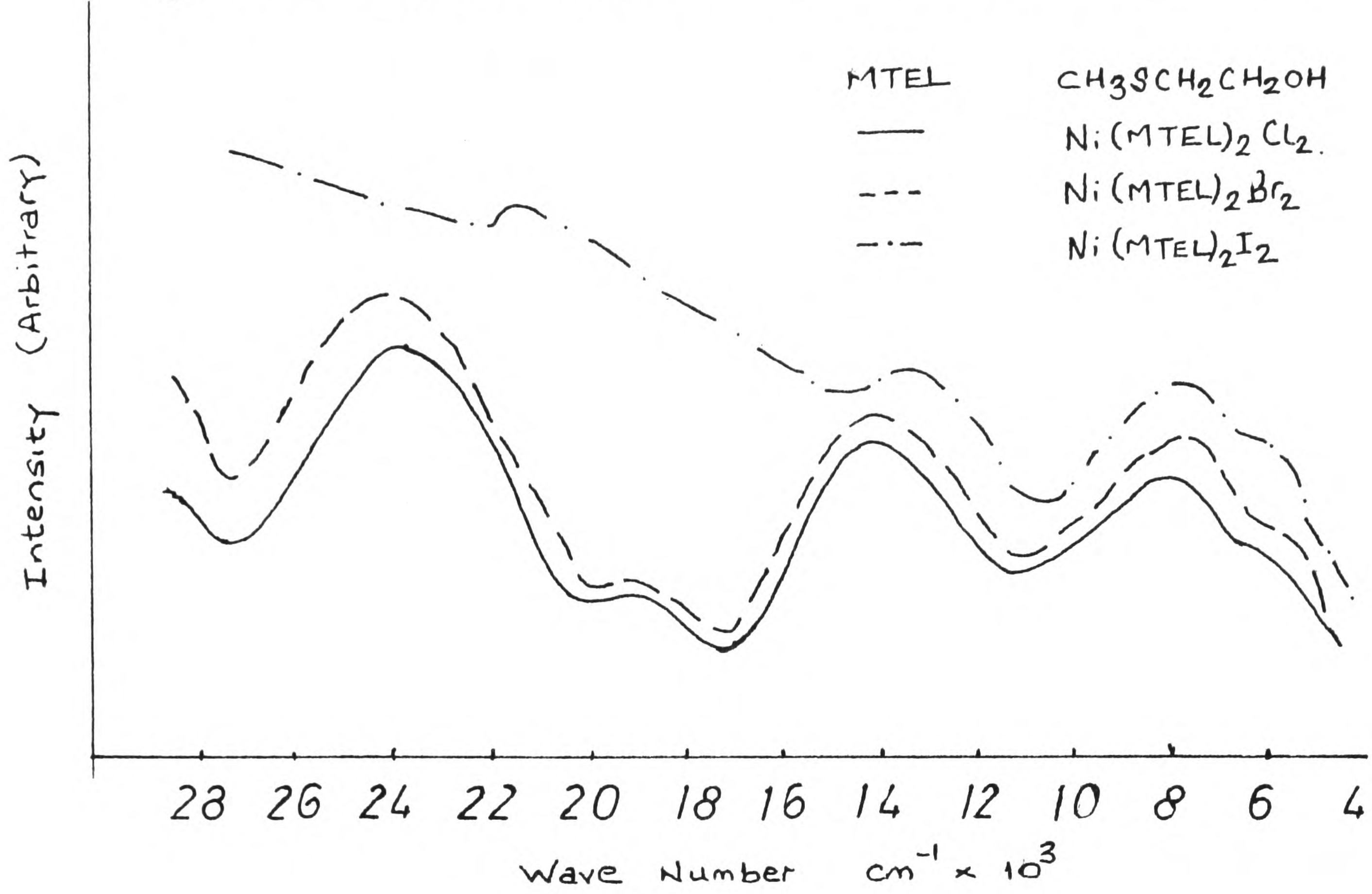
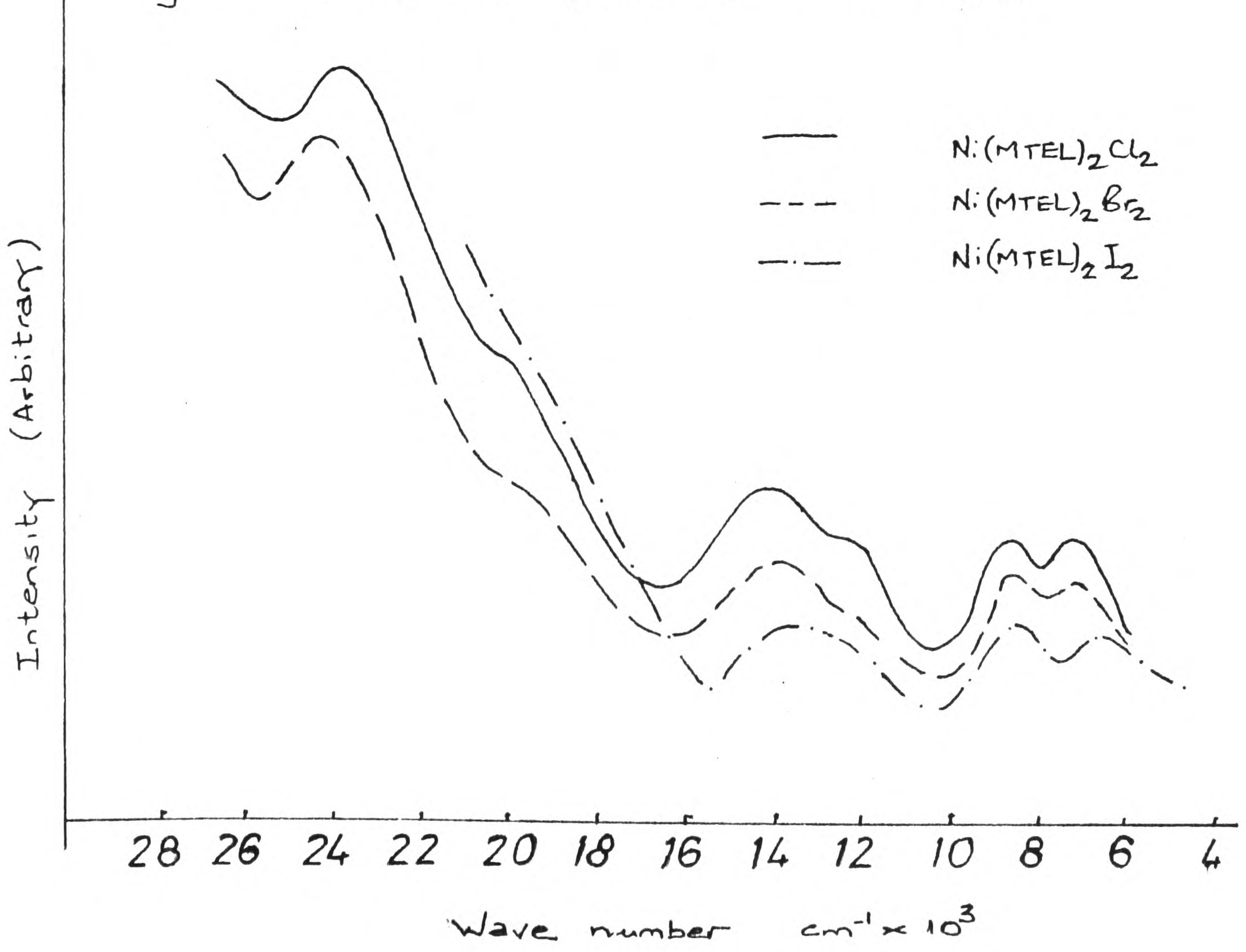


Fig. 4.2 Solution spectra of $Ni(MTEL)_2X_2$



due to $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1), $^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2) and $^3T_{2g}(P) \leftarrow {}^3A_{2g}$ (ν_3), respectively.

The tetragonal distortion is reflected in the splitting of the ν_1 band into two components at about 8700 and 7800 cm^{-1}. This splitting is clearly resolved in the solution spectra but not so in the reflectance spectra of the solid. The relationship between the free-ion octahedral and tetragonal field splitting of the d orbital is discussed in the Theory Section (p.40) and schematically illustrated in the diagram in Figure 2.3, p. 40. The two near infrared transitions are assigned to the transitions arising from the splitting of the $^3T_{2g}(F)$ in octahedral symmetry on going to D_{4h} symmetry (strictly speaking the symmetry should be D_{2h} as the in-plane ligands consists of two oxygens and two sulphurs) and have energies of $10Dq^E$ and $10Dq^E - 35Dt/4$. In the case of $Ni(MTEL)_2X_2$, Dt is positive as the halides are lower down in the spectrochemical series[26] than the oxygen and sulphur, the bands are assigned as $10Dq^E$ (ca. 8700 cm^{-1}) and $10Dq^E - 35Dt/4$ for the transitions $^3B_{2g} \leftarrow {}^3B_{1g}$ and $^3E_g \leftarrow {}^3B_{1g}$, respectively. The calculation is tabulated in Table 4.1, p.134. The in-plane field strength of about 870 cm^{-1} is found to be between that of $Ni(O_4)X_2$ and that of $Ni(S_4)X_2$ which are in the range of 830-860 cm^{-1} and 920-1020 cm^{-1}, respectively[45,46,81,82] (where (O_4) and (S_4) indicated the in-plane ligands are four oxygen and four sulphur atoms, respectively). The result is as expected because the co-ordination is probably through the oxygen of the hydroxyl group and sulphur of the thioether group of the molecule and this would involve two oxygen and two sulpur atoms for the in-plane field.

The axial field strengths calculated at about 690-720 cm^{-1}

Compound	$^3B_{2g} \leftarrow {}^3B_{1g}$ cm^{-1}	$^3E_g \leftarrow {}^3B_{1g}$ cm^{-1}	Dq^E cm^{-1}	Dq^A cm^{-1}	β_{35}
$Ni(MTEL)_2Cl_2$	8750	7975	875	720	0.77
$Ni(MTEL)_2Br_2$	8700	7875	870	705	0.75
$Ni(MTEL)_2I_2$	8710	7800	870	690	0.75

Table 4.1 Low energy bands, Dq^E, Dq^A and β_{35} parameters for $Ni(MTEL)_2X_2$.

Compound	$^3B_{2g} \leftarrow {}^3B_{1g}$ cm^{-1}	$^3E_g \leftarrow {}^3B_{1g}$ cm^{-1}	Dq^E cm^{-1}	Dq^A cm^{-1}	β_{35}
$Ni(MTOE)_2Cl_2$	8600	7950	860	740	0.78
$Ni(MTOE)_2Br_2$	8605	7900	861	725	0.77
$Ni(MTOE)_2I_2$	8500	7750	859	717	0.76

Table 4.2 Low energy bands, Dq^E, Dq^A and β_{35} parameters for $Ni(MTOE)_2X_2$.

are similar to those expected for a MX_6 compound (X=Cl, Br, I). These results (Table 4.1, p. 136) are in accordance with the stereochemistry of the compounds as the in-plane ligands MTEL is non-bulky and should not interfere with the axial positions. Furthermore the axial field strength decreases as the halogen changes from chloride to bromide to iodide (720, 705 and 694 cm^{-1}, respectively), which strongly support the suggestion that the halogens are co-ordinated in the axial position[44].

As pointed out in the Theory Section (p.42), the splitting of the higher energy transition bands are not likely to be resolved at room temperature spectra. However, it is observed that the bands are asymmetric, showing pronounced shoulders on the lower energy side (Figure 4.1 and 2, p.134) which are due to singlet-triplet transitions. The asymmetric appearance of the bands also indicates tetragonal distortion of the structure[70].

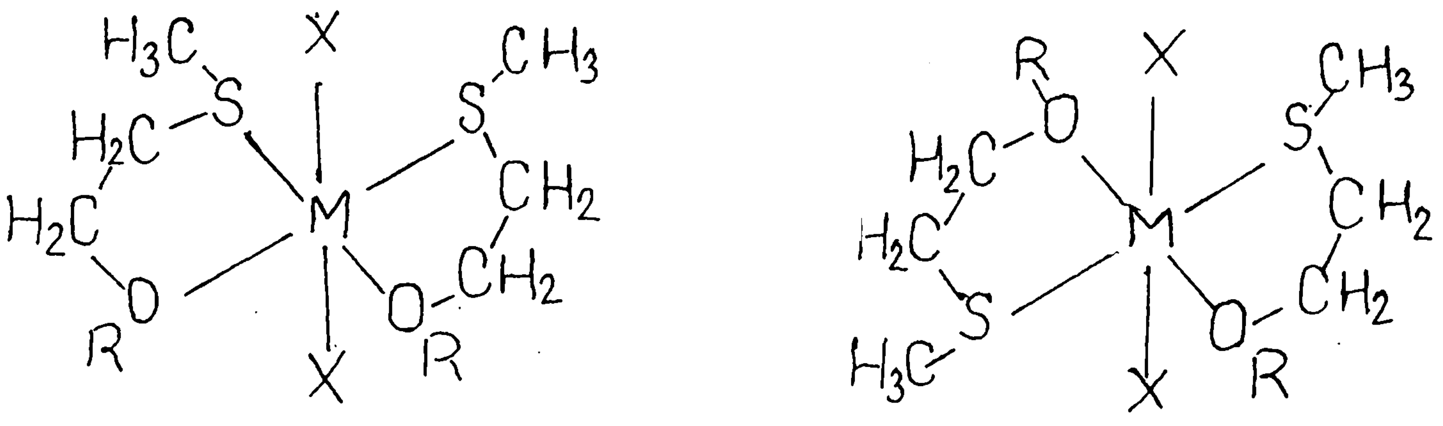
Further evidence for the terminal metal halogen bond is the intense charge transfer band which moves from the chloride to the iodide to lower energy so that the bands of the $Ni(MTEL)_2I_2$ are not well defined.

<u>Infrared Spectra (4000-450 cm^{-1})</u>: The infrared spectra of the complexes are similar in appearance but all differ considerably from that of the ligand itself. Shift to lower frequencies and broadening of the (OH) stretching frequency is observed in all the spectra of complexes, which strongly supports the assumption that the hydroxyl group acts as a co-ordination site[119]. It is difficult to assigned a "structurally altered" band to indicate the thiol-ether co-ordination. This is due to the fact that thiol-ether has very weak vibrational absorption bands[120] in this region and these are normally hidden by other

stronger modes of vibration exhibited by the ligand. However, the observed change in the spectra in the region 1300-450 cm^{-1} strongly suggests that a deformation of the vibration modes of the ligand occurs on chelation. In addition to this change, there is also an overall shift of the absorption bands in this region to lower frequencies (Figure IR 11, p.102) which may be caused by a slight resonance effect resulting from ring formation on chelation. The sulphur and oxygen atoms in the ligand are well positioned for a five membered metal-chelate ring.

Far Infrared Spectra (450-80 cm^{-1}): The spectrum of the ligand showed four weak absorptions at 446, 402, 384 and 332 cm^{-1}, all the complex spectra are very similar in appearance (Figure fir 1, p.115) and six to eight absorption bands are found of which none could be related to the free ligand vibration. Due to the complexity of the complex spectra in this region, it is not possible to assign individual bands to their vibrational origin It is tentatively assumed that the bands between 450-350 cm^{-1} are mainly due to ν(Ni-O) stretching frequencies[101-5] and ligand internal vibration modes and those at 280-350 cm^{-1} are the ν(Ni-S) absorption band[99-100]. In contrast to the metal-ligand situation, very strong halogen sensitive bands are observed at 246 cm^{-1} for chloride, 198 cm^{-1} for the bromide and 150 cm^{-1} for the iodide. The band positions and their relative energies are consistent with their assignment as stretching vibrations for terminal ν(Ni-X) band in an octahedral nickel complex[95].

Thus the spectral evidence strongly supports the assumption that the ligand MTEL is bidentate and the co-ordinating centres are sulphur and oxygen atoms. With nickel halides the ligand forms high spin octahedral complexes and all the halides are co-ordinated to the metal ion as shown in Figure 4.3, below. No definite assignment as to which of the cis and trans structure is the correct one for the complex could be made.



Cis (a) Trans (b)

Figure 4.3 Proposed structures for Ni(MTEL)$_2$X$_2$
(M=Ni, X=Cl, Br, I; R=OH, CH$_3$)

4.2 Nickel(II) halides complexes of 1-methoxy-3-thiabutane $[CH_3SCH_2CH_2OCH_3]$ MTOE

The complexes prepared by reacting nickel halides and the ligand MTOE under anhydrous conditions are very similar to corresponding MTEL (3-thiabutanol) nickel(II) halides complexes. This is in some ways expected since the MTEL differs from the MTOE only by the presence of a hydroxyl group instead of a methoxy group and complexation reaction of MTEL does not involve the loss of hydrogen proton from the hydroxyl group.

All the complexes are soluble in nitromethane and acetone, although solvolysis does occur in the latter, which is indicated by the high conductance of the complexes in acetone. In nitromethane at concentration 10^{-3}M, the nickel complexes are essentially non-electrolytes with Λ at ca. 15 $cm^2 ohm^{-1} mole^{-1}$ (Table 3.8, p.95). Molecular weight determination in chloroform indicated that the complexes are monomeric with molecular weight corresponding to their stoichiometric formula obtained from the elemental analysis (Table 3.2, p. 85), which is $Ni(MTOE)_2X_2$ (X=Cl, Br, I). The magnetic susceptibilities (μ_{eff} = 3.4-3.5 B.M.) are characteristic of nickel in high spin octahedral stereochemistry.

Electronic Spectra: The reflectance spectra of the complexes (Table 3.8, p.95) showed absorption bands at 23900-22800, 15000-13000 and 9000-7000 cm^{-1} which are characteristic of Ni(II) ion with a co-ordination sphere of approximately octahedral stereochemistry. The tetragonal distortion (as with the case of MTEL complexes) is reflected by the splitting of the lowest energy electronic transition at about 9000 and 7800 cm^{-1}. Similar to the MTEL complexes the axial co-ordination of the halides is indicated by the decrease in the axial field strength from chloride to bromide to iodide. The solution spectra of these complexes in nitromethane at concentration 10^{-3}M are very similar to their reflectance suggesting that the complexes retain the same stereochemistry in solution (Table 3.8b, p.96). The coefficient of extinction obtained from the solution spectra listed in Table 3.8b are in the low range values expected of nickel(II) ion in octahedral environment.

The Dq^E, Dq^A and β_{35} values calculated from the spectra are compared with those obtained for the MTEL complexes (Table 4.2, p.136). The similarities between the corresponding sets of crystal field parameters (MTOE: Dq^E = 860 cm^{-1}, Dq^A = 760 cm^{-1} for Cl and β_{35} = 0.77; MTEL: Dq^E = 870 cm^{-1}, Dq^A = 720 cm^{-1} for Cl and β_{35} = 0.78), indicated strongly that the ligand MTOE and MTEL have the same chelation reaction, chelating through oxygen of the ether and sulphur of the thio-ether groups.

Far Infrared Spectra (450-80 cm^{-1}): Table 3.14, p.110 listed the results of the far infrared spectra of the ligand and the nickel halides complexes. The ligand MTOE has three broad and weak bands observed at 450, 420 and 310 cm^{-1}, and the lower region is, like MTEL, transparent. These bands for the ligand are not observed in the complex spectra. This may be due to their weak absorption or more likely the deformation of the ligand on chelate formation yields different absorption bands. The spectra of the complexes have general similarities in their appearances and are all complicated with a number of absorption bands. Except for the halogen to metal bands which are easily identified because of their high intensity and their sensitivity to the change of the halide ions, the rest of the spectra could not be analysed effectively.

The halogen sensitive bands are observed at 280 cm^{-1} for chloride, 220 cm^{-1} for bromide and 155 cm^{-1} for iodide. It is interesting to note that these halogen sensitive bands for the MTOE complexes are found at higher frequencies than those of MTEL complexes which showed absorptions at 246 cm^{-1} for chloride, 198 cm^{-1} for bromide and 150 cm^{-1} for iodide. This suggests that the halogen co-ordinates more strongly to the metal in MTOE complexes than those of MTEL complexes. A possible explanation for this observation is that MTOE is a weaker ligand. This is also reflected on the crystal field parameters of both ligands. The MTEL has a higher Dq^{E} value (MTEL = 875, MTOE = 860 cm^{-1}) and a lower Dq^{A} value (MTEL = 720, MTOE = 740 cm^{-1} for the chloride complexes), which may be interpreted as the MTOE co-ordination to nickel ion is stronger than that of MTEL and vice versa with the halide ions in the corresponding sets of complexes.

The infrared spectra of the complexes in the middle infrared range (4000-450 cm^{-1}) are very similar to each other but different from the free spectrum, as illustrated by the spectra of $Ni(MTOE)_2Cl_2$ and MTOE in Figure IR 12,p.103. The difference in the spectra of complexes suggests that there is a deformation of the vibration modes of the free ligand on chelation. Though, it is difficult to assign any individual change on the spectra to its origin, the overall shift of the bands to the lower frequency region is indicative of ring formation (p.138). As with the ligand MTEL the oxygen and sulphur atoms in the ligand MTOE are favourable positioned for the formation of a stable five-membered ring[121]. This lends further support to the proposed chelation mode of the ligand which was via the oxygen and sulphur atoms and the complexes formed are likely to have a structure illustrated in Figure 4.3, p.139.

4.3 Nickel(II) halides complexes of di-(2-methylthioethyl) disulphide, $\boxed{(CH_3SCH_2CH_2S)_2}$,MTD

The two bidentate thio-ether and ether ligand MTEL and MTOE (p.133 and p.140, respectively) studied have both shown better co-ordinating properties towards nickel(II) than the monodentate thio-ether ligand, dimethyl sulfide[27]. It appears that the additional chelating site enhances the co-ordinating properties of the ligand. Thus, it would be interesting to investigate the co-ordinating properties of ligands with more than two potential sites for comparison.

The disulphide, di-(2-methylthioethyl) disulphide (MTD) found as a breakdown product in the Tinox formulation offers an opportunity for this investigation, because there are four thio-ether atoms present in this molecule, thus representing four potential co-ordinating sites.

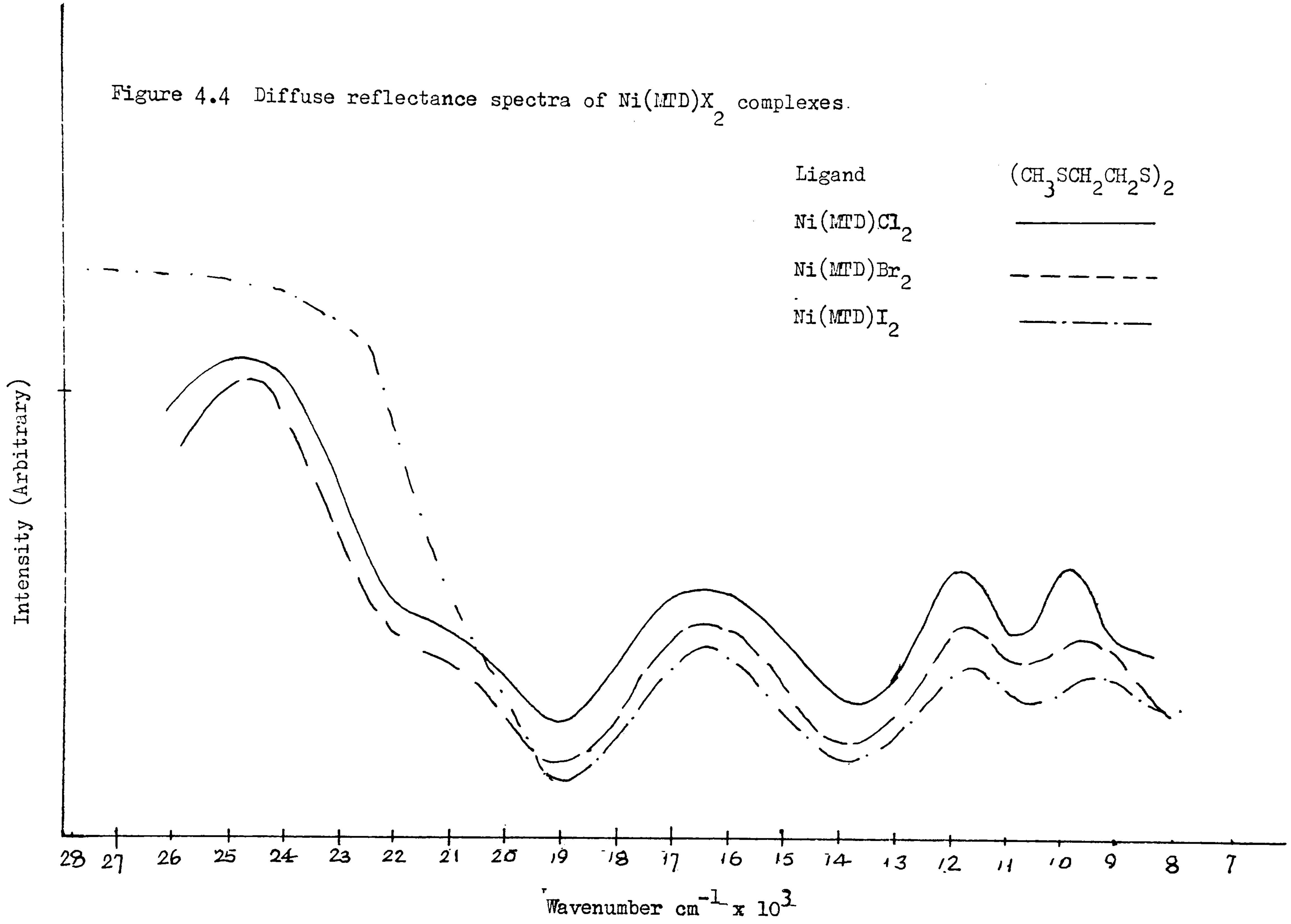
Under the same experimental conditions as those used for the preparation of nickel complexes with neutral ligands like MTEL and MTOE, complexes of nickel(II) halides with the disulphide ligand (MTD) of the type Ni(MTD)X_2 (X=Cl, Br, I) were obtained. The complexes with bromide and iodide were isolated pure and although the chloride complex was also obtained, the analysis resulted (Table 3.3, p.86) showed that there is a small excess of ligand. Once formed the complexes are insoluble in most organic solvents but dissolve with decomposition in polar solvents. Hence, it was not possible to measure the conductance behaviour of the complexes and no molecular weight determination was made. The complexes are highly hygroscopic and decompose if exposed to the atmosphere.

The magnetic moments reported in Table 3.9, p.97 are in the range of 3.3-3.4 B.M. indicating that the nickel ion is present as high spin and the stereochemistry of the complexes is likely to be octahedral. This is confirmed by the reflectance spectra of the complexes.

Electronic Spectra: The spectral results for the three complexes are given in Table 5.9, p.97. The spectra showed characteristic absorptions of Ni(II) ion with a co-ordination sphere of approximately octahedral stereochemistry. The tetragonal distortion is reflected on the splitting and the positions of the lowest energy transition and also the presence of a shoulder at about 20000 cm^{-1} on the lower energy side of the highest energy transition d-d band occuring at 24000 cm^{-1} (Figure 4.4, p.146). The splitting of the lowest energy transition is due to the splitting of the $^3T_{2g}(F)$ in octahedral symmetry on going to D_{4h} symmetry. A consideration on the ligand strength of the halides and the thio-ether leads to the following band assignments of the two bands. The lowest energy transition occurring at 8900 cm^{-1} is assigned to the ^3E_g transition and the next higher energy to the ^3B_g transition at ca. 1100 cm^{-1}.

No splitting of the $^3T_{1g}(F)$ and $^3T_{2g}(P)$ transitions were observed. The pronounced shoulder on the lower energy of the transition at 24000 cm^{-1} is probably due to the two spin forbidden transitions ^1E_g $^1T_{2g}(D)$ and $^1A_{1g}$ $^1A_{1g}(G')$. The large splitting of the $^3T_{2g}$ transition strongly suggests that the complexes have trans octahedral structures with the halides co-ordinated in the axial positions. This assumption is supported by the value of the Dq^A calculated from the complex apectra (Table 4.3, p.148) with chloride = 715, bromide = 694 and iodide = 673 cm^{-1}, which are very similar to those expected for MY_6

Figure 4.4 Diffuse reflectance spectra of Ni(MTD)X_2 complexes.



compounds which have Dq($NiCl_2$) = 720, ($NiBr_2$) = 700 and (NiI_2) = 680 cm^{-1} [83]. This agreement would be expected for the trans stereochemistry with non-bulky in-plane ligands. Table 4.3,p.148, lists a series of octahedral nickel complexes with in-plane su sulphur ligand and axial halogen co-ordination and other axial halogen co-ordinated complexes with various non-bulky in-plane ligands. A comparison of the low energy band, Dt, Dq^E and Dq^A parameters of these complexes leads to the supposition that the complexes of nickel halides with MTD are co-ordinated by four sulphur atoms on the in-plane and two halide ions in the axial positions. Significantly lower band energies would be expected if the structure of the complexes were cis octahedral for Dq^E and higher for Dq^A(p.40).

The Dq^E value further substantiates the argument that the in-plane environment of the nickel complexes is 4(S), as the value (ca.11000 cm^{-1}) is expected for such an arrangement.

Infrared Spectra (4000-450 cm^{-1}): The spectra of the complexes are almost identical to each other and is illustrated in Figure III 13, p.104, by the spectrum of the chloride complex. The difference of the spectra of complexes from the free ligand spectrum is attributed to the restricted configuration of the ligand on chelation.

Far Infrared Spectra (450-80 cm^{-1}): Table 3.15, p.111 lists the far infrared spectra of the ligand and various complexes. Over this range the ligand is essentially transparent and only three weak bands are observed at 450, 410 and 380 cm^{-1}. Only one of these bands (450 cm^{-1}) was observed in the complex spectra. In spectra of complexes halogen sensitive bands are observed at 235 and 260 cm^{-1} for the chloride, at 183 and 200 cm^{-1} for

Table 4.3

Comparison of low energy band Dt, Dq^E and Dq^A parameters of $Ni(MTD)X_2$ complexes with other similar systems

Compound	$^3B_{2g} \leftarrow {}^3B_{1g}$	$^3E_{2g} \leftarrow {}^3B_{1g}$	D_t	D_q^E	D_q^A	ref.
$Ni(MTD)Cl_2$	11050	9100	222.8	1105	715	this work
$Ni(MTD)Br_2$	11000	8970	232	1100	694	"
$Ni(MTD)I_2$	11000	8864	244	1100	673	"
$Ni(2,5dithiahexane)_2Cl_2$	10600	9000	182	1060	743	44
$Ni(2,5dithiahexane)_2Br_2$	10600	8910	193.1	1060	723	44
$Ni(2,5dithiahexane)_2I_2$	10900	8800	240.1	1090	670	44
$Ni(Etu)_4Br_2$	8550	7460	125	855	636	93
$Ni(Etu)_4Cl_2$	8550	7800	86	855	705	93
$Ni(bme)Br_2$	10200	8850	154.2	1020	740	47
$Ni(bme)I_2$	10300	8750	177.1	1030	730	47
$Ni(bmp)I_2$	10300	8930	156.5	1030	750	47
$Ni(TTP)Cl_2$	10640	9260	157.7	1064	710	46
$Ni(TTP)Br_2$	10640	9010	186	1064	739	46
$Ni(TTP)I_2$	10990	8960	232	1099	699	46

Etu: ethylene thiourea, bme: 1,2 bis(θ-methylthiophenylthio)ethane, bmp: 1,3 bis(O-methylthiophenylthio)propane,

TTP: **1,4,8,11-tetrathiacyclotetradecane**, the bromide and at 140 and 157 cm^{-1} for the iodide. The band positions are consistent with their assignment as Ni-X stretching vibrations in an octahedral nickel complexes[93-95]. In particular the energies reflect the presence of terminal nickel-halogen bands, rather than bridging bonds[95]. A weak band at about 350 cm^{-1}, which is observed in all the complexes may be associated with the Ni-S stretching vibration[99].

All the spectral evidence is consistent with the proposition that the complexes are octahedral in structure with halide ions co-ordinated terminally on the z axis. For the complexes to attain an octahedral symmetry under these conditions, it would be necessary, for all the four sulphur atoms in the ligand molecules to be co-ordinated. The linearity of the ligand molecule would prevent all the four sulphur atoms to be attached to one metal ion, thus it would be reasonable to expect that the structure of the complexes to be polymeric with each ligand attached to two metal ions as shown in Figure 4.5, below,

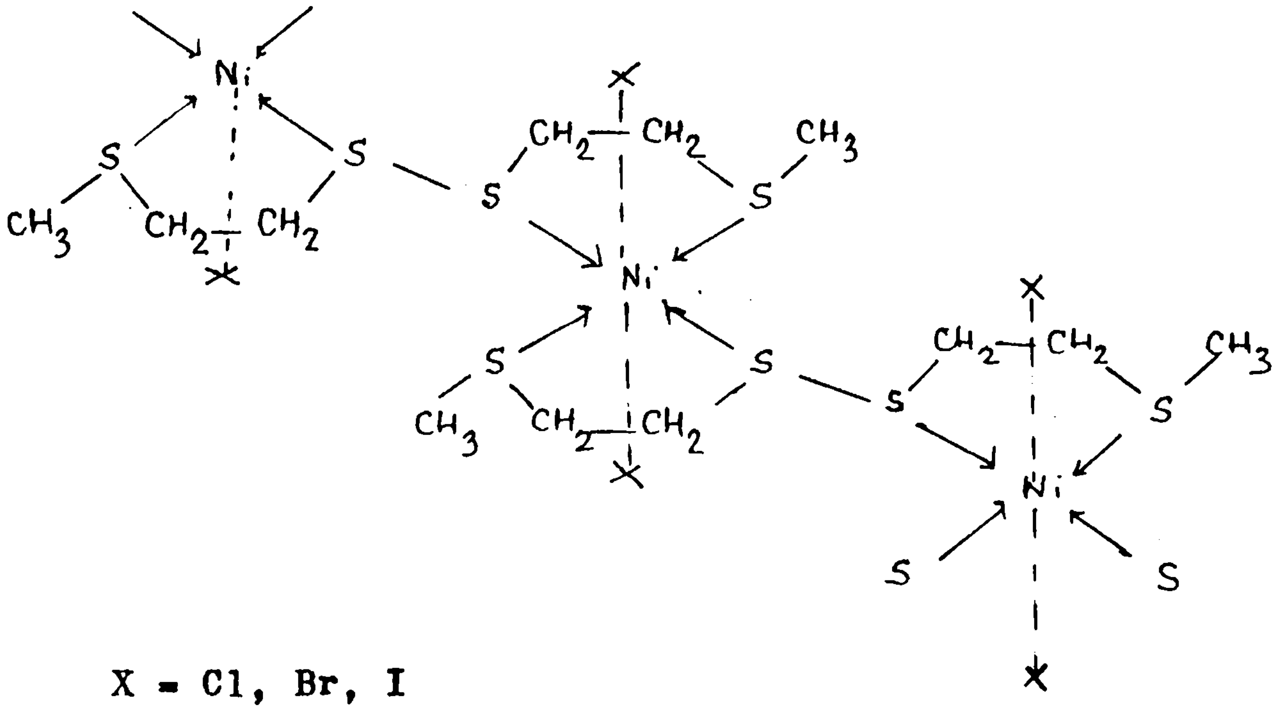


Figure 4.5

4.4 Nickel(II) halides complexes of 1-mercapto-3-thiabutane, $[CH_3SCH_2CH_2SH]$, MMTH

The replacement of the hydroxyl group of the MTEL (3-thiabutanol) by the thiol group to form the compound MMTH (1-mercapto-3-thiabutane) gives a ligand of entirely different co-ordinating properties. The ligand complexes with the loss of the proton from the thiol group and forms a variety of complexes under different conditions. Under stringent anhydrous conditions the proton is not dissociated and no complex was isolated with nickel(II) halides.

Hydrated nickel(II) halides react with the ligand MMTH in alcohol to gives complexes of the formula $Ni_2(MMT)_2\ X_2$ (X=Cl, Br, I). The complexes are diamagnetic and non-electrolytes. Their molecular weight determinations in chloroform indicated that they are dimeric and the molecular formula is the same as their corresponding stoichiometric formula (analysis results in Table 3.4, p.87).

Electronic Spectra: The reflectance spectra of the $Ni_2(MMT)_2\ X_2$ are difficult to interpret because of the large charge transfer bands which come well into the visible region. Dilution with magnesium carbonate does not yield well resolved bands and as the spectra of the complexes in nitromethane at concentrations ca. 10^{-3}M showed similar absorption but better resolved bands (Figure 4.6, p.151), the solution spectra of the complexes are used for the discussion.

Table 3.10, p.98 lists the absorption of the complexes $Ni_2(MMT)_2\ X_2$. The spectra are very similar with a high intensity band (ε = 500 $cm^{-1}M^{-1}$1) found in the region 17000-18000 cm^{-1} with a shoulder at 13000 cm^{-1}. The lack of any transition occurring below 10000 cm^{-1} is indicative of a large crystal field separation characteristic of the square nickel (II) complexes invariably exhibit a crystal field separation, between the lowest d orbital and the next, greater than 10000 cm^{-1} [83].

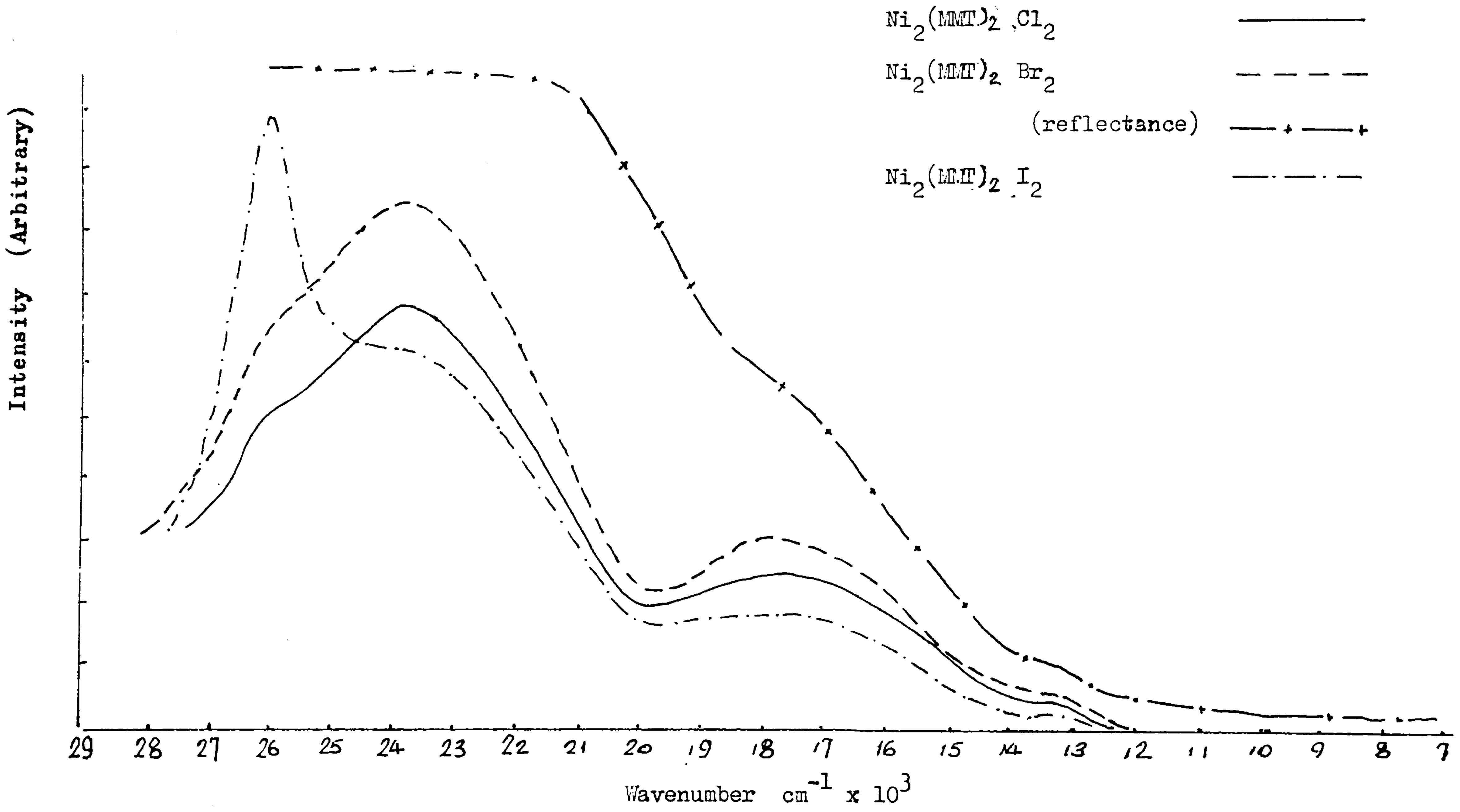
The first band observed as a shoulder on the larger band is assigned to the transition $^1A_{2g} \leftarrow {}^1A_{1g}$. The second band is assigned to be the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition (p. 44).

The presence of a high intensity multiple band in the region 28000-20000 cm^{-1}, is thought to be of charge transfer in origin. The high ε value of this band (about 1200 cm^{-1}M^{-1}l) plus the fact that similar absorption is observed in cobalt(II) complexes of the same ligand, strongly support this idea.

However, the possibility of the absorption at ca.25000 cm^{-1} being a d-d transition can not be ruled out entirely. In the absence of any orbital interaction between the metal and the ligand, it is likely that the three d orbitals e_g and b_g lie fairly close together and thus resulting only one transition from this group i.e. $^1B_{1g} \leftarrow {}^1A_{1g}$ at ca. 17000 cm^{-1}. If orbital interaction occurs, the e_g orbital become dissimilar in energy from the b_g and extra bands may be observed [83]. This situation could occur with ligands of high nephelauxetic effect and sulphur being strongly polarisable generally exhibits high nephalauxetic effect on co-ordination. Figure 4.7, p.153 is a diagrammatic representation of the d orbital splitting pattern in a square planar ligand field.

Infrared Spectra (4000-450 cm^{-1}): The infrared spectra of the complexes are very similar but distinctly different to the ligand, indicating a deformation of the vibrational modes of the ligand molecule on chelation. The loss of the thiol absorption band at 2500 cm^{-1} in the complex spectra showed that the co-ordination involves the thiol group with the loss of the proton;

Figure 4.6 Solution spectra of Ni(II) halide complexes with 1-mercapto-3-thiabutane (MMTH)



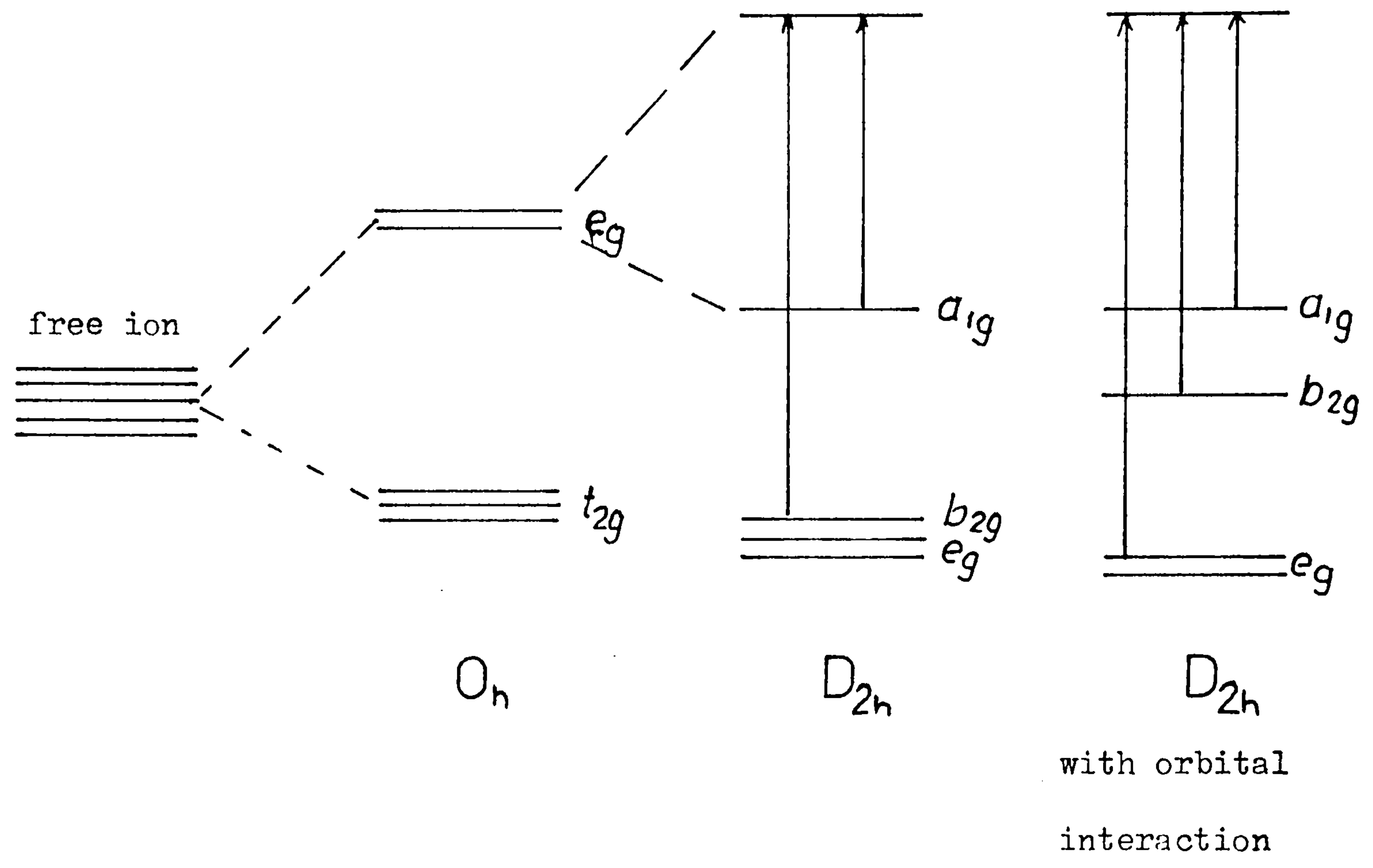


Figure 4.7 d orbital splitting of Ni(II) ion in a square planar ligand field

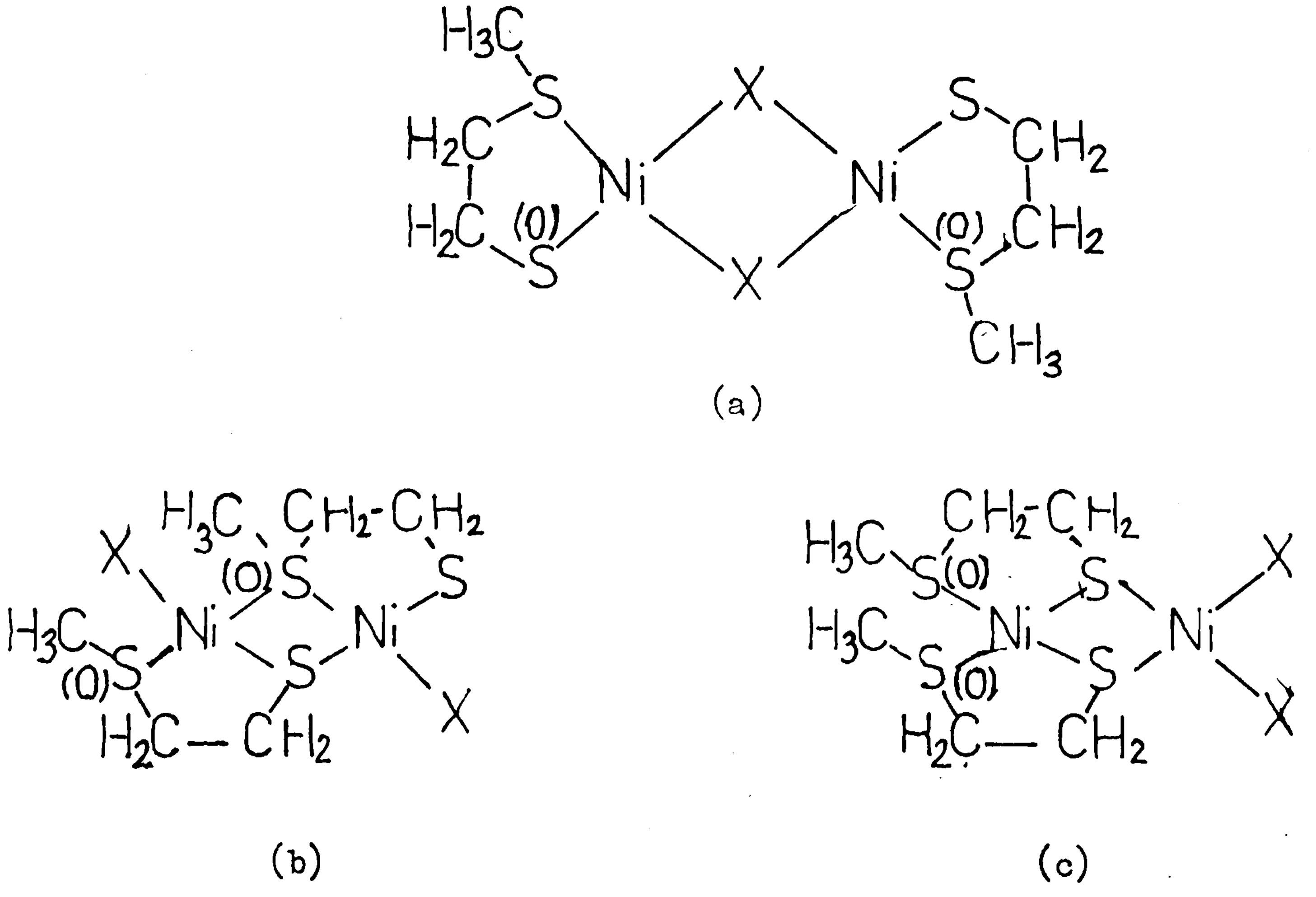


Figure 4.8 Proposed structures for Ni$_2$(MMT)$_2$ X$_2$ and Ni$_2$(MME)$_2$X$_2$

however, comparison of the spectra of the ligand with the chloride complex (IR 14, p. 105) does not show any significant overall shift of the bands to lower frequencies, hence, no indication of ring formation on chelation may be drawn. The change in the vibration modes of the ligand suggests that the co-ordination is likely to be affected by more than one point i,e. not by the thiol group alone, and the only other atom apart from the thiol that is likely to co-ordinate is the thio-ether sulphur. From the results obtained by the ligands 3-thiabutanol (p.131) and 1-methoxy-3-thiabutane (p.140), the thio-ether is likely to take part in the chelation and may form a five-membered metal-ligand ring.

Far Infrared Spectra (450-80 cm^{-1}): The spectra of the complexes are shown in Figure fir 4, p.118 and the assignment of the bands are listed in Table 3.16, p.112. Due to the coupling effects, most of the assignment of the bands can only be tentative and by comparison with reported data on stretching frequencies of ν(Ni-S)$^{97-100}$, ν(Ni-O)$^{101-5}$ and ν(Ni-X)^{92,93}. The metal-halogen vibration gives rise to the most intense features of the spectrum and together with the wavelength shift that occurs when one halogen is substituted for another, these bands are unambiguously identified. The absence of bands which could be related to halogen bridging mode^{95}, rules out the structure involving halogen bridging (Figure 4.8a, p. 153). The structures of the complexes are likely to be as shown in Figure 4.8 (b & c), p.153. Structure shown in Figure 4.8c is very similar to a *cis* square planar system and would give rise to two absorptions in the regions 325, 260 and 210 cm^{-1} for chloride, bromide and iodide, respectively. This is not observed in the spectra. Instead, a broad band sensitive to halogen at ν_{max} 378 cm^{-1} for chloride, ν_{max} 342 cm^{-1} for bromide and ν_{max} 270 cm^{-1} for iodide complexes is observed. The frequencies and the relative positions of the halogen sensitive bands indicated that they are terminal in nature[92,96], thus strongly supporting the trans structure proposed in Figure 4.8b, p.153.

The planar structure is also in accord with the magnetic behaviour of the complex. The complexes are diamagnetic which shows that all the d electrons are paired. The thiol ion is thought to be responsible for the square planar symmetry as the thio-ether group generally leads to high spin complex formation (p.17). This difference in behaviour is usually attributed to the higher polarisability of the thiol sulphur when compared with the thio-ether sulphur, thus allowing a greater π-bonding between the metal ion and the ligand in the case of the thiol sulphur ligand complexes. In the present study, the thio-ether sulphur ligands 3-thiabutanol (p.131), 1-methoxy-3-thiabutane (p.140) and the di-(2-methylthioethyl) disulphide (p.144) all give high spin nickel(II) complexes.

The mode of chelation of MMTH is similar to the ligand 2(2-mercapto-ethyl)pyridine[31] but differs from the ligand 2-mercapto-ethyl amine[30] indicating that the nature of the second co-ordination ligand atom (i.e. the thio-ether, the amino and the pyridino) affects the co-ordination mode, leading to different stereochemistry of the complexes formed. Hence, to complete the study of this effect, the thio-ether group is replaced by an ether group and the resulting ligand 1-mercapto-2-methoxyethane, was studied.

4.5 Nickel (II) halides complexes of 1-mercapto-2-methoxyethane, $\boxed{CH_3OCH_2CH_2SH}$, MMEH

Like MMTH (1-mercapto-3-thiabutane) p.150, the complexes of nickel(II) halides are readily prepared by mixing ethanolic solutions of the hydrated salts and ligand. The resulting precipitate was washed with ether and dried under vacuum. The purity of the complexes prepared was checked by elemental analysis (Table 3.3, p.88), which indicated a stoichiometric formula $Ni_2(MME)_2X_2$ (X=Cl, Br, I).

Electronic Spectra: The solution spectra (Table 3.11,p.99) of the nickel complexes are essentially the same as the diffuse reflectance spectra except for a slight shift of the absorption peaks maxima to higher energy (ca.50 cm^{-1}). These spectra are similar to those of the corresponding 2-mercapto-3-thiabutane nickel(II) complexes $Ni_2(MMT)_2X_2$ and are characteristic of a square planar structure (p.44). The $^1A_{2g} \leftarrow {}^1A_{1g}$, $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$ transitions occurs in the region 12000-13000, 16000-19000 and 23000-24000 cm^{-1}, respectively. The last band at 23000-24000 cm^{-1} although assigned as d-d transition is unlikely to be pure d-d in nature because of its high intensity (ε = 15000 l $cm^{-1}M^{-1}$). Perhaps the d-d band is superimposed on the stronger charge transfer band which also occurs in this region. The evidence to support this statement is found in the cobalt complexes of this ligand, which has a band of very high intensity (ε = 1200 l $cm^{-1}M^{-1}$) occurring in the same region. As this band does not alter through the series chloride, bromide and iodide, it can be concluded that the charge transfer is probably caused by the sulphur ligand and not by the halides[81].

Conductivity measurement in nitromethane at concentration about 10^{-3}M, shows that the above complexes are essentially non-electrolytes, which is indicative of the halide ion co-ordination. The diamagnetism of the complexes are in accord with the square planar structure.

As in the case of $Ni_2(MMT)_2\ X_2$, the infrared spectra (4000–450 cm^{-1}) of the MME complexes showed there is a deformation of vibration modes of the ligand on chelation and the disappearance of the thiol (SH) absorption peak at 2500 cm^{-1} showed that the chelation involves the mercaptide group with the loss of the proton. A comparison of the spectra of the free ligand and the chloride complex (Figure IR 15, p.106) showed that there is an overall change of the vibrational modes of the ligand making identification of individual band shift impossible. It is assumed (as in the case of MMTH complexes) that the configurational hindrance on chelation is largely responsible for the change of the vibration modes of the ligand.

Far Infrared Spectra (450–80 cm^{-1}): The spectra of the complexes have a generally similar appearance and different from the free ligand as illustrated by the spectra of the chloride complex and the ligand in Figure fir 6, p.120. The prominent feature of the spectra is the halogen sensitive bands which are assigned to chloride at 370 cm^{-1}, bromide at 340 cm^{-1} and iodide 290 cm^{-1} (Table 3.17, p.113). The positions of the halogen absorption bands leaves little doubt that the halogens are not bridged and attached terminally and in square configuration[93].

Thus on the spectral and analytical evidence, it is concluded that the ligands MMEH and MMTH have similar chelating properties and the structure of the complex formed is probably the one illustrated in Figure 4.8b, p.153.

It is relevant at this point to mention the study done on bidentate ligand by Busch and co-workers[30-33] noted in the introduction (p.18). In their study, they reported the preparation of dichlorobis-2-(2-mercaptoethyl)-pyridino dinickel (II) $Ni_2(mep)_2Cl_2$ (mep= ligand) and proposed two possible structures for this compound as shown in Figure 1.8 & 9, p.19. The authors were unable to establish which structure was the correct one, though they strongly suggested that it would be the more symmetrical structure in Figure 1.

In view of the study of the ligands MMEH and MMTH with nickel halides, the far infrared evidence strongly supports a *trans* structure in the halide complex, which is equivalent to the structure shown in Figure 1.9. It would be reasonable to suggest that this would be the correct structure for $Ni_2(mep)_2Cl_2$.

If it is assumed that the first band in the region 12000 cm^{-1} of the nickel complexes arises as a consequence of a transition from the d_{xy} orbital to the $d_{x^2-y^2}$ orbital, (illustrated in diagram 2.1, p.36) whose electron energy separation is $10Dq^E$ a comparison of the energy of this transition for the nickel complexes of MMEH and MMTH would reflect the ligand field strengths of the two ligans. From this, it is observed that the replacement of the thio-ether with oxo-ether group had very little effect on the crystal field strength of the ligand. This is to be expected from the study of the thio-ether and the ether ligands(MTEL, p.131; MTOE, p. 140; MTD, p.144) indicated that the two ligands process similar crystal field strength towards nickel(II) ion and the replacement of one for the other is unlikely to cause any observable change in the

the crystal field strength which may be reflected by the electronic transitions. It is unfortunate that Busch and co-worker[30-33] did not quote any electronic transition results of the nickel complexes of mep and thus no direct comparison with the ligand could be drawn.

It must be noted that although the co-ordination sites of the mep are said to be nitrogen and the thiol group, replacement of the pyridine nitrogen with the amine nitrogen as in the ligand 2-mercaptoethyl amine (p.18), does not give complexes of analogous composition. The complexes formed by this ligand are said to be planar in structure but are trimeric with the structure shown in Figure 1.7,p.18. This indicates that the replacement of the sulphur ligand atom (the thio-ether sulphur) by an atom of different ligand field strength (e.g. the much stronger nitrogen atom) may lead to different chelating properties.

4.6 Cobalt(II) halides complexes of 3-thiabutanol, $[CH_3SCH_2CH_2OH]$, MTEL

It is a fairly general observation that the equilibrium constant for the formation of analogous complexes of the divalent metal ion of Mn through Zn with the same ligands fall in the following order[27] of metal ions: $Mn^{2+} < Fe^{2+} < Co^{2+} \leq Ni^{2+} < Cu^{2+} > Zn^{2+}$. Although it may be deduced from this series that nickel and cobalt divalent metal ions would form similar complexes with a particular ligand, it is often observed that the stereochemistry of the complexes formed by the two metal ions with the same ligand are quite different from each other. This is attributed to the effect of Ligand Field Stabilisation Energy on the two metal ions, such as the fact that tetrahedral complexes of Co(II) are relatively stable while those of Ni(II) are not[81].

Thus it is not altogether surprising that the ligand MTEL yields different type of complexes with cobalt halides. Under the same experimental conditions as those used for the nickel salts, ligand MTEL reacts with cobalt(II) halides to yield purple coloured high spin complexes. Elemental analysis (Table 3.1, p.83) gives a stoichiometric formula of $Co(MTEL)_2X_2$ (X=Cl, Br, I). Conductivity measurement in nitromethane at concentration ca. 10^{-3}M, showed that the complexes are 1:2 electrolytes (Table 3.7, p.94) which strongly indicates that the halide ions remain ionic in the complexes. Molecular weight determination could not be carried out accurately as no suitable solvent was found to dissolve the complexes to the required concentration (ca. 10^{-1}M) for accurate evaluation. Room temperature magnetic susceptibility

Table 3.7, p.94 measurement yield μ_{eff} values in the range of 4.2-4.3 B.M. which is in the region of values characteristic for Co(II) ion in a tetrahedral environment[88].

Electronic Spectra: The diffuse reflectance spectra of cobalt(II) halide complexes are characteristic of the tetrahedrally co-ordinated metal ion (p. 46). The transitions in the spectra of the cobalt complexes (Table 3.7, p.94) are classified on the assumption of T_d symmetry throughout, although the effective symmetry may be lower for the co-ordination sites of the ligand are not equivalent (it is assumed that the ligand co-ordinates through the oxygen and sulphur atoms in the molecule). The energy correlation for a d^7 ion in a tetrahedral field is shown in Figure 4.9, p.162. The free ion spin quartet of d^7 are ^4F and ^4P. These will split up in a tetrahedral field into $^4A_{2g}$, $^4T_{2g}$, $^4T_{1g}(F)$ and $^4T_{1g}(P)$. The $^4A_{2g}$ level being lowest, the transitions $^4T_{2g} \leftarrow {}^4A_{2g}(\nu_1)$, $^4T_{2g} \leftarrow {}^4A_{2g}(\nu_2)$ and $^4T_{2g}(P) \leftarrow {}^4A_{2g}(\nu_3)$ are expected. The crystal field splitting parameter is determined by the energy of the first transition (i.e. ν_1 = 10Dq) (p. 46). However, due to the low energy of this transition (ca. 4000 cm^{-1}), it is masked by the vibration overtone absorption of the ligand in this region and could not be identified accurately from the spectra. Hence, the crystal field splitting and the electronic repulsion term B'(p. 52) were estimated from the method suggested by Konig[90]. In the calculation the energies of the transition $^4T_{1g}(F) \leftarrow {}^4A_{2g}$ at about 6000 cm^{-1} and $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ at about 16000 cm^{-1} were assumed to correspond to the centres of gravity of the multiple band ν_2 and ν_3 , respectively. As the cobalt complexes retain their stereochemistry in nitromethane and that

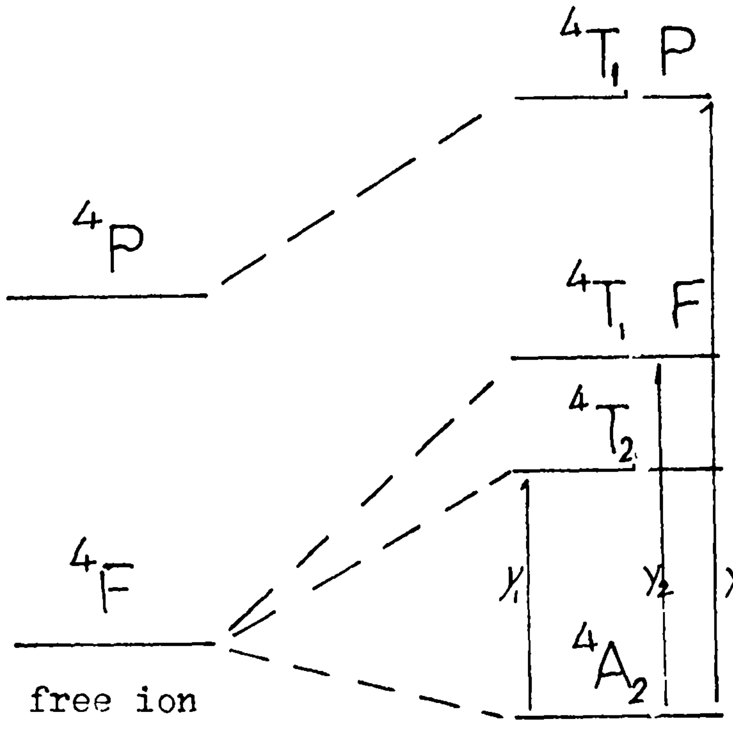


Figure 4.9

Energy Correlation Diagram

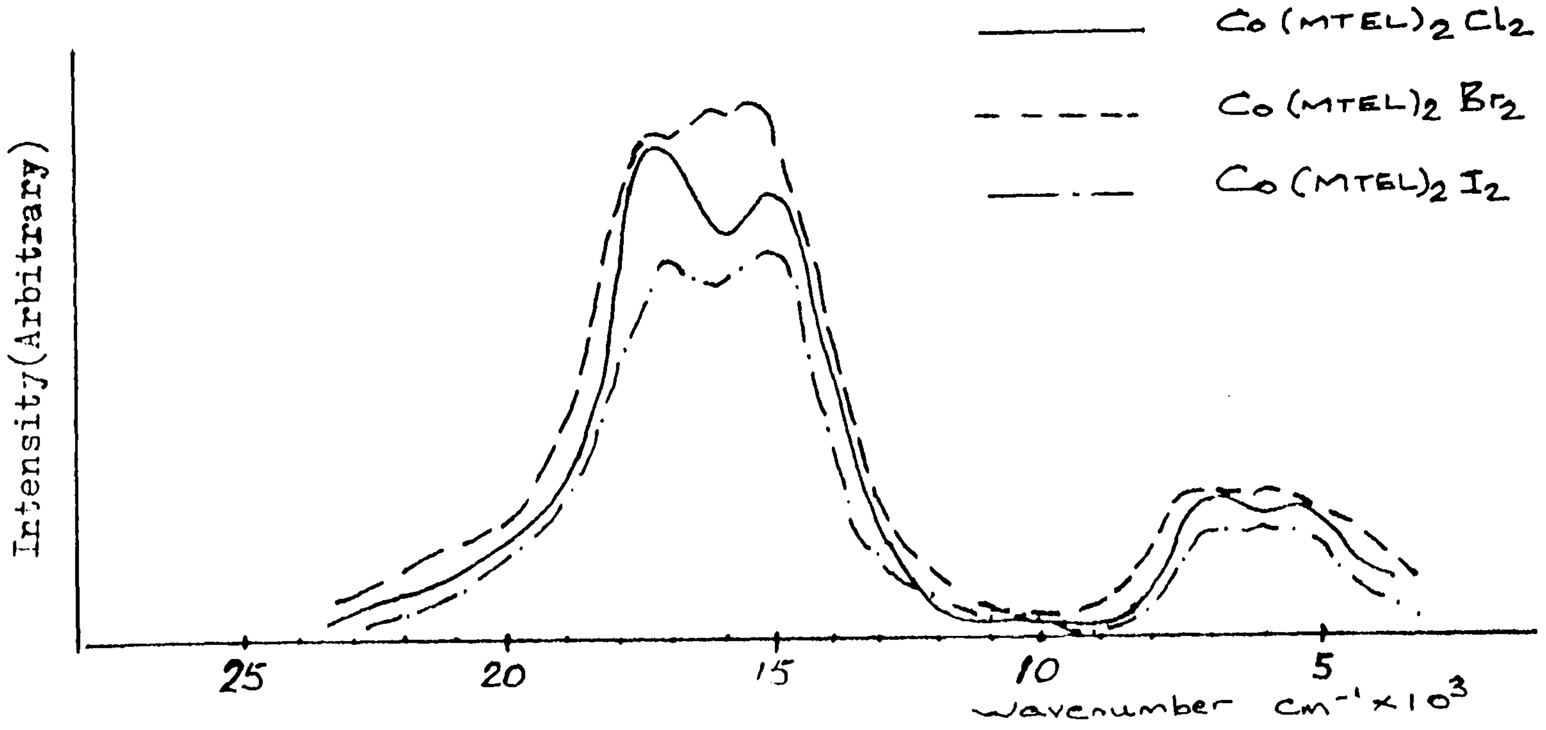


Figure 4. 10

Electronic Spectra of Cobalt Complexes

the absorption spectra are better resolved than the reflectance spectra of the solid diffuse reflectance spectra, all the calculations are based on the values found in the solution spectra (Figure 4.10, p.162).

All the cobalt complex spectra show two characteristic absorption bands ν_2 and ν_3 , which appear as multiple absorption bands with high intensity. The coefficient of extinction of the peaks are of the order 90-98, and 350-400 cm^{-1} $mole^{-1}$ l. for ν_2 and ν_3 , respectively. This further supports the assumption that the cobalt ion is in a tetrahedral environment.

Values of Dq and β_{35} derived are given in Table 4.4, p.164. Data are also collected in Table 4.5, p.164 concerning the Dq and values previously been determined for model CoS_4 and CoO_4 tetrahedral chromophores. As may be seen the Dq and β_{35} ranges for the CoS_4 lie within 396-450 cm^{-1} and 0.57-0.65 respectively, while the corresponding ranges for the CoO_4 chromophores are 365-398 cm^{-1} and 0.75-0.81 respectively. As seen from the Table the crystal field parameters of cobalt complexes of MTEL ($Dq=398-401$ cm^{-1}, $\beta_{35}=0.65-0.71$) lie between the values found for CoS_4 and CoO_4 chromophores. Further, using the "law of average environment"[83] the Dq and β_{35} values of $Co(MTEL)_2X_2$ may be calculated by taking the averages of the Dq and β_{35} values of CoO_4 and CoS_4 ions, a satisfactory agreement between the observed and calculated data (Table 4.6, p.165) supports the assumption that the ligand co-ordinate through the oxygen and sulfur atoms.

<u>Infrared Spectra (4000-450 cm^{-1})</u>: All the spectra of cobalt complexes are very similar but distinctly different to the spectrum of the free ligand. The noticeable broadening and a shift to lower

Compound	10Dq cm^{-1}	B cm^{-1}	β_{35}
$Co(MTEL)_2Cl_2$	3984	695	0.71
$Co(MTEL)_2Br_2$	4000	663	0.68
$Co(MTEL)_2I_2$	4010	634	0.65

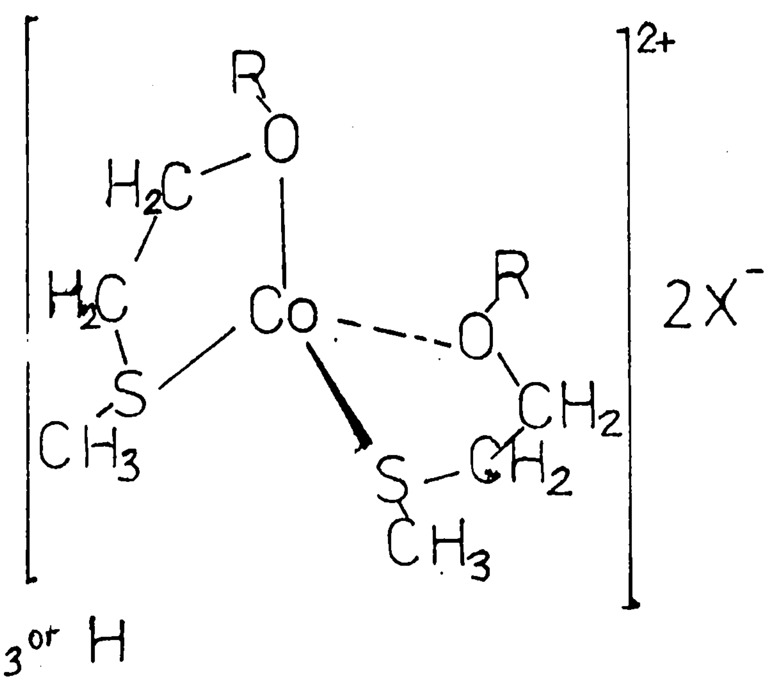
Table 4.4 Calculated Crystal Field Parameters of $Co(MTEL)_2X_2$

	Compound	Dq	B	β_{35}	ref
CoS_4	$Co(PySH)_4(NO_3)_2$	450	587	0.59	97
	$Co(PySH)_4(ClO_4)_2$	396	635	0.65	97
	$Co(Su)_4(ClO_4)_2$	403	575	0.59	130
	$Co(Su)_4(NO_3)_2$	405	620	0.63	130
CoO_4	$[Co(MeAsO)_4](ClO_4)_2$	398	786	0.81	63
	$[Co(MeAsO)_4]Br_2$	384	738	0.76	63
	$[Co(MeAsO)_4]Cl_2$	365	728	0.75	63

Table 4.5 Dq and B values for tetrahedral CoS_4 and CoO_4 chromophores

	D_q cm^{-1}		β_{35}	
Compound	Observed	Calculated	Observed	Calculated
$Co(MTEL)_2Cl_2$	398	395	0.71	0.69
$Co(MTEL)_2Br_2$	400	395	0.68	0.69
$Co(MTEL)_2I_2$	401	395	0.65	0.69

Table 4.6 Comparison of observed and calculated D_q and β_{35} values



$R = CH_3$ or H

X = Cl, Br, I

Figure 4.11 Proposed structure of cobalt complexes with MTEL and MTOE ligands frequencies of the OH stretching frequency (ca. 3300 cm^{-1}) in the spectra of complexes indicates that the hydroxyl group is involved in the chelation. The changes in the bands observed in the region 1200-900 cm^{-1} suggests that there is conformational changes in the free ligand on chelation. This is expected as the more restricted system in the complexes would lead to different type of vibrational modes in this region. Two bands observed in the complex spectra of the nickel halides of the same ligand. (820 and 660 cm^{-1}) are also observed in the cobalt complex spectra. Since these bands are not found in the free ligand, they are assumed to arise from the chelation. An additional band at 520 cm^{-1} which is not found in the nickel complexes, is observed in all the cobalt complexes. The low frequency of this band suggests that it is likely to be metal-ligand in origin. However, no individual band has been assigned, because of the difficulty in distinguishing any particular vibration mode from all the others. It may be concluded from the infrared spectra that chelation of the ligand is effected through more than one site and strongly indicates that the sulfur atom also take part in the chelation. The spectra of the cobalt chloride complex and the free ligand are shown in Figure 3.11, p.103 to illustrate the difference between them.

Far Infrared Spectra (450-80 cm^{-1}): The spectra of the three halides reported in Table 3.13, p.109, are very similar in appearance. This points to the mode of chelation is affected by the same method with all the three complexes. Like the nickel complexes of this ligand the spectra are very complicated in the higher energy region (450-300 cm^{-1}) with six to eight strong and weak bands. Figure fir 1, p,115, shows the spectra of the ligand MTEL, the nickel(II) chloride complex and the cobalt(II) chloride complex. The essential difference between the two infrared spectra is the absence of any halogen sensitive band in the cobalt spectra, which is in agreement with the high conductance exhibited by the cobalt complexes. The high conductance (Table 3.8,p.95) suggests that the halide ions are present in ionic form and therefore, no halogen-metal band would be expected in the far infrared spectra of the complexes. The large number of absorption bands present in the cobalt complex spectra would include other vibration modes such as ligand internal vibration frequencies and other stretching frequencies arising from coupling processes, thus, assignment of individual bandsto metal-sulphur and metal-oxygen vibration could only be made tentatively. The bands observed in the regions 280-350 and 350-450 cm^{-1} are assigned to ν(Co-S) and ν(Co-O) modes, respectively (Table 3.13, p.109).

The spectral and analytical evidence strongly support a tetrahedral high spin structure for the cobalt complex with ligand MTEL and it is likely that the chelation sites of the ligands are the oxygen and sulphur atoms of the ligand molecule as observed in the case with nickel and the proposed structure of the complex is illustrated in Figure 4.11, p. 165.

4.7 Cobalt(II) halides complexes of 1-methoxy-3-thia-butane, $[CH_3OCH_2CH_2SCH_3]$, MTOE

MTOE forms similar complexes with cobalt halides to those formed by the ligand MTEL under the same experimental conditions. The analytical results yield a stoichiometric formula of $Co(MTOE)_2X_2$ (Table 3.2, p.84). The complexes are slightly soluble in nitromethane which allows their conductance to be determined, but the solubility is too low for accurate molecular weight determination by the ebullioscopic method (p.124-5). The conductance reported in Table 3.8,p.95 showed that the complexes are 1:2 electrolytes, suggesting the presence of the complex $[Co(MTOE)_2]^{2+}[2X^-]$. Magnetic moments of the complexes obtained are between the value expected for the high spin tetrahedral stereochemistry (μ_{eff} =4.3-4.9 B.M. Table 3.8).

Electronic Spectra: Diffuse reflectance spectra of the complexes reported in Table 3.8,p.95 show characteristic absorption bands of cobalt(II) ion in tetrahedral environment with two intense bands assignable to the $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ (ν_3) and $^4T_{1g}(F) \leftarrow {}^4A_{2g}(\nu_2)$ transitions of the $\underline{d}^7$ high spin ion at ca. 16000 cm^{-1} and 6000 cm^{-1}, respectively. The band in the region of 16000 cm^{-1} is split into three components at approximately 17400, 15000 and 13800 cm^{-1} for chloride and bromide and at 16900,14940 and 14200 cm^{-1} for iodide as expected from the spin orbital coupling for the tetrahedral stereochemistry of cobalt(II) ion[83]. As with the MTEL complexes the low energy transition band $^4T_{2g} \leftarrow {}^4A_{2g}(\nu_1)$, is obscured by the ligand bands and 10Dq has to be calculated. The electronic parameters of the complexes calculated, together with those obtained for the MTEL complexes are listed in Table 4.7,p.169. As seen from the table

	D_q		β_{35}	
	MTOE	MTEL	MTOE	MTEL
Cl^-	420	398	0.73	0.71
Br^-	410	400	0.72	0.68
I^-	390	401	0.72	0.65

Table 4.7 Dq and β_{35} values of Co(MTOE)$_2$X$_2$ and Co(MTEL)$_2$X$_2$.

the magnitudes of the data in both ligands are very similar with 10Dq=390-420 and 398-420 cm^{-1} for the MTOE and MTEL ligands respectively, and β_{35}=0.72-0.73 and 0.65-0.71 for MTOE and MTEL ligands respectively. This suggests that the two ligands share the same mode of co-ordination and the chelation is effected through the sulphur and oxygen atoms.

Infrared Spectra (4000-450 cm^{-1}): All the cobalt spectra are essentially similar but differ from the free ligand. The broadening of the band at about 1100 cm^{-1} which has been observed in the nickel complexes of the same ligand is also a prominent feature in the cobalt complexes. Since this region includes the vibration modes of the ether and the carbon chain, it indicates that there is a conformational change on the vibration modes on chelation and strongly suggests that the ether group is involved in the co-ordination process. The bands occurring at the lower regions are not so prominent as in the complex spectra of the MTEL ligand. The bands observed at 670 and 520 cm^{-1} are probably metal-ligand bands as these are not seen in the spectrum of the free ligand. Thus, the overall change of the vibration modes of the ligand in complexes may be taked as evidence of chelation. The spectrum of the chloride complex together with the spectra of the free ligand and that of the analogous nickel complex are shown in Figure IR 12, p.103.

Far Infrared Spectra (450-80 cm^{-1}): The analysis used for the MTEL complexes (p.166) may be applied in the spectra of the MTOE complexes. The spectra are very similar in appearance which supports the assumption that co-ordination is identical with the different halides as suggested by their electronic spectra. No halogen sensitive bands are observed, which is expected from the result of the conductance measutement which indicated that the halides are present in ionic form and not co-ordinated to the metal ion. Beside the band due to the ligand there are a number of additional bands which are listed in Table 3.14, p.110. However, the complexity of the spectra makes it difficult to identify the origin of each vibration mode individually, thus no individual band is assigned. Comparison with the spectra of the MTEL complexes suggests that the bands at ca. 390 and 280 cm^{-1} are probably cobalt-ligand stretching modes with the one at higher frequency due mainly to the ν(Co-O) and the one at lower frequency due to ν(Co-S).

It may be pertinent to point out that although as with the nickel halides, the co-ordination modes of the two ligands MTOE and MTEL with cobalt halides are very similar, in the case of the nickel complexes the ligand MTOE is found to have a relatively weaker crystal field splitting energy than that of the MTEL (ca. 15 cm^{-1} lower), this is not found in the cobalt analogous complexes. The similarity of the Dq and β_{35} values of the cobalt complexes of the two ligands reflects on the equal co-ordinating strength of the two ligands. A possible explanation is that the calculation of the values of Dq and β_{35} is dependent on the accuracy in determining the centres of gravity of the two absorption bands observed. Due to the wide spread of these bands the possible error in determining the centres of gravity could be up to ± 100 cm^{-1}(60). With such a spread of possible values, it is unlikely for the small difference of the two ligand crystal splitting values to be reflected in the calculated resulted.

The MTOE ligand is likely to co-ordinate through the ether oxygen and the thio-ether sulphur and the complexes obtained would have structures illustrated by Figure 4.11, p.165.

4. 8 Cobalt(II) halide complexes of 1-mercapto-3-thiabutane, $\boxed{CH_3SCH_2CH_2SH}$, MMTH

In the study of the nickel halide complexes, it is observed that the replacement of the hydroxyl group in 3-thiabutanol by the thiol group to yield the ligand 1-mercapto-3-thiabutane MMTE, which exhibits completely different co-ordination properties. This pattern of behaviour is repeated with the cobalt complexes. The ligand MMTH reacts with hydrated cobalt halides readily in ethanol to yield complexes of the stoichiometry $Co_2(MMT)_2 X_2$. Magnetic moment measurement showed that the complexes are all low spin with μ_{eff}= ca.2.2 B.M. (Table 3.10, p.98). This indicates that the electronic ground state of the cobalt ion in the complex is spin paired with $S=\frac{1}{2}$ [49], which points to a square planar stereochemistry (p. 47). Conductance measurement (Table 3.10,p.98) showed that the complexes are essentially non-electrolytes in nitromethane and molecular weight determination in chloroform gives a formula in agreement with the dimeric stoichiometric formula stated above.

Electronic Spectra: Although there is still confusion over the interpretation of the square planar spectra of the cobalt complexes, enough data have been accumulated for the identification of such complexes by the electronic spectra. As early as 1954 Nyholm and Figgis[131] have stated that square planar complexes of cobalt(II) can be distinguished from tetrahedral complexes both spectroscopically and magnetically.

Nishida and Kida [88] have made a comparatively detailed study of magnetic and optical properties of some low spin square planar cobalt complexes and have shown that in near infrared and visible regions, these complexes show three bands mainly due to the transitions, $^2E_g \leftarrow {}^2A_{1g}$, $^2B_{1g} \leftarrow {}^2A_{1g}$ and $^2E'_{1g} \leftarrow {}^2A_{1g}$ appearing at about 5000, 7000 and 18000 cm^{-1} respectively. The bands observed on the spectra of $Co_2(MMT)_2 X_2$ are at about 4000, 7000 and 21000 cm^{-1}. The shape and intensities of the first two bands (the first band is broad and of low intensity with $\varepsilon = 20$ cm^{-1} M^{-1} l, and the second band is sharp and very low intensity with $\varepsilon = 8$ cm^{-1} M^{-1} l) are characteristic of the transitions pertaining to the square stereochemistry (Figure 4.12, p.174).

The band at 21000 cm^{-1} is unlikely to be a *d*-*d* band due to the high extinction coefficient it exhibits ($\varepsilon = 1000$ cm^{-1} M^{-1} l) and as in the nickel complexes of MMTH it is considered to be of charge transfer in origin. This band may also obscure the higher energy transition band which is predicted to occur at about 18000 cm^{-1} for a square planar stereochemistry.

Recent detailed analysis of the electronic spectra of cobalt (p. 47) is in agreement to the assignment of the transitions. The splitting of the energy levels of the cobalt(II) ion in square planar stereochemistry (p. 47) is illustrated diagramatically in Figure 2.8,p.49 and the bands observed are interpreted accordingly.

$$\nu_1 = {}^2E_g \leftarrow {}^2A_g$$
$$\nu_2 = {}^2B_g \leftarrow {}^2A_g$$
$$\nu_3 = {}^2E'_g \leftarrow {}^2A_g$$

Infrared Spectra (4000-450 cm^{-1}): The spectra of the complexes are very similar to those of the nickel complexes and may be

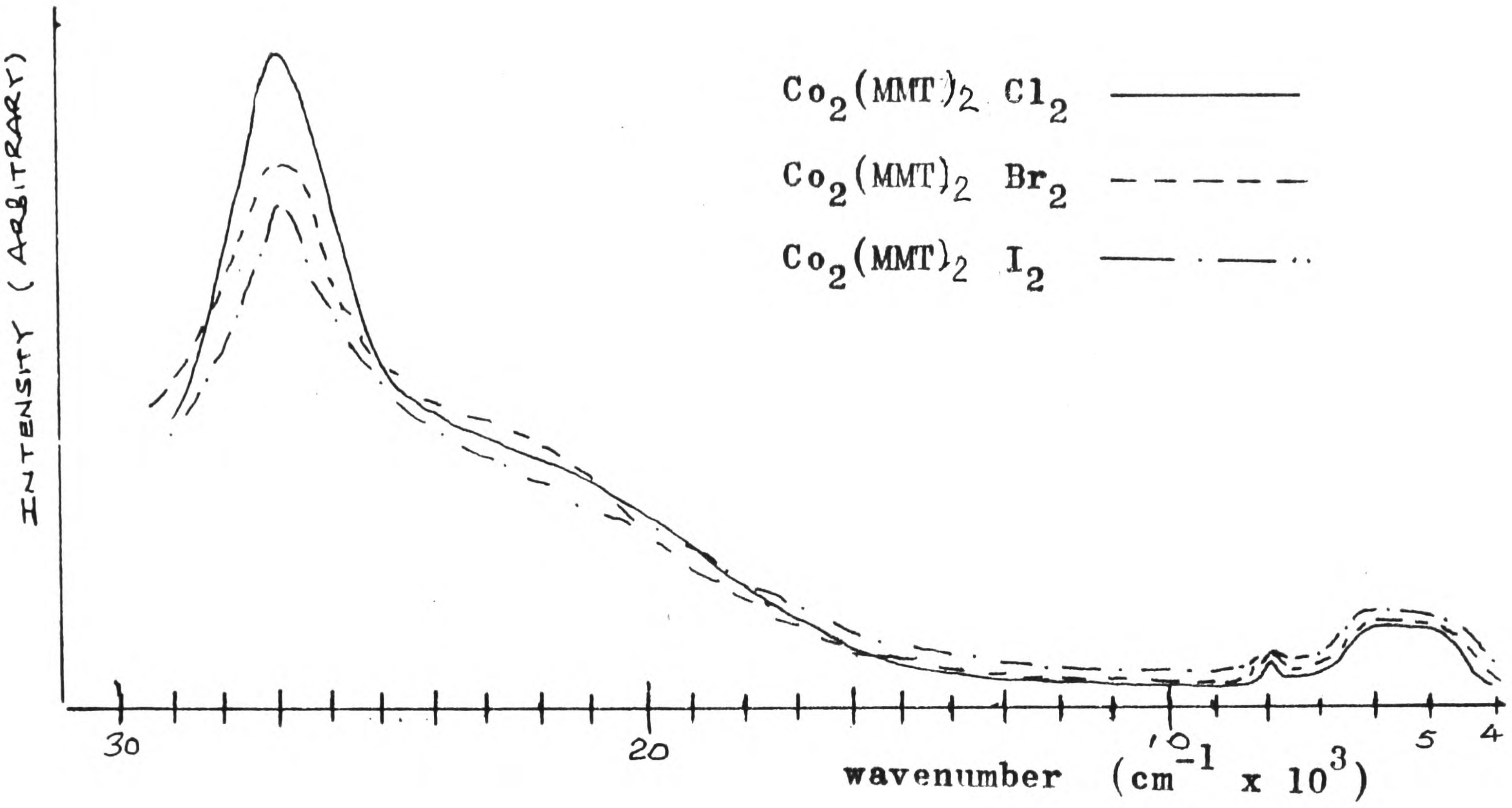


Figure 4.12 Electronic spectra of Co(II) halide complexes of 1-mercapto-3-thiabutane (MMTH)

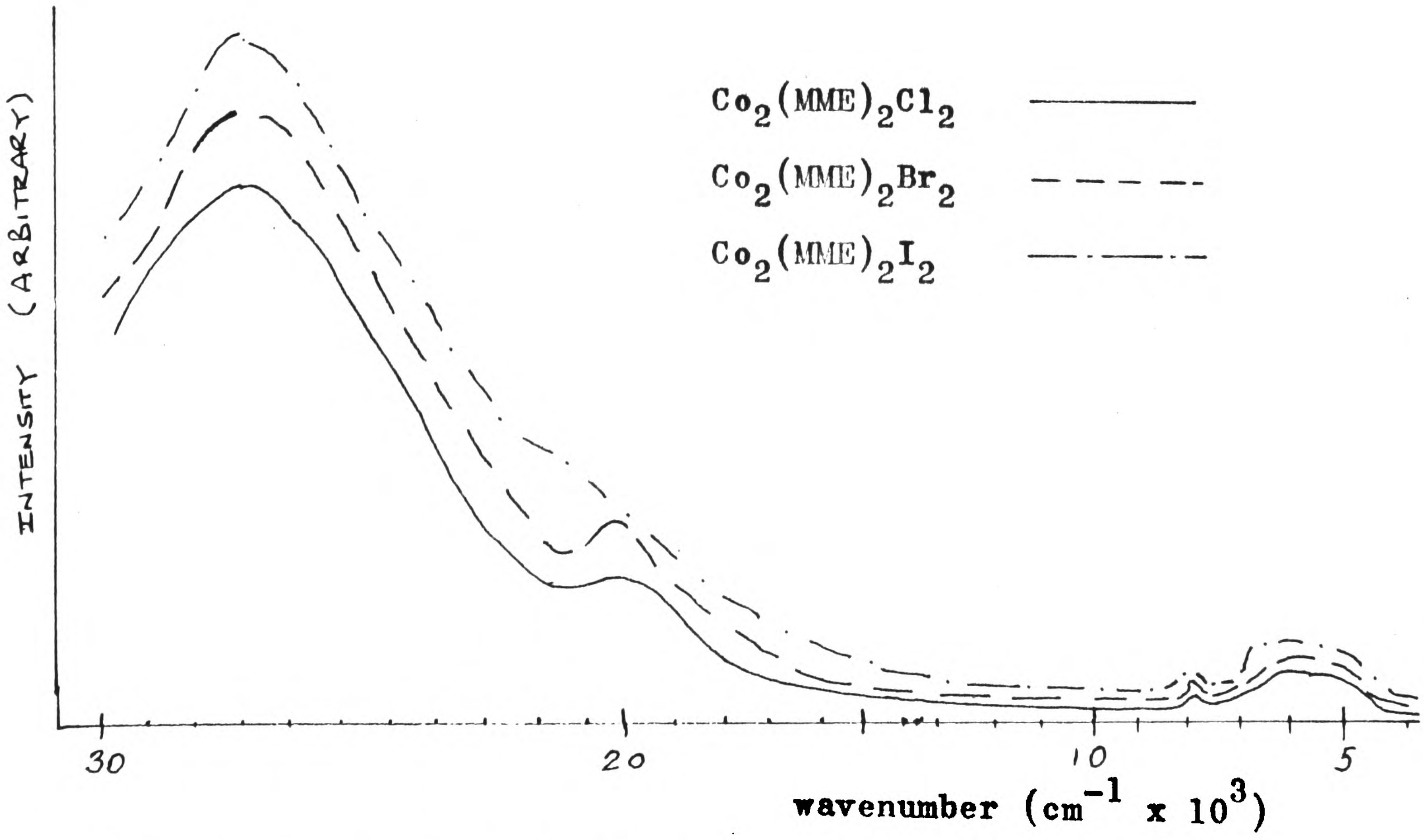
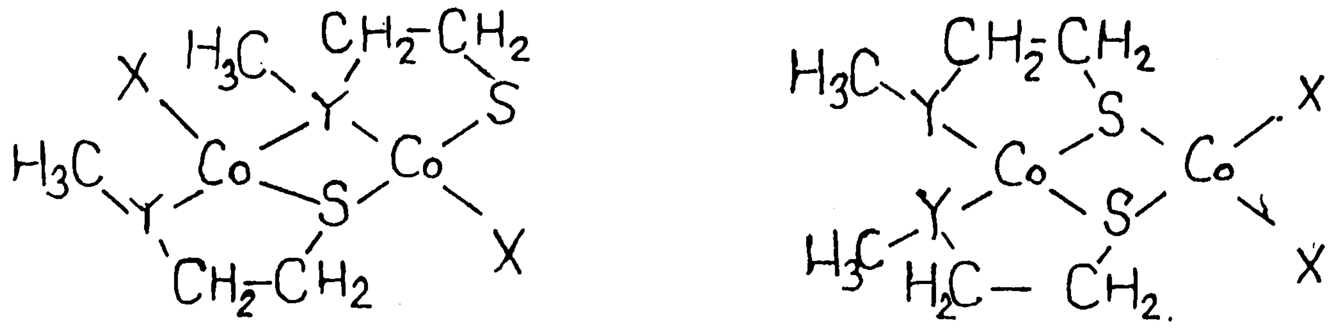


Figure 4.13 Electronic Spectra of Co(II) halide complexes of 1-mercapto-2-methoxyethane (MMEH)

analysed accordingly (Figure IR 14, p.105) the loss of the thiol (2500 cm^{-1}) absorption peak in the complex spectra indicates that the mode of co-ordination involves the thiol group with the loss of the proton. The overall change in the vibration modes of the ligand on chelation suggests that the co-ordination is not restricted to the end thiol ion only and points to the participation of the thio-ether group, which is situated favourably for the formation of a five membered metal-ligand chelation ring. Such a method of co-ordination would undoubtedly lead to a change in the conformational modes of the ligand, thus explains the observed change in the vibration modes of the ligand on chelation. The two bands observed at the lower frequency region in the nickel complexes (ca. 800 and 500 cm^{-1}) are observed in the cobalt complaxes with higher intensities. These bands obviously arise from the chelation. The band at 500 cm^{-1} is probably a metal-ligand vibration band. However, due to the overlapping and coupling of the absorption bands, it is not possible to assign the bands observed to their origins. Nevertheless, the spectra of the complexes strongly suggest that the mode of co-ordination of the ligand is effected by more than one site and may be taken as an indication of the participation of the thio-ether group on chelation.

Far Infrared Spectra (450-80 cm^{-1}): The vibrational bands observed in the spectra of the complexes are reported and assigned in Table 3.16, p.112. The spectral analysis described for the nickel complexes (p.154) is applicable in this complex and the halogen sensitive bands are easily recognised because of their high intensity and their sensitivity to the halide ions. The bands are found at 372 cm^{-1} for chloride, 342 cm^{-1} for bromide and 290 cm^{-1} for iodide. The shift of the band maxima are illustrated in Figure fir 5, p.119 which showed the spectra of the three complexes. The assignment of the metal to ligand bands can only be tentative as in the case of nickel complexes. The positions of the halide bands suggest that the structure of the complexes is likely to be *trans* rather than *cis* as illustrated in Figure 4.14, below. Similar argument as applied in the nickel complexes may be used in the cobalt complexes and it is likely that the structure shown in Figure 4.14b is the correct structure.



(a) (b)

X = Cl, Br, I

Y = O, S

Figure 4.14 (a & b) Proposed structures of Cobalt(II) halides complexes of ligands MMTH and MMEH.

4.9 Cobalt(II) halides complexes of 1-mercapto-2-ethane $\boxed{CH_3OCH_2CH_2SH}$ MMEH

The cobalt halide complexes of MMEH are all square planar dimeric compounds as deduced from the characteristic square planar electronic spectra (Table 3.11, p.99), the low magnetic moments of the compound (μ_{eff}=ca.2.2 B.M.) and molecular weight determination. This result is somewhat expected from the study of the ligand behaviour of MMTH and MMEH in the nickel halide complexes (p.150 and p.156 , respectively). Elemental analysis indicated that the complexes are pure and therefore no further purification of the crystals obtained was carried out.

The spectral analysis and interpretation not only give conclusion on the stereochemistry of the complexes but also support the argument used for the co-ordination properties of the MMTH ligand. The expected loss of the thiol vibration at 2500 cm^{-1} in the complex spectra is observed and is evidence for the thiol group co-ordination in the complexes.

In the electronic spectra (Table 3.11, p.99) of the ~~com~~ complexes, the expected high energy transition $^2E_g \leftarrow {}^2A_{1g}$ for the square planar cobalt ion, occuring at about 18000 cm^{-1}, which is obscured by the intense charge transfer band in the MMTH complexes, is observed for both the chloride and bromide as a shoulder on the charge transfer. With the iodide, this band is not observed because the charge transfer band for the iodide complex extends further into the visible spectrum, and covered any d-d transfer band above 15000 cm^{-1}. Figure 4.13, p.174 showed the solution spectra of the $Co_2(MME)_2X_2$ complexes in nitromethane, The high intensity which is observed in all the nickel and cobalt halide complexes of MMT and MME occurs at approximately the same wavenumber (ca.27000 cm^{-1}) is assumed to be charge transfer. The fact that this occurs with all the thiol complexes at the same wavenumber strongly pointed that this band is associated with the thiol group. It may be concluded that this charge transfer band is metal to ligand in origin. Such absorption is expected when the ligand has low lying empty π orbitals and thiol with empty π orbitals is an obvious candidate.

The observed halogen sensitive bands with vibration frequencies 380, 345 and 300 cm^{-1} for the chloride, bromide and the iodide complexes, respectively, are similar to the corresponding halogen sensitive bands of $Ni_2(MMT)_2 X_2$ (Table 3.16, p.112), $Ni_2(MME)_2X_2$ (Table 3.17, p.113) and $Co_2(MMT)_2 X_2$(Table 3.16) which support to the proposed mode of co-ordination of the halide ion in these complexes. Thus, it may be concluded that the ligands MMTH and MMEH form similar complexes with cobalt and nickel bivalent halides and the replacement of the sulphur (thio-ether group) by the oxygen (ether group in MMEH)has little effect to the co-ordination properties of these two ligands. Hence using the same argument as with the nickel complexes (p.150 and p.156), the structure of the cobalt complexes with MME is as shown in Figure 4.14, p.176.

It is generally observed observed that square planar complexes of cobalt(II) occur with relatively strong field ligands such as ethylenediamine and triethylene-tetramine[87] which co-ordinate through the nitrogen which is a strong field ligand. In fact, in a recent publication, Singh and

Shukla[122] postulated that (1) all ligands having ethylenediamine moiety will form square planar complex with Co(II) ions; (2) all ligands which are capable of forming five-membered aliphatic chelate ring are likely to form square planar complex and (3) to acquire a planar configuration the ligand field should be stronger than a certain threshold value, below which the Co(II) ion will prefer to acquire tetrahedral configuration.

Although the ligands MMTH and MMEH fulfil the second condition, their relatively low ligand field strength should not lead to square planar complex formation. At present there is no clear explanation why thiol ligands form square planar complexes with metal ion like Co(II) and Ni(II), but the high nephelauxetic effect of the thiol sulphur is considered to be one of the main contributory factors.

4.10 Thiophosphoryl Ligands

As mentioned in the introduction, there is much confusion on the co-ordination properties of the phosphoryl sulphur (P=S) with class 'a' metals. Counter claims on the co-ordination[66-68] properties of similar ligands are common in literature and it would seem that a great deal more information is needed before a precise evaluation on the co-ordination properties of the sulphur atom linked to phosphorus as in P=S is possible. A major reason for the unclear picture is caused by the variable polarisability of the sulphur atom when linked to some other group. The polarisability of the sulphur atom, which is determining factor in its co-ordinating strength towards class 'a' metals is dependent on the chemical nature of the other substituents. This is reflected by the fact that $R_3P=S$ (R= methyl or ethyl) does not form complexes with class 'a' metals but replacement of the alkyl groups by the aminoalkyl groups, thus increasing the basic character of the P=S group gives a ligand that would co-ordinate with class 'a' metals e.g. the compound tris(dimethylamino) phosphine forms complexes with cobalt(II) and nickel(II) halides[66] .

The phosphorus compounds investigated in the present study are esters of the thiophosphoric and thiophosphonic acid(phosphine esters may co-ordinate through the phosphorus atom). These compounds are listed below and are discussed in details in turn.

The four thiophosphate compounds and the thiophosphonate compound are the methyl thiophosphate, ethyl thiophosphate, 0,0-dimethyl methyl phosphorodithioate, 0,0-dimethyl (2-methylthioethyl) phosphorodithioate and 0,0-dimethyl methylthioethyl thiophosphonate.

a). Methyl thiophosphate and ethyl thiophosphate, $[(CH_3O)_3PS]$ and $[(C_2H_5O)_3PS]$

These compounds unlike their oxygen analogues, the tri-alkyl phosphate[65], do not form complexes with the metal halides of nickel(II) and cobalt(II) under the same experimental conditions. This result is contrary to expectation as the compound $(CH_3N)_3PS$ is reported to form metal complexes with these two metal ions[68]. One possible explanation is that the stronger basic (CH_3N)- group is better in stabilising the metal complex formation than the less basic (OR)- group.

b). O,O-Dimethyl methyl phosphorodithiolate, $[(CH_3O)_2P(S)SCH_3]$

From the negative result obtained for the thiophosphate compounds, it is unlikely that this compound would exhibit any co-ordinating behaviour towards class 'a' metal ions under the same conditions. The presence of a sulphur atom attached directly to the phosphorus would not enhance the co-ordination properties of the ligand because atoms attached directly to the phosphorus atom, apart from the phosphoryl group do not participate in co-ordination reaction (p.188). In addition, the replacement of the oxygen by the sulphur would only decrease basicity of the P=S group, rendering the phosphoryl sulphur weaker in its relative co-ordinating strength towards class 'a' metal ion. As expected this ligand does not form complexes with cobalt(II) nor nickel(II)

c). O,O-Dimethyl (2-methylthioethyl) phosphorodithiolate. $[(CH_3O)_2P(S)SCH_2CH_2SCH_3]$

The addition of this ligand to a solution of metal halide (cobalt(II) or nickel(II) halides) causes a change in the colour of the solution, indicating complex formation. However no pure metal complexes could be isolated. The product from cobalt(II) or nickel(II) halide is generally a viscous oil, which does not yield consistent results in elemental analysis. Also a large amount of solvent is trapped in this product making infrared analysis of the substance not practicable.

d). 0,0-Dimethyl (methylthioethyl) thiophosphonate, $[(CH_3O)_2P(S)CH_2CH_2SCH_3]$

Like the previous ligand, the addition of this ligand causes a colour change in the solution of metal (Ni or Co bivalent) halide, indicating that there is complex formation. However, no pure complex was isolated and vacuum distillation of the organic solvent left a gummy substance with inconsistent analysis result.

4.11 Nickel(II) halides complexes of 0,0-dimethyl S-(2-methylthioethyl) phosphorothioate, $[(CH_3O)_2P(O)SCH_2CH_2SCH_3]$, DSPD

Among all the phosphorus-sulphur and oxygen ligands investigated in the present study DSPD is the only compound which yielded crystalline complexes suitable for spectral analysis. As mentioned in the experimental section, the complexes are prepared in dichloromethane and not in butanol (p. 80). This is because the latter solvent tend to co-ordinate with the nickel and is not replaced readily by the ligand as in other sulfur ligands studied (e.g. MMTE, MTEL etc). This was avoided by the use of the dichloromethane as solvent for the preparation. The complexes formed are highly hygroscopic and must be kept in dry conditions. The elemental analysis of the complexes gives a stoichiometry of $Ni(DSPD)X_2$ and the conductance measurement indicates that the complexes are essentially non-electrolytes and the small conductance exhibited by the complexes is probably caused by partial dissociation of the complexes in solution. The limited solubility and the dissociation of the complexes in solution prevent an accurate determination of the molecular weight of the complex by ebullioscopic method. It must also be noted (as explained in the latter part of the discussion) that there is a change in stereochemistry of the complex in solution, thus the results obtained in solution may not be a true reflection of the structure of the solid complex

Electronic Spectra: The diffuse reflectance spectra of the complexes shown in Figure 4.15, p.184 are confusing. The high intensity charge transfer band which comes into the region 17000 cm^{-1} makes analysis of the spectrum difficult. The two other transitions occuring at 15000 cm^{-1} and 8500 cm^{-1} may

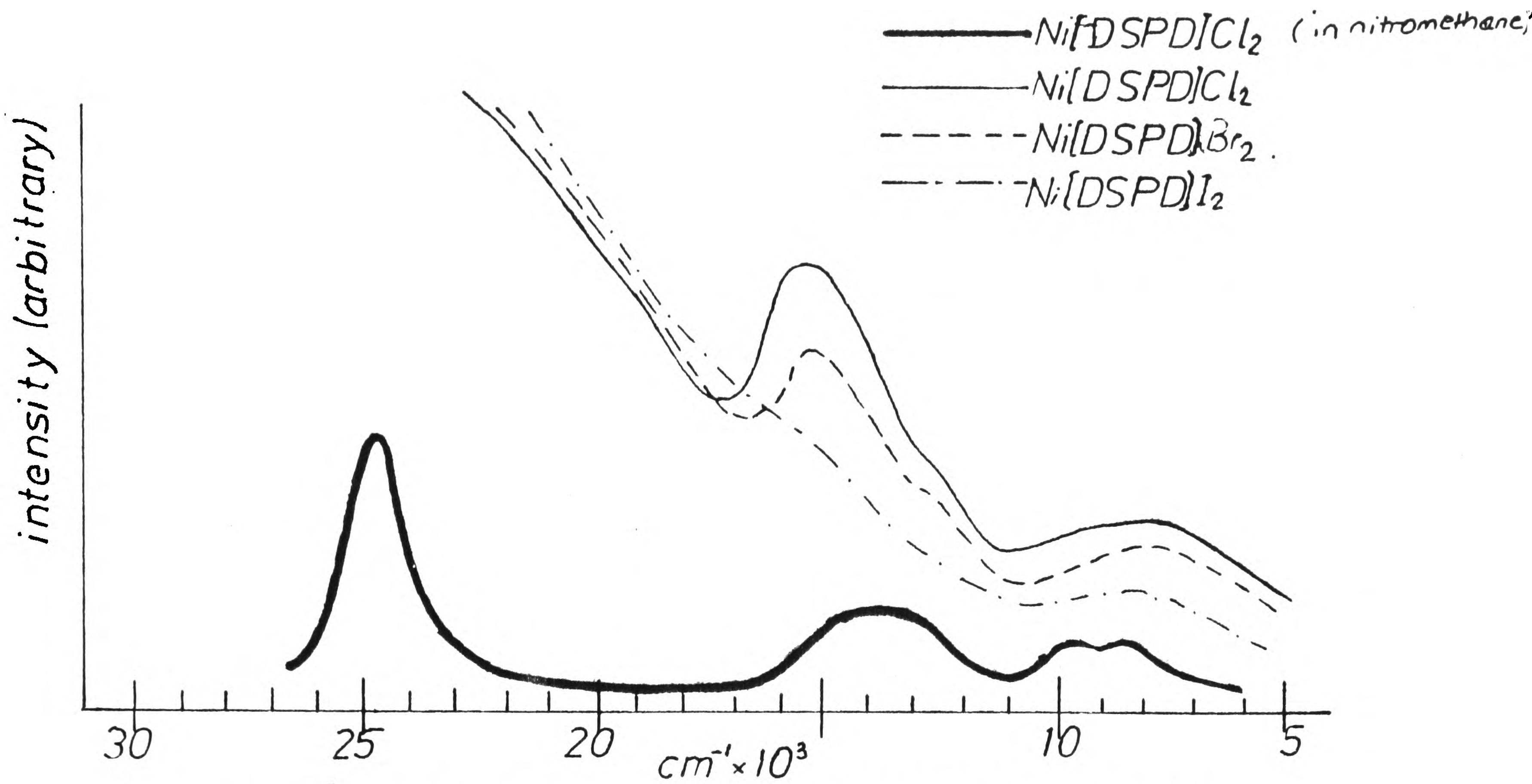


Figure 4.14 Electronic Spectra of Ni(DSPD)X_2 (X=Cl,Br,I)

Compound	10Dq	β_{35}	ref
Ni(DSPD)Cl_2	4020	0.75	this work
Ni($Ph_3PO)_2Cl_2$	3960	0.80	65
Ni(DSPD)Br_2	4000	0.75	this work
Ni($Ph_3PO)_2Br_2$	3950	0.82	65
Ni(DSPD)I_2	3980	0.73	this work
Ni($Ph_3PO)_2I_2$	3820	0.79	65

Table 4.8 10Dq and β_{35} values of Ni(DSPD)X_2 and Ni($Ph_3PO)_2X_2$ (X=Cl,Br,I)

at first appear to be the first and second transitions of Ni(II) ion in an octahedral environment. However calculation of the B value using these two bands leads to unacceptable result for all the three complexes (B=1050 and ν_3 = 30000 cm^{-1} for chloride complex). If these two bands are assumed to be the second and third transitions of Ni(II) ion in a tetrahedral environment, the calculated values of 10Dq and B are of comparable magnitudes to those of nickel complexes known to have a tetrahedral symmetry (Table 4.8,p.184). It is thus assumed that the nickel(II) complexes are tetrahedral and not octahedral. The two absorption peaks observed are readily assignable to the electronic transitions $^3T_1(P) \leftarrow {}^3T_1(F)$ ν_3 , and $^3A_2 \leftarrow {}^3T_1(F)$ ν_2. The last band ν_3 occurs at 15000 cm^{-1} is clearly shown in the complexes of chloride and bromide but in the case of iodide, this occurs as a shoulder on the charge transfer band, barely discernable at the same frequency range. The expected first d-d transition band $^3T_2(F) \leftarrow {}^3T_1(F)$ ν_1 of tetrahedral nickel complexes is not identified in these complexes due to the large overtone of the ligand bands in this region. This is quite common with tetrahedral complexes because the first transition ν_1 is usually of low energy and is found at the near infrared region of the spectrum, and is often hidden by the ligand vibration in this region.

Included in the Figure 4.15,p.184 is the solution spectrum of the Ni(DSPD)Cl_2 in nitromethane, which is representative of the three solution spectra of the Ni(DSPD)X_2 complexes. The spectrum shows characteristic absorptions of Ni(II) ion in an octahedral environment and this is supported by the low extinction coefficient value (ε = 6 cm^{-1} M^{-1} 1) of the band at 26000 cm^{-1} which is typical of Ni(II) ion in octahedral symmetry. The change in the spectra of the nickel complexes in solution is an indication of a change in the stereochemistry of the complex in solution. The change of stereochemistry of a complex when dissolved in solution is a common phenomenon and is due to the higher degree of freedom enjoyed by the molecules in solution as compared to the rigid conditions in solid. In the present case, there is also indication from the conductance measurement (Table 3.12, p.100) that complex dissociation occurs in solution thus change in the stereochemistry of the complex may be a result of many factors and there may even a decomposition of the complex.

The crystal field splitting energies and the effective values of the Racah interelectronic repulsion term B', for the complexes of DSPD are calculated according to the equations given on page 45 . These results together with those reported in the literature for the phosphorus-oxygen (P=O) ligands with nickel(II) halide tetrahedral complexes are tabulated in Table 4.8, p.184.

The similarity between the 10Dq values of the DSPD ligand and those ligands quoted suggests that the ligand DSPD co-ordinates through the phosphoryl oxygen.

It is noteworthy that the β_{35} value of the nickel(II) DSPD complexes obtained averaging 0.75 are consistently lower than those of the bis-phosphorus-oxygen complexes which are about 0.81. As the β_{35} value is related to the degree of metal ligand covalency, the lower value exhibited by this ligand indicates that the mode of chelation involves ligands with a higher nephelauxetic effect than oxygen and strongly points to the participation of the sulphur atom in the complex co-ordination.

Infrared Spectra (4000-450 cm^{-1}) The infrared spectra of the complexes are similar to each other and show a significant shift of the ν(P=0)frequency to the lower frequency. This is illustrated in Figure III 16,p.107, which showed the spectra of the nickel chloride complex and that of the free ligand. The observed large reduction in the (P=0) band (30-50 cm^{-1}) in the complex spectra points to the co-ordination is through the phosphoryl oxygen. There are no other observable changes in the spectra and the very strong absorption of the ν (P-0-C) band would renders any small change caused by the thio-ether co-ordination (which occurs in the same region) not observable.

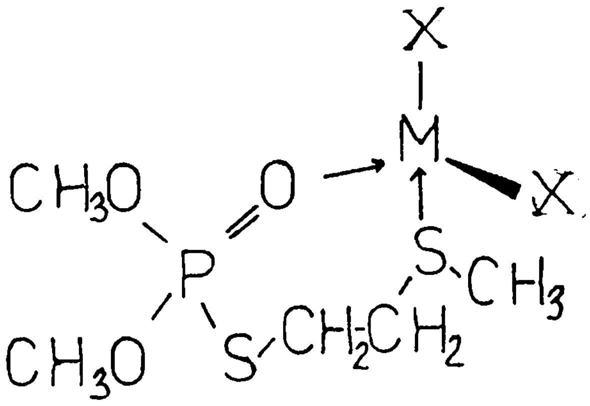
Far Infrared Spectra (450-80 cm^{-1}): The free ligand exhibits a very broad and strong absorption in the region 180-80 cm^{-1} and no individual bands can be distinguished. In the region 450-180 cm^{-1} the ligand shows three medium bands at 450, 418 and 320 cm^{-1} and two weaker bands occuring at 389 and 260 cm^{-1} (Table 3.18,p.114).

The spectra of the Complexes are very complicated with seven to eight bands found in the region 450-180 cm^{-1}. The lower regions are obscured by the ligand band. The complex spectra are not similar to each other (Figure fir 8,p.122), each with bands not found in the others. They are all different from the ligand spectrum with three to four additional bands. There is obviously a slightly shift of most of the ligand bands on chelation, but due to the complicated nature of the spectra and the overlapping of the bands, only two strong bands can be identified as metal-ligand in origin, which are found at ca. 445 and 415 cm^{-1}.

The metal-halogen bands are identified by their sensitivity to the halogen and their high intensity. The lack of halogen sensitive bands in the lower region 260–180 cm^{-1} suggests that the chloride and bromide are not bridged. The positions of the halogen bands (Table 3.18, p.114), 320 cm^{-1} for chloride, 270 cm^{-1} for the bromide and 240 cm^{-1} for the iodide strongly supports that the halides are terminally and tetrahedrally co-ordinated.

The analysis result (Table 3.6, p.89) of the complexes showed that the metal to ligand ratio in the complex is 1:1. For the complex to be tetrahedral with non-bridging halide ion, it is necessary for the ligand to bidentate. The co-ordinating sites of the ligand apart from the phosphoryl oxygen is the thio-ether sulphur on the side chain as co-ordinating agents such as oxygen, sulphur and nitrogen when attached directly to the phosphorus atom as the methoxy, thio-alkyl and aminoalkyl group respectively, do not normally participate in co-ordination reaction.

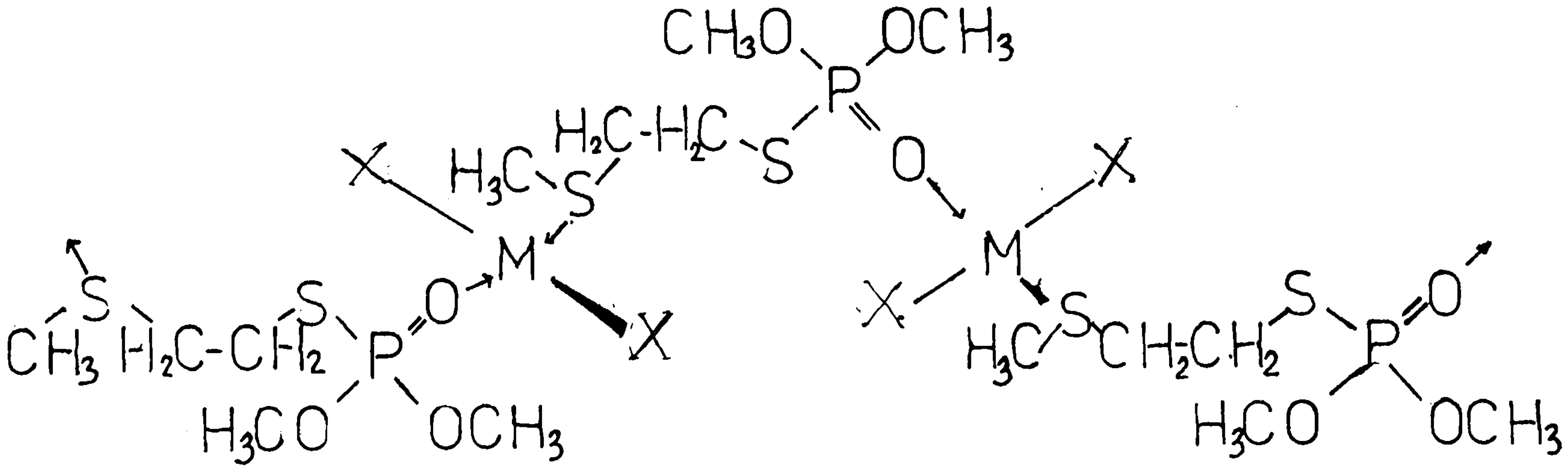
It is unlikely for the sulphur and oxygen atoms of the same ligand molecule to co-ordinate to the same metal ion, as this would result the formation of an unstable seven-membered metal-ligand chelation (Figure 4.16, p.189). It is more probable that the sulphur atom is co-ordinated to another metal ion resulting a polymeric structure as shown in Figure 4.17, p.189. The limited solubility of the complexes in organic solvents suggests that the complexes are likely to be polymeric.



M = Co, Ni

X = Cl, Br, I

Figure 4. 16



M = Co, Ni

X = Cl, Br, I

Figure 4. 17

4.12 Cobalt(II) halides complexes of 0,0-dimethyl S-(2-methylthioethyl) phosphorothiolate, $[(CH_3O)_2P(O)SCH_2CH_2SCH_3]$, DSPD

Cobalt halides react with ligand DSPD in anhydrous conditions to yield complexes of stoichiometry $Co(DSPD)X_2$. No pure cobalt iodide DSPD complex could be isolated and vacuum concentration of the solvent resulted a gummy substance which could not be crystallised. The complexes obtained are very hygroscopic and decompose rapidly when exposed to air. Conductance measurement (Table 3.12,p.100)shows that the complexes are non-electrolytes and the small conductivity showed by the complexes are likely to have caused by small dissociation of the complexes in solution. The limited solubility of the complexes in organic solvents makes it difficult to determine the molecular weight of the complexes by ebullioscopic method accurately.

Electronic Spectra: The diffuse reflectance of the cobalt DSPD complexes suggest tetrahedral structure for the two compounds (p. 45). The bands observed and their assignment are tabulated in Table 3.12,p.100.The ${}^4T_1(P) \leftarrow {}^4A_2$ ν_3 and ${}^4T_1(F) \leftarrow {}^4A_2$ ν_2 transitions appear as multiple absorption in the region 16000-13000 cm^{-1} and 7400-5000 cm^{-1}, respectively.

The values of the electronic parameters calculated from the spectra are listed in Table 4.9,p.191. The availability of reliable 10Dq and β_{35} values for $Co[(CH_3)_3PO]_2X_2$ (X=Cl, Br) complexes makes it possible to compare the ligand field strength of the DSPD ligand with the phosphoryl oxygen ligands. As with the nickel DSPD complexes such a comparison shows that the phosphoryl oxygen is involved in the co-ordination by the similarity of the crystal field splitting energy of both ligands (10Dq=3810

Compound	10Dq cm^{-1}	β_{35}	$-\lambda$ cm^{-1}	ref.
$Co(DSPD)Cl_2$	3810	0.76	152	this work
$Co(Me_3PO)Cl_2$	3730	0.76	145	65
$Co(DSPD)Cl_2$	3812	0.71	156	this work
$Co(Me_3PO)Cl_2$	3590	0.76	147	65

Table 4.9 10Dq, β_{35} and $-\lambda$ values of $Co(DSPD)X_2$, and $Co(Me_3PO)X_2$ (X=Cl,Br)

for DSPD and 3730 for $(CH_3)_3PO$ in the chloride complexes) and that the lower β_{35} value of the DSPD complexes (β_{35} =0.72 for DSPD and β_{35} =0.76 for $(CH_3)_3PO$ suggests that there is appreciably more orbital overlapping than the $(CH_3)_3PO$ ligands, which strongly supports the assumption that the sulphur atom is also involved in the co-ordination.

Infrared Spectra(4000-450 cm^{-1}): As in the case of nickel DSPD complexes only the ν(P=0) at 1250 cm^{-1} was shifted to lower frequency by 30-50 cm^{-1} in the complex spectra. No other observable change is noted on other ligand absorption band in this region, which suggests that there is no overall change in the conformation mode of the ligand and indicates that the chelation is unlikely to involve ring formation (p.138). The shift of the ν(P=0) absorption band is in agreement with the assumption that the co-ordination is through the phosphoryl oxygen. The infrared spectra of the two halide complexes are similar, thus only the spectrum of the chloride complex is included in the Figure IR 16, p.107 for illustration.

Far Infrared Spectra (450-80 cm^{-1}): The far infrared spectra of the complexes are similar in appearance to those of the nickel complexes and as those have already been discussed in detail (p.187), it is therefore sufficient to say that, the complexity of the spectra makes the assignment of the absorption bands apart from the high intensity halogen sensitive bands, tentative. The band assignments and their frequencies are listed in Table 3.18,p.114.The positions of the halogen sensitive bands (315 cm^{-1} for chloride and 260 cm^{-1} for bromide) suggest that the halides are co-ordinated tetrahedrally which supports the tetrahedral structure as indicated by the electronic spectra of the complexes.

Magnetic Susceptibility: The magnetic moments of the complexes listed in Table 3.12, p.101 with μ_{eff}=4.6 B.M. for chloride and 4.7 B.M. for the bromide are in the upper limit of values typical of cobalt ion in tetrahedral structure. It is possible to calculate values of the spin-orbit coupling coefficient from the spectroscopic and magnetic measurements[83,123]. It has been pointed out by Owen[123] that the lowering of the spin-orbital coupling λ', in the complexes as compared to the λ value in the free ion is related to orbital overlapping resulting in delocalization of the d electron, hence λ' value as in the case of β_{35} value is related to the degree of metal-ligand covalency. It might be supposed that a lower β_{35} value leads to a lower value. Thus, even though the λ' value obtained from this calculation is subjected to considerable error, it is of interest in the present study to provide a way to test the validity of the supposition that there is higher covalency the complexes of DSPD relative to the phosphorus-oxygen complexes. As expected, the λ value calculated for the cobalt DSPD complexes are lower than those of the $(CH_3)_3PO$ complexes (Table 4.9,p.186).

The spectral evidence, magnetic moments, elemental analysis and conductance measurement all indicate that the complexes formed by the DSPD ligand with cobalt halides are tetrahedral. The co-ordination is likely to be effected as in the nickel complexes (p. 183) through the phosphoryl oxygen and the thioether sulfur present in the side chain and the structure of the complex is likely to be polymeric as shown in Figure 4.16, p.184.

4.13 Preliminary investigation of reaction of ferric chloride with the sulfur and phosphorus-sulphur and phosphorus-oxygen ligands

a) Initially, it was thought that the **sulphur ligand in** the present study MTEL (p.131), MTOE (p.140), MMTH (P.150), MMEH (p.156) and MTD (p. 144) would exhibit stronger co-ordinating properties towards the more covalent (compare to nickel(II) and cobalt(II) ions) ferric ion. Under the same experimental conditions no crystalline product of any of the ligands with the ferric ion was obtained, although there is indication (colour change on addition of the ligands to the metal salt solution) that complexation may occur in solution.

The lack of crystalline product does not necessarily reflect on the lesser tendency of complex formation of the ferric ion towards these ligands in comparison to the nickel and cobalt bivalent ions. It is more likely that the solubility of the ferric complexes in the organic solvent is greater than the corresponding nickel or cobalt complexes. However, the lack of solid product of ferric ion prevents any direct comparison of the complex structure between the metal complexes.

b) Ferric chloride complexes with the thiol ligands MMTH and MMEH

The thiol ligand MMTH and MMEHformed complexes with ferric chloride in aqueous conditions. The black crystalline solid formed contained no chloride ion and the analytical results (Table 3.19,p.124) give a stoichiometric formula of FeL_3(L=MMTH or MMEH). The molar ratio of ligand to metal is three to one, which is expected from the balance of the charges of the compound, The analytical results are not very consistent, even after re-crystallisation of the solid, which is probably due to the partial reduction of the ferric ion on chelation. The complex also showed abnormal magnetic behaviour with μ_{eff}=4.3 B.M. which could only be explained by the existence of both high spin (sextet) and low spin(doublet) states in the complex[124]. This may also explain the complicated electronic spectrum of this complex. As the present study involves with complexes prepared in non-aqueous conditions, this compound was not investgated any further.

c) Ferric chloride complexes with the phosphoryl compounds

With the phosphoryl compounds, ferric chloride only forms crystalline complexes with the phosphoryl oxygen compound and no phosphoryl-sulfur complex was obtained, but it is observed that there is generally a colour change in the ferric solution on the addition of the phosphoryl-sulfur compounds, indicating that some complexation may have occurred. This phenomenon was investgated by the use of the 0'0-dimethyl (2-methylthioethyl) phosphorodithioate, which has a well defined ν(P=S) absorption band at 652 cm^{-1} in the infrared spectrum.

d) Ferric chloride study with ligand 0,0-dimethyl (2-methylthioethyl) phosphorothiolate (DSPD)

A set of solution of 0,0-dimethyl((2-methylthioethyl) phosphorothiolate (0.01M in xylene), increasing amount of ferric chloride was added. The series of solution obtained were investigated by infrared spectroscopy It was observed that the addition of the ferric ion caused a gradual broadening of the ν (P=S) band, which disappeared completely when ferric chloride was added in large excess (Figure 4.18, p.190). From

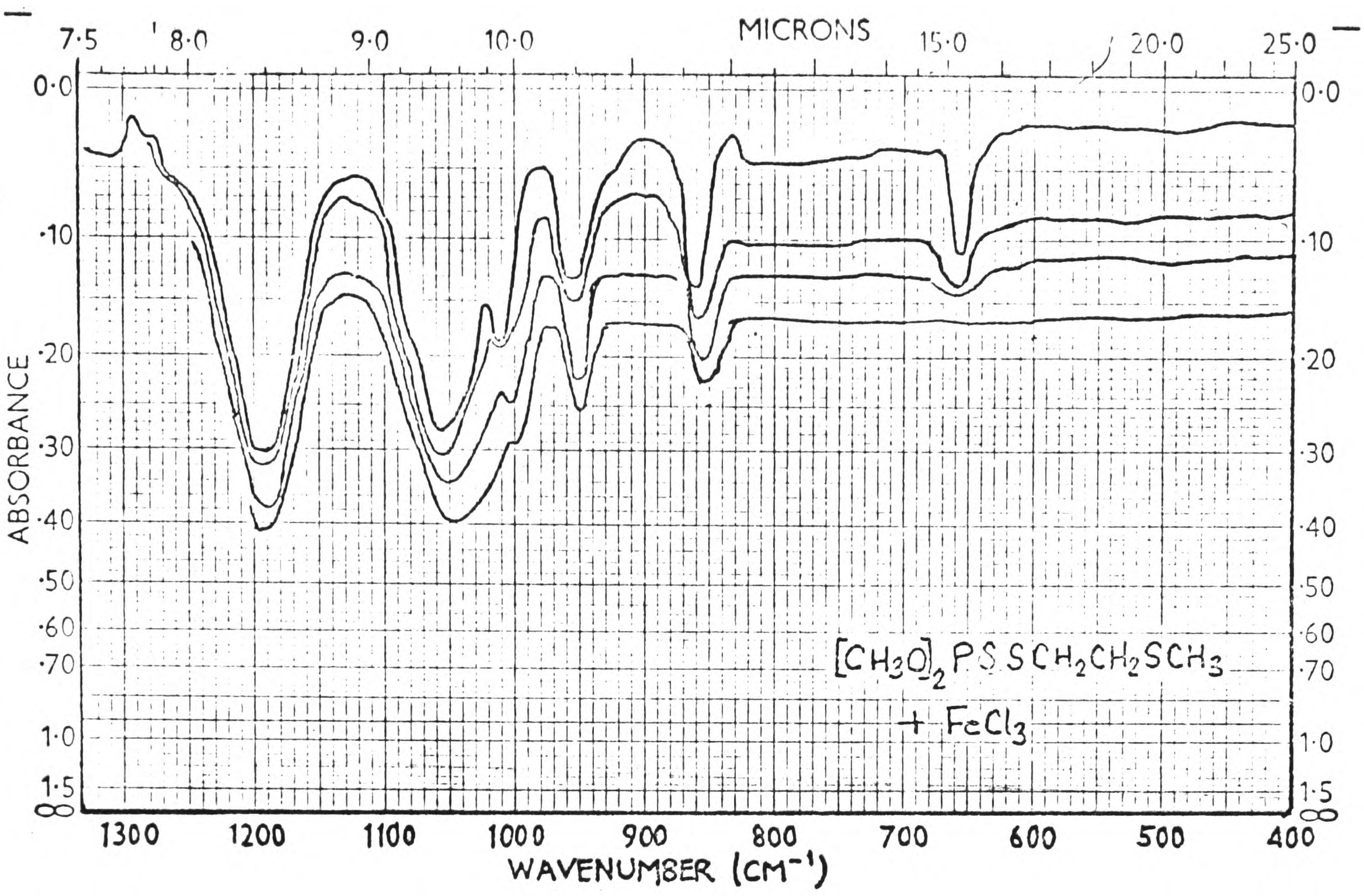


Figure 4. 18 Infrared spectra of $FeCl_3$ and 0,0-dimethyl (2-methylthioethyl) phosphorodithioate

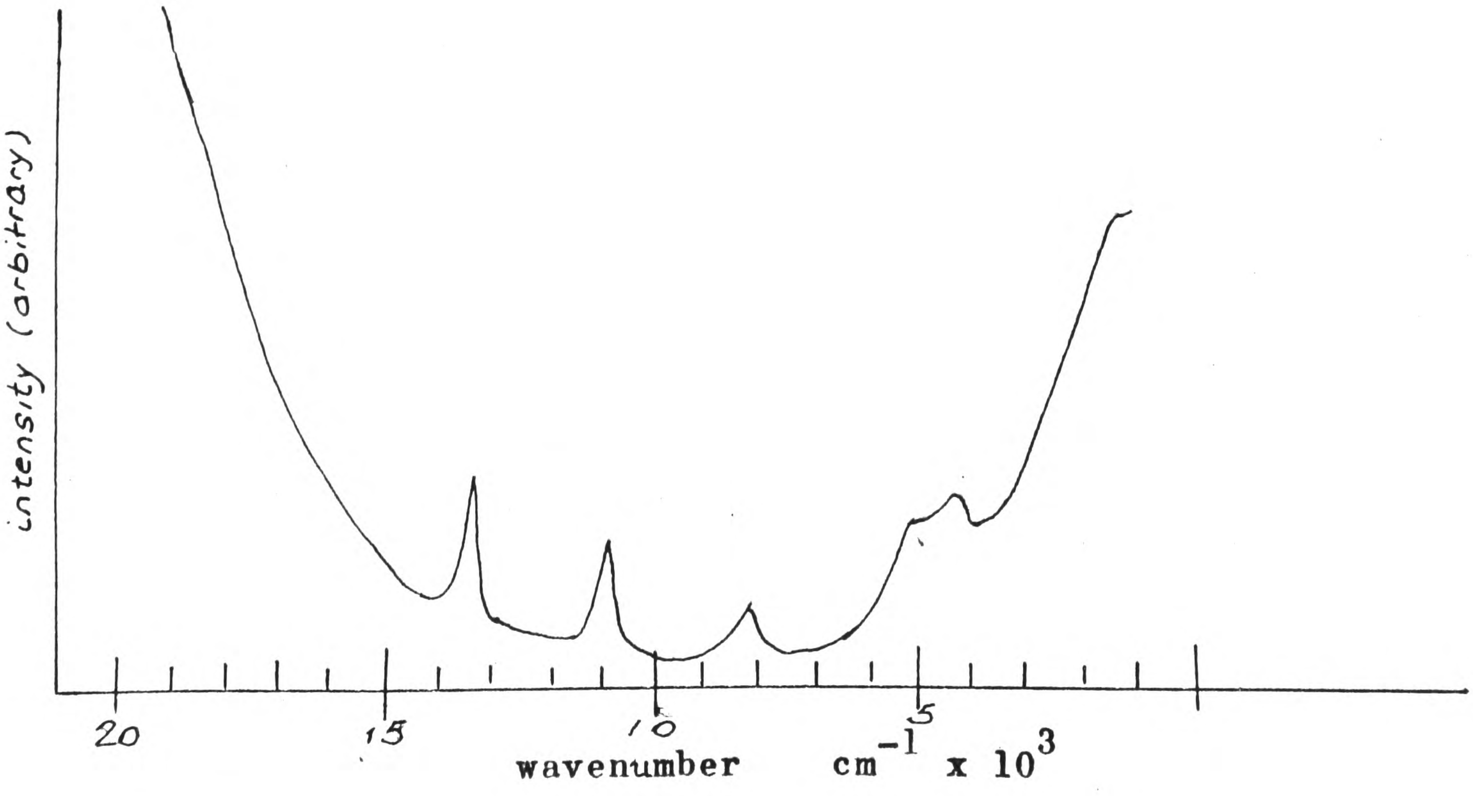


Figure 4. 19 Electronic Spectra of $Fe(DSPD)Cl_3$

the infra spectra and the colour change on addition of the ligand to the metal chloride solution, it may be concluded that the phosphoryl-sulphur ligands co-ordinate with ferric ion in solution via the phosphoryl-sulfur atom. As there is no observable change with all other major bands of the spectrum of the ligand even in the present of excess ferric ion, no conclusion in the possible participation of the thio-ether sulphur present in the side chain, in the chelation may be drawn.

e) Ferric chloride complex with 0,0-dimethyl S-2-methyl thioethyl phosphorothiolate (DSPD)

The ferric complex obtained with DSPD (experimental method C, p.80), is pale brown in colour, It is not hygroscopic and is quite stable in atmosphere. Elemental analysis (Table 3.19a, p. 124) gives a stoichiometric formula of $Fe(DSPD)Cl_3$, which agrees with the molecular weight formula obtained from the ebullioscopic determination in acetone. The magnetic moments of the complex (μ_{eff}=5.5 B.M.) suggests a high spin ground state ($^6A_2$)[123].

The predominent feature of the electronic spectrum is an intense charge transfer band, which extends far into the visible region (18000 cm^{-1}) as shown in Figure 4.19,p.195 obscuring most of the crystal field transitions. Two narrow bands are observed at the tail end of the charge transfer band.

From the magnetic moments measurements the ground state of the ferric complex corresponds to five unpaired electrons. This is in fact a half-filled d shell and is therefore spherically symmetrical. Thus the ground state term is derived from the ^6S term of the spherically perturbed free ion. This is unaltered by all operations of the octahedral or tetrahedral group and belongs to $^6A_2$. All transitions from the ground state (in a weak field) are spin forbidden. Thus, if transition occur, it would be very weak, this is in agreement to the weak narrow bands observed in the spectrum. This very weak transition is also reflected on the very pale brown colour of the complex.

Due to the large intense charge transfer band which covered most of the visible spectrum, conclusion on the stereochemistry could not be drawn on the electronic spectrum of the complex, although the bands observed are compatible with a tetrahedral stereochemistry[124].

Infrared Spectrum (4000-450 cm^{-1}): The infrared spectra of the ligand and the complex are shown in Figure IR 17, p.108. Apart from the large shift of the ν(P=0) at 1250 cm^{-1} for the ligand to 1170 cm^{-1} in the complex, no observable shift on all other major bands of the ligand is noted. The shift of the ν(P=0) band confirms that the co-ordination is through the phosphoryl-oxygen of the molecule. The lack of observable change on other major bands suggests that the chelation does not cause any major conformational change to the ligand molecule indicating that the co-ordination is probably through the oxygen atom only.

Far Infrared Spectrum (450-80 cm^{-1}): The far infrared spectra of the ligand and the complex are shown in Figure fir 9 p.123. The spectrum of the complex showed two intense bands occuring at 380 cm^{-1} and 240 cm^{-1} and a medium strength band at 320 cm^{-1}. Apart from the 320 cm^{-1} band, which also occurs as a strong band in the ligand, none of the other ligand bands is observed in the complex spectrum. The band assignment is listed in Table 3.20, p.124 and the band at 380 cm^{-1} is probably due to the stretching vibration of Fe-Cl [105] and the lower band at 240 cm^{-1} is assignable to ligand-metal vibration mode.

From the results obtained, it is likely that the ferric ion complex has tetrahedral structure with the metal co-ordinated to three chloride ions and one ligand molecule. The ligand co-ordinates through the phosphoryl-oxygen and it is unlikely that the thio-ether sulfur on the side chain of the ligand is involved in the co-ordination.

f) Ferric chloride complex with Tinox

The complex obtained using purified Tinox as ligand with ferric chloride is identical to that obtained with the thiolo isomer, as seen by their identical spectroscopic properties. This is expected from the previous experiments which indicated that only the phosphoryl-oxygen compounds form crystalline solid complex with ferric chloride.

This led to the suggestion, that the two isomers in the formulation may be separated by the selective precipitation of the thiolo-isomer by ferric chloride. For this method to be of practical use, the precipitation of the thiolo-isomer must be complete. However, further experimental work showed that the precipitation of the thiolo isomer as a complex of ferric chloride was not complete, with a large percentage of the thiolo isomer left in the residual solution. Excess ferric chloride could not induce complete precipitation, as the complex has a notable solubility in most organic solvents. Hence, it is not possible to utilise this property for the separation of the two isomers.

g) Ferric Thiocyanate Experiment

(experimental detail on p. 128)

It has been shown that the selective precipitation of the thiolo isomer using ferric chloride (p,187) is not feasible as a quantitative analytical method for the determination of the thiolo isomer. In the course of examining organophosphorus compounds, it has been noted that a number of phosphates are used to extract metal ions from aqueous solution[125-7], and it has been found that the amount of metal ion extracted is dependent on a number of factors, among these, such as the pH of the solution the coefficient of partition of the metal between the two phases and it also varies directly to the concentration of the phosphate used. This led us to design an experiment to test the extracting property of the thiolo isomer (which may be regarded as a phosphate) on the ferric thiocyanate and to investigate the feasibility of this property for the basis of a quantitative test for the thiolo isomer.

The reason for the choice of ferric thiocyanate are three fold (1) extraction of ferric thiocyanate by organic solvent has been well studied[128-9] and the results obtained may be comparedwith those reported in the literature;(2) ferric thiocyanate exhibits an intense charge transfer band, which is quantitatively related to the amount of ferric thiocyanate present and this band is intensified in the organic solvent, thus making the exact amount of ferric present readily established;(3) the presence of water prevents interference from the thiono isomer and other sulphur breakdown products to co-ordinate to the ferric ion and any ferric-thiol complex formed would go into the aqueous layer and therefore would not interfere.

Table 3.20,p.129 shows the results of extracting 15 ml. of 1 mole solution of ferric thiocyanate with solution of thiolo isomer in Xylene of various concentrations (20 ml.). Ferric thiocyanate extracted is proportional to the absorbance reading at 560 cm^{-1}. A graph of absorbance against the concentration of thiolo is plotted (Figure 3.1,p.129).

The linearity of the graph indicated that the extraction is directly proportional to the concentration of the thiolo concentration. However, both the low sensitivity (detection limit at about 0.1 mole solution) and the accuracy (± 5%) would require improvement before this method become suitable for quantitative analysis of the Tinox isomer. However, the simplicity of this method is a great advantage and should be explored further.

V

CONCLUSION

V. CONCLUSION

The results obtained for the thio-ether ligands highlighted two points (i) thio-ether and ether have very similar spectrochemical behaviour towards nickel(II) and cobalt(II) metal ions, which substantiates the proposed position of the thio-ether in the spectrochemical series as between H_2O and NCS^-; (ii) although generally π-bonding between the metal ion and the ligand in nickel(II) and cobalt(II) complexes is regarded as being of limited importance, the consistently higher nephelauxetic effect of the thioether ligand over ether ligand, indicates that some π-bonding character must be present in these metal complexes. This is well illustrated by the relatively lower values obtained for the thio-ether ligand as for example β_{35} values for nickel(II) halides complexes for MTEL[+], MTOE[++] and MTD[+++] are 0.77, 0.77 and 0.76, respectively and for cobalt(II) halides complexes for MTEL[+] and MTOE[++] are 0.68 and 0.72, respectively. (The β_{35} values for $Ni(O)_4$ and $Co(O)_4$ complexes with the corresponding stereochemistry are 0.79 and 0.77, respectively.)

The stereochemistry of the ligand is in some cases a major factor in the complex formation. This is shown by the fact that the ligand MTD (p.144) forms complexes with nickel(II) halides but no crystalline product of cobalt(II) halide could be obtained under the same experiment conditions. This is thought to be caused by the fact that nickel complexes of thioether ligands are normally octahedral whereas the cobalt complexes are tetrahedral and that the favoured stereochemistry of the cobalt complexes may not be compatible with the configuration of the ligand, thus no complex could be obtained.

[+] 3-thiabutanol

[++] 1-methoxy-3-thiabutane

[+++] di-(2-methythioethyl) disulphide

The results of the mercapto-ligands reflect on the difference of their electronic states between thiol and thio-ether. An entirely different stereochemistry is obtained for the complexes with the thiol ligands. The tendency of forming square planar complexes with nickel(II) and cobalt(II) metal ions is obviously due to the high polarisability of the thiol ion rather than its ability in accepting d electrons for which the thio-ether is known to be better[35].

With the aid of far infrared spectroscopic technique, identification of the correct structure from the two possible structures of the metal complexes with the ligand MMTH and MMEH has been made and it is concluded that the trans structure (p.150, 156, 172 and 177) with sulphur bridging is the one which fits best all the available evidence.

The phosphoryl compounds exhibit different co-ordinating behaviour to the aliphatic sulphur and oxygen compounds. The phosphoryl sulphur is a very weak co-ordinating ligand when compared to the oxygen analogue. This is reflected by the formation of complexes of nickel(II) and cobalt(II) halides with ligand 0,0-dimethyl S-(2-methylthioethyl) phosphorothiolate and only an oily impure product was obtained with phosphoryl sulphur analogue 0,0-dimethyl (2-methylthioethyl) phosphorodithiolate. The relatively stronger oxygen towards the class 'a' metal is in agreement with the higher electronegativity of oxygen relative to the sulphur atom. It is observed from the results obtained, that the predominant factor on the co-ordination strength for the two ligands above towards the class 'a' metal is the electronegativity of the co-ordination atoms and that the polarisability of the atom is not an important factor.

The stereochemistry of the complexes formed by the thiophosphoryl ligands is tetrahedral for both the nickel(II) and cobalt(II) halides. The consistent lower values of β_{35} of both complexes when compared to the analogues oxygen complexes (bis-phosphorus-oxygen metal halide complexes, p.186) leaves little doubt that the sulphur atom in the side chain is also involved in the co-ordination.

Hence, with the use of nickel(II) and cobalt(II) bivalent salts, it has been shown clearly that the Tinox isomers exhibit chelating properties in solution, although only the thiolo isomer (0,0-dimethyl S-(2-methylthioethyl) phosphorothiolate) would form crystalline solid complexes, whereas the thiono isomer (0,0-dimethyl 0-(2-methylthioethyl) phosphorothionate) with the weak phosphoryl sulphur atom would not form crystalline product with nickel(II) and cobalt(II) halides.

For ecological reasons discussed on page 30, these two metal ions are not suitable for industrial use. However, their use in the investigation has led to the establishment of the chelation sites of the Tinox isomers.

The possible use of ferric ion for complexation has been studied. The results indicate complexation takes place, but the mode of co-ordination apparently involves only phosphoryl group and not the thio-ether group present in the side chain. The complex formed is found to be high spin and has a tetrahedral stereochemistry. It has also been demonstrated that only one ligand acting as monodentate co-ordinating agent is attached to the complex and the halide ions are also co-ordinated.

The formation of a solid complex does not automatically prove the feasibility of the ferric ion as a stabilisation agent. To establish this, it would be necessary to study the thermodynamic properties of the complex formed in solution, the stability constant, the dissociation constant and the solubility products. In addition, the hydrolysis of the complex by water would require more detailed study, to ensure that the hydrolysis of the complex would yield the active ingredient in full and no undesirable side reaction was catalysed by the presence of the metal ions.

The investigation of the chelating properties of the breakdown leads to the conclusion that no practical photometric method may be developed for the analysis of the active ingredients in ®Tinox using nickel(II) and cobalt(II) salts. The feasibility of such a method is hindered by the fact that the phosphoryl sulphur and oxygen are the weakest co-ordinating agents in the formulation (relative to the co-ordinating agents present) and it is unlikely that conditions may be found which would eliminate the interference from othe chelating agents present and allow selective complexation of the metal by the ®Tinox isomers.

The special affinity of ferric ion towards the phosphoryl oxygen leads to the investigation of the potential of using ferric thiocyanate for the analysis of the thiolo isomer. The apparent low sensitivity of this method seems to render the analysis unsuitable. However, the full potential of this method has not been fully tested. The effects of altering other parameters which would affect the extraction have not been fully investigated. Further work on the line of improving the sensitivity and accuracy of this method is necessary before a definite conclusion on the feasibility of this method can be drawn.

VI

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