AN INVESTIGATION OF THE STRUCTURES, PROPERTIES AND POSSIBLE APPLICATIONS OF COMPLEXES OF METALS WITH ORGANOTELLURIUM COMPOUNDS

by

VICHITR RATTANAPHANI

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ABSTRACT

Organic telluride complex forming ability was investigated. It is found that tellurides form quite stable complexes with metals of class (b) or softish character. Copper(I), rhodium(III) and rhodium(I) complexes with diaryltellurides were synthesised. Their structure, properties and uses were investigated with the help of various physical techniques.

Copper(I) halides and tellurides were found to form complexes with definite compositions irrespective of the ratio of metal: ligand used. A 2:1 ligand to metal ratio was preferentially formed among the copper(I) complexes. The structures of these copper(I) compounds were found to range from tetrahedral, four-coordinated copper(I) halogen bridged dimers, trigonal planar and three coordinated copper(I) halogen bridged dimers. The copper-halogen stretching vibrations $\nu(Cu - X)$; (X = Cl, Br, I) were found to be rather low compared with the available literature values.

Rhodium(III) halides with tellurides were found to form complexes of the type ML_3X_3; (L = diaryltelluride; X = Cl, Br) to which a configuration was assigned with the aid of far infra-red and n.m.r. spectroscopy. mer RhL_3X_3 was found to form in good yield under dinitrogen. The preparation carried our under air yielded the complex fac RhL_3X_3 in lower yield. Reactions using $[Rh(Ph_2Te)_3Cl_3]$ as a synthetic intermediate in preparing complexes of the type $[Rh(Ph_2Te)(chelate)Cl_3]$; (chelate = 2,2'bipyridyl, 1,10'phenanthroline, di-2-pyridylketone, di-2-pyridylamine) were carried out. A rhodium(I) complex with telluride was found to be stable only in the presence of CO; a complex formulated as $[Rh(Ph_2Te)_2(CO)Cl]$ was synthesised. Reactions using telluride to stabilise rhodium(I) compounds in the presence of ethanolic KOH and borohydride were unsuccessful.

Reactions to test the complex $Rh(Ph_2Te)_3Cl_3$ as a homogeneous hydrogenation catalyst were carried out. It was found that $Rh(Ph_2Te)_3Cl_2$ did not catalyse the homogeneous hydrogenation reaction contrary to the complexes (RhL_3Cl_3); (L = Et_2S, $(PhCH_2)_2S$) which are known to be active.

The role of di-2-pyridylketone as ligand was investigated. Some complexes of cobalt, iron, nickel and copper with di-2-pyridylketone were synthesised and characterised by various techniques. An explanation for the anomolous magnetic behaviour of cobalt complex reported by a previous worker is given. *Tris* complexes of di-2-pyridylketone were found to exist. The ligand field parameters of some complexes are given, and di-2-pyridylketone was found to be a weak field ligand.

It was noted that under some circumstances the carbonyl group of the ligand became readily aquated or alcoholated. The ease of formation of these acetal or hemicetal deriviatives is discussed and it is concluded that, contrary to the previous suggestion, steric strain within the carbonyl ligand need not be a major cause.

All complexes prepared are discussed in terms of their analytical data and spectra, including in the case of iron(II) and iron(III) complexes their ^{57}Fe Mössbauer spectra. In one case good evidence for an(N,O)mode of coordination for di-2-pyridylketone was found.

This work was carried out between 1970 and 1973 at The University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

V. Rattanaphani

V. RATTANAPHANI

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CHAPTER ONE

INTRODUCTION

As part of a programme of research in the area of organotellurium chemistry being carried out in this laboratory; an investigation of the potentialities of organictellurides as ligands in the formation of complexes was carried out. Although sulphur-containing ligands have now been widely studied(1,2), only a handful of tellurium-containing ligands have been investigated.

The ligands chosen for this study are of the type R_2Te where [$R = C_6H_5$ -, p-$CH_3C_6H_4$-, p-$EtOC_6H_4$-],some reactions and properties of these diaryl tellurides will be mentioned here. Tellurides can be prepared by the reduction of bis(organo)telluriumdihalides by a variety of reducing agents, e.g. Na_2SO_3, $NaHSO_3$, $Na_2S.9H_2O$, tin(II)chloride in hydrochloric acid, and lithium aluminium hydride. The tellurides undergo a wide variety of reactions. The chemical changes take place preferably on the tellurium atom or affect the tellurium-carbon linkages. Some of the reactions of tellurides which have been investigated are

a) The reactions which increase the valency of tellurium.

1. The addition of two halogen atoms to form bis(organo) tellurium halides

$$R_2Te + X_2 \longrightarrow R_2TeX_2$$

This reactions is very useful in purifying tellurides. The halides are recrystallised and reduced back to give pure tellurides(3). McWhinnie and Patel(3) have studied isomorphous series Ph_2TeX_2 [$Ph = C_6H_5$, X = Cl,Br,I] and have suggested the assignment of tellurium-halogen stretching vibrations, ν(Te-X) and concluded that the structure of all Ph_2TeX_2 compounds is ψ-trigonal bipyramidal with axial halogen atoms regardless of the nature of substituents in the aryl ring.

2. Metal chlorides, for example, $FeCl_3$, $HgCl_2$, and $CuCl_2$ were reduced to the lower chlorides when heated in a sealed tube in glacial acetic acid with bis(p-tolyl)telluride. The bis(p-tolyl) telluride dichloride was isolated from these reactions(4).

$$2FeCl_3 + R_2Te \longrightarrow R_2TeCl_2 + 2FeCl_2$$

$$2CuCl_2 + R_2Te \longrightarrow R_2TeCl_2 + 2CuCl$$

Silver chloride was only reduced slightly and most of the telluride was recovered unchanged. When hydrated ferric chloride was used in the reaction with toluene as the solvent, the anhydride of bis (p-tolyl)tellurium hydroxychloride was obtained. Anhydrous $FeCl_3$ did not give this product.

b) Reactions of tellurides which affect the tellurium-carbon bond. The example for these reactions is the exchange of a tellurium atom for a sulphur atom(5) e.g.

$$C_6H_5TeC_6H_5 + S \longrightarrow C_6H_5SC_6H_5 + Te$$

An extensive survey of the relative affinities of ligand atoms for metal ions was made by Ahrland, Chatt and Davies(6) who divided metals into two classes (a) those which form their most stable complexes with the first ligand atom of each group, i.e. with N, O and F, (b) those which form their most stable complexes with the second or subsequent ligand atoms. For class (a) the stabilities of the complexes will be 0 >> S > Se > Te; for class (b) metals S >> 0 but almost any sequence of S, Se and Te may occur. Class (b) metals form a triangular area in the centre of the periodic table with a somewhat diffuse border. Metals of pronounced (b) character are in the centre of this area for examples Cu(I), Rh(I), Pd(II), Ag(I), Pt(II) and Hg(II). Molecules such as C_2H_4, CO and CNR will co-ordinate only with metals of pronounced (b) characters. The oxidation state of metals affects the degree of (b) character, which is strongest for transition metals in low oxidation states, i.e. metals having non-bonding d electrons so they are capable of forming d_π - p_π and d_π - d_π bonds by donating a pair of electrons to the ligand. Craig and Nyholm(7) have given a semi-quantitative explanation of class (a) and class (b) behaviour toward halides ions.

Another classification of metals and ligands into hardish and softish lewis acids and bases was done by Pearson(8) which is very similar to the preceding (a) and (b) characters. A general rule for this principle is that hardish acids will bind strongly to hardish bases and softish acids to softish bases. Hardish acids are those that bind to bases which bind strongly to the proton, softish acids bind strongly to highly polarisable or unsaturated bases which have very small affinity to bind with protons, e.g. R_2S, R_2Se, R_2Te. In some cases it is possible for a base to be soft and bind strongly to the proton, e.g. the highly polarisable S^{2-} ion.

As organictellurides could be classified as softish bases or class (b), they should form a very stable complexes with acceptor of class (b) and softish characters. According to Jørgensen(9) class (b) contains three categories: (1) metals with unusually low oxidation numbers; (2) metals with certain high oxidation numbers, (3) the S^2 family Sn^{II}, Sb^{III}, $T\ell^{I}$, Pb^{I}, Bi^{III} showing (b) character to heavy halides and chalcogenides but (a) toward σ-bonded cyanides and amines. Low-spin d^8 ions Pd^{II}, Pt^{II}, Au^{III} and d^{10} ions, Cu^{I}, Ag^{I}, Au^{I} and Hg^{II} have the highest formation constants with the heavy halides and with sulphur ligands(1a). Being softish or (b) characters they form strong σ-bonds with softish ligands and also d_π - d_π bond by donation of a pair of electrons to the ligands. In general, donor atoms which give large ligand-field splitting energy (which could be deduced from the spectrochemical series(10)) form more stable complexes with metals which are especially sensitive to ligand field stabilisation (class b), whereas donor atoms which produce small ligand fields tend to form more stable complexes with metals which are insensitive to ligand-field stabilisation (class a)(11).

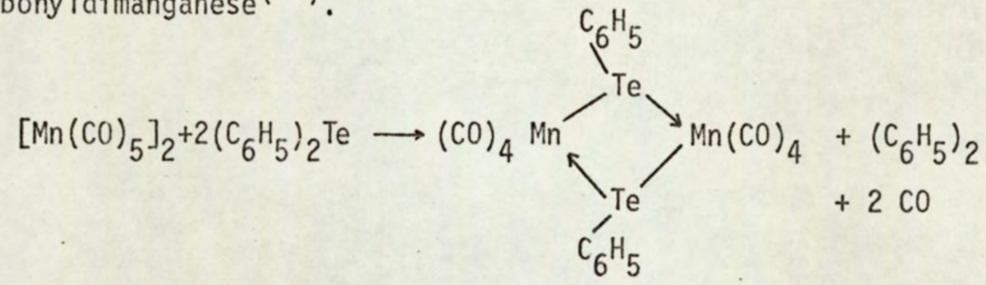
Organic tellurides have been known to form complexes with platinum as indicated by the work of Fritzman in 1915-1938(12); a formula of $[(C_6H_5CH_2)_2Te)_2PtCl_2]$ was proposed for one compound which probably has a trans configuration as it is soluble in chloroform. It is stable in the solid state but rapidly decomposes in solution to platinum, tellurium and bibenzyl; no isomers are known; cis $[((C_6H_5)_2Te)_2Pt\ Cl_2]$ was made by Jensen(13) by reacting K_2PtCl_4 with Ph_2Te by using H_2O and C_2H_5OH as a solvent.

Chatt and co-workers(14) in their investigations of inductive and mesomeric effects in platinum (II) and palladium (II) complexes prepared three types of complex with the general formula L_2MCl_2, $L_2M_2Cl_4$ and L, $amMCl_2$; [M = Pt(II), Pd(II), am = piperdine or p-toluidine, L = aliphatic telluride]. The bridged complexes $L_2M_2Cl_4$ reacted with amines to form mixed complexes trans L,$amMCl_2$. These complexes disproportionate spontaneously into L_2MCl_4 and am_2MCl_2. The stability of the bridged complexes $L_2Pt_2Cl_4$ and those of group V ligands fall in the order of $R_3P \sim R_2S > R_3As >$ amine $> R_2Te > R_3Sb > R_2Se$. The analogous Pd^{II} complexes $L_2Pd_2Cl_4$ are more soluble and less stable than the platinum complexes, but more stable when L = R_2Se. The stability sequence of the Pd complexes is $R_3P > R_3As \sim R_2S > R_2Se > R_2Te > R_3Sb$. The reverse order of stability for R_2Te and R_2Se complexes of palladium may be due to the relative size of the orbitals used for σ-bonds Se being comparable to Pd and Te with Pt. From a study of the N-H stretching frequencies in complexes $LamPtCl_2$ it was concluded that telluride ligands influence the N-H bond mainly through an inductive effect, back bonding from metals to ligands being unimportant. The ligand field splittings inferred from the energies $d_{xy} \leftrightarrow d_{x^2-y^2}$ transition in the complexes trans-[L-piperidine $PtCl_2$] decreases when L are arranged in the sequence. $P(OMe)_3 > Pr_3P >$ piperidine $> Pr_3As > Et_2S > Et_2Se > Et_2Te$. The range of energies is small varying from 33,400 cm^{-1} when L = $P(OMe)_3$ to 29,400 cm^{-1} when L = Et_2Te.

A new series of organopalladium complexes of the type trans-[PdL_2RX]; [L=$SeEt_2$, $TeEt_2$; R = aryl group; X = halogen] containing σ-bonded organic substituents have been prepared by Faraone et al. from trans $[PdL_2X_2]$ complexes and the appropriate Grignard reagents(15). The stabilities of the complexes vary and are markedly dependent on the ability of SEt_2, $SeEt_2$ and $TeEt_2$ to stabilize the complexes. The stability increases in the order $SEt_2 < SeEt_2 < TeEt_2$ i.e. with increasing atomic number of the donor atom. This trend has no significant difference in the case of platinum(II) compounds(16). The observed trend could be related to the polarizability of the donor atom. In addition, Π-bonding between palladium and sulphur (in thioether) has been reported to be insignificant(17) whereas the overlap between the filled 4d orbitals of palladium(II) and the empty 4d and 5d orbitals of selenium and tellurium respectively seems to be important. The view that Π-interaction is more important in the Pd-Te than in the Pd-Se bond is supported by the work of Pluscec and Westland(18).

Considerations of the work done by Chatt et al.(14) on the bridged complexes of palladium $Pd_2L_2Cl_4$ and those of Faraone et al(15) on complexes of the type trans $[PdL_2RX]$ there seems to be some disagreement on the explanation of the stabilities of the complexes. Whilst Chatt favoured the R_2Se complexes of palladium to be more stable than R_2Te, Faraone claimed the opposite stability sequence to hold. It should be observed that there is no strong evidence to prove that σ-bonding or Π-bonding are important for the two types of complex described above, it is known that Π-bonding could be invoked to explain some stabilities of the complexes which could also be approached by other explanations.

Several organotellurium-containing metal carbonyl compounds are known$^{(19)}$. Diphenyltelluride was known to react with decacarbonyldimanganese at 130°C in p-xylene forming di-μ-phenyltelluro-octacarbonyldimanganese$^{(19)}$.



one of the tellurium-carbon bonds is broken during this reaction, the dinuclear structure was supported by a molecular weight determination in benzene and the diamagnetism of the compound. Halopentacarbonylmanganese was found to react much more readily than pentacarbonylmanganese. In boiling diethyl ether two CO groups were exchanged.

$$Mn(CO)_5X + 2(C_6H_5)_2Te \longrightarrow [Mn(CO)_3(Te(C_6H_5)_2)_2X] + 2\ CO$$

where X = Cl, Br, I.

The reactivity of $Mn(CO)_5X$ decreases in the sequence Cl > Br > I. The complex $Mn(CO)_3(Ph_2Te)_2Cl$ reacted with NO to form $Mn(NO)_3(Ph_2Te)Cl$. It was not possible to isolate monosubstituted compounds in which more than two CO ligands were replaced by diphenyltelluride. Di-n-butyltelluride was recovered unchanged after boiling with $Mn(CO)_5Cl$ but dimerisation occurred in the reaction.

$$2Mn(CO)_5Cl + 2Te(C_4H_9)_2 \rightleftharpoons 2Mn(CO)_4[Te(C_4H_9)_2]Cl + 2CO$$

$$2Mn(CO)_4[Te(C_4H_9)]Cl \longrightarrow [Mn(CO)_4Cl]_2 + Te(C_4H_9)_2$$

The catalytic conversion of the mononuclear into dinuclear species is thought to be caused by the instability of the Mn-dialkyltelluride bond. In the case of aryl telluride complexes they are stabilised by $d_{\Pi} - d_{\Pi}$ back-bonding which is made possible by electron withdrawing phenyl groups. The alkyl groups in dialkyl telluride increase the electron density on tellurium atom thus decreasing $d_{\Pi} - d_{\Pi}$ interactions and weakening Mn-Te such that dialkyl telluride complexes have only transitory existence.

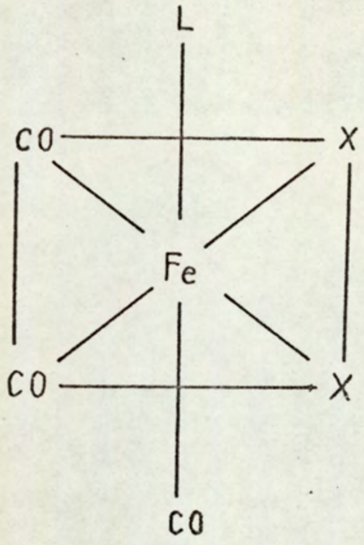
Dodecacarbonyl tri-iron and diphenyl telluride in boiling cyclohexane yielded $Fe(CO)_4Te(C_6H_5)_2$ with a trigonal bipyramidal structure

$$[Fe(CO)_4]_3 + 3Te(C_6H_5)_2 \longrightarrow 3Fe(CO)_4Te(C_6H_5)_2$$

Diphenyl telluride could also replace one CO ligand in $Fe(CO)_4X_2$ at room temperature

$$Fe(CO)_4X_2 + Te(C_6H_5)_2 \longrightarrow Fe(CO)_3Te(C_6H_5)_2X_2 + CO$$
$$[X = Br, I]$$

Dipole moment studies showed that 2 iodine atoms in $Fe(CO)_4I_2$ are in the cis position. From this fact and the trans effect of the CO group the following structure was proposed for the complex $Fe(CO)_3Te(C_6H_5)_2X_2$



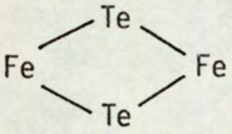
L = $(C_6H_5)_2Te$,   X = Br, I

Diphenyltelluride also reacted with $Fe(NO)_2(CO)_2$ at room temperature to give $Fe(NO)_2CO(Te(C_6H_5)_2)$,when diphenyl telluride was treated with octacarbonyldicobalt both Te-C bonds were cleaved forming the paramagnetic $[Co_2Te(CO)_5]$. Chromium carbonyl did not react with telluride when kept at 125^o for several days. When diphenyl telluride was heated with nickel carbonyl only elemental nickel and elemental tellurium were formed.

Faraone and co-workers$^{(20)}$ have studied ligand effects on oxidative addition reactions of d^8 metal complexes. They prepared complexes of the type <u>trans</u> $[Rh(CO)L_2Cl]$, where L = $S(C_2H_5)_2$, $Se(C_2H_5)_2$, $Te(C_2H_5)_2$. The reactions of these complexes with Cl_2, Br_2, I_2,HCl, CH_3I, $C_6H_5SO_2Cl$ are described. The strong tendency of the complexes <u>trans</u> $[Rh(CO)L_2Cl]$ to undergo oxidative addition could be attributed to a balance of σ and Π bonding factors, the former being dominant in the case of the ligands considered.

Other metal halides which have been found to form complexes with tellurides are HgX$^{(21)}$ which forms adducts of the type RR^{1}Te - HgX$_2$ (R,R^1 = C_6H_5, X = Cl, Br, I), AgI, CdI$_2^{(22)}$,AuCl$_3$ and BCl$_3$.

Ditellurides, R_2Te_2, were investigated as ligands by Heiber and Kruck$^{(23)}$ who prepared the complex $[(p\text{-}CH_3OC_6H_4Te)Fe(CO)_3]_2$ by reacting $[p\text{-}CH_3OC_6H_5Te]_2$ with $[Fe(CO)_4]_3$. This red-brown compound is quite unstable, its diamagnetism can be interpreted by the existence of an Fe - Fe bond with electron spins paired. A non-planar structure of the type



is suggested.

Baddley and Schermer$^{(24)}$ have also studied the role of ditellurides as ligands. They have done the reactions of diphenyldichalcogenides Ph_2E_2[E = Te, Se] with $[(\Pi\text{-}Cp)Fe(CO)_2]_2$ from which many new complexes were isolated and characterised. These include mononuclear $[(\Pi\text{-}Cp)Fe(CO)_2EPh]$ (E = Te,Se) and dinuclear $[(\Pi\text{-}Cp)Fe(CO)(EPh)]_2$. In the case of dinuclear compound, two isomers were obtained which could be separated in the case of selenium, only a mixture of isomers was obtained for tellurium. Greater stabilities of the dinuclear selenium and tellurium compounds over the analogous sulphur compounds were explained in terms of the reactions of softer selenium and tellurium ligands with soft subtrates $[(\Pi\text{-}Cp)Fe(CO)_2]_2$.

Reactions of $[M_3(CO)_2]$ (M = Fe,Ru) with diphenyldiselnide and diphenylditelluride were studied(25). In the case of M = Fe, the dinuclear compound of the type $[M(CO)_3(EPh)]_2$ (E = Se,Te) was the only product obtained, but for M = Ru the dinuclear species was only a minor product while the major products were two forms of polymeric $[Ru(CO)_2(EPh)_2]_n$ (E = Se,Te).

The first practical use of the complex $[RhCl(PPh_3)_3]$ for the homogeneous reduction of alkane, alkyne and other unsaturated compounds at 25^{0}C and 1 atm Pressure of hydrogen in benzene solution was pioneered by Wilkinson and his group(26). Since then the investigations and applications of other transition metal complexes in homogeneous catalysis have grown rapidly.

Trichloro<u>tris</u>diethylsulphide rhodium(III); $[RhCl_3(SEt_2)_3]$ was first prepared by Dwyer and Nyholm(27), its configuration was assigned to be <u>mer</u>(28). Its potential use as a hydrogenation catalyst was studied by James and co-workers(29). They found that the complex is a good hydrogenation catalyst in N,N' dimethylacetamide [DMA] at 50^{0}C with 1 atom of H_2. In the presence of alkene, dihydrogen reduces $[Rh(SEt_2)_3Cl_3]$ to the Rh(I) olefin complex. The rate-determining reduction is the reaction of the Rh(I) olefin complex with dihydrogen to give product and more rhodium(I). The catalytic effect was found to be dependent on the solvent which plays an important role in promoting dissociation of sulphide ligands from the rhodium(III) complex. The reaction scheme proposed was as follows

$$RhCl_3(Et_2S)_3 \rightleftharpoons RhCl_3(Et_2S)_2 + Et_2S \qquad (1)$$

$$RhCl_3(Et_2S)_2 + H_2 \longrightarrow HRhCl_3(Et_2S)_2^- + H^+ \qquad (2)$$

or

$$HRhCl_2(Et_2S)_2 + H^+ + Cl^-$$

(solvent molecules presumably complete octahedral coordination)

These reactions were considered to be followed by the faster steps shown

$$Rh^{III}H \longrightarrow Rh^I + H^+ \qquad (3)$$

$$Rh^I + \text{olefin} \longrightarrow Rh^I\ (\text{olefin}) \qquad (4)$$

$$Rh^I(\text{olefin}) + H_2 \longrightarrow [H_2Rh^{III}(\text{olefin})] \longrightarrow Rh^I + \text{saturated product} \qquad (5)$$

In addition to $RhCl_3(SEt_2)_3$ which was found to activate molecular hydrogen, James also prepared another complex of rhodium with the more bulky sulphide ligand (dibenzyl sulphide), $[Rh((PhCH_2)_2S)_3Cl_3]$ (30). They found that the complex would catalyse the homogeneous hydrogenation of maleic acid but the kinetic dependences were different from those of the $RhCl_3(Et_2S)_3$-maleic acid system(29). This rhodium dibenzylsulphide-maleic acid system was found to be similar to the $RhCl_3(Et_2S)_3$-cinnamic acid system(30). This system showed that the rate increases with rhodium at lower concentration and is first order in hydrogen and is independent of cinnamic acid concentration. It showed an inverse dependence on both added sulphide and chloride. They suggested that the dissociation of either Et_2S or Cl^- from $L_3Rh^I[CA]$; [L = Cl, Et_2S or DMA; CA = cinnamic acid] is necessary before rate determining reaction with dihydrogen.

$$L_3Rh^I[CA] \overset{k}{\rightleftharpoons} L_2Rh^I[CA] + L\ (= Et_2S \text{ or } Cl^-] \qquad (1)$$

$$L_2Rh^I[CA] + H_2 \xrightarrow{k} [L_2Rh^{III}(CA)H_2] \longrightarrow Rh^{(I)} + \text{product} \quad (2)$$

In the case of the dibenzyl sulphide complex dissociation of the more bulky sulphide ligand is considered to occur prior to the formation of the cis dihydride complex. Cattalini and his co-workers(31) have noted that in $AuCl_3(Bz_2S)$, the sulphide is more labile than chloride and this was attributed to steric factors. It should be noted that the rhodium(I)-dibenzyl sulphide catalyst system does not catalyse the reduction of cinnamic acid, even at lower temperatures around 50°C, dihydrogen treatment yielded metals. This was explained as the steric effect of bulky sulphide ligand and trans olefin make stabilisation of rhodium(I) by olefin difficult.

As tellurium is also potentially a Π-acceptor belonging to the same group as sulphur, the rhodium complexes containing tellurium as a donor atom of the type $Rh(R_2Te)_3Cl_3$ may possibly behave as homogeneous catalysts for the hydrogenation of alkenes and other organic subtrates.

Apart from the complexes $[Rh(Et_2S)_3Cl_3]$ and $[Rh((PhCH_2)_2S)_3Cl_3]$ mentioned above, complexes of the type MX_3L_3; [M = Rh, Ir, Ru; X = Cl, Br, I; L = Et_2S, Pr^n_2S, Et_2Se have been investigated by Fergusson and co-workers(32). They obtained the above complexes via the direct reaction of L with RhX_3. The method is essentially the same as that previously reported by Dwyer and Nyholm(27) for L = Et_2S. The i.r. spectra (below 400 cm^{-1}) suggested sulphur and selenium are less effective Π-acceptor ligands than phosphine. The bonds assigned to $\nu(M - Cl)$ are some 20-30 cm^{-1} higher in energy than the corresponding bonds assigned for the tris phosphine complexes $MX_3(R_3P)_3$. The disparity in the metal-halogen stretching frequency as between sulphide (selenide) and phosphine complexes has been observed for divalent platinum complexes(33). Greater competition between halogen and ligand for the metal $d_\pi$electrons in the phosphine complexes would give rise to an overall decrease in the M-X bond order compared to sulphide and selenide complexes. It is also found that halogen ligands can have a considerable effect on the bonding of other ligands, especially when the donor atom can participate in Π-bonding, e.g. the stabilities of the metal diethylsulphide complexes vary with the halogen in the order $RhCl_3 > RhBr_3 > RhI_3$(32a).

Chatt and co-workers have prepared some complexes of the type $[RhCl_3(PhSR)_3]$, $[R = Me, Et, Pr^n, Bu^n]$(34) by reacting the sulphide PhSR with $RhCl_3XH_2O$ in methanol to give $[RhCl_3(PhSR)_3]$. They were able to isolate both mer and fac isomers. The mer isomers were obtained in all reactions, but only fac-$[RhCl_3(PhSR)_3]$; ($R = Et$ or Pr^n) could be obtained in a pure state. The chloride ligand could be replaced by reacting mer $[RhCl_3(PhSEt)_3]$ with lithium bromide to give impure $[RhBr_3(PhSEt)_3]$. Diphenyl sulphide could also be reacted with $RhCl_3xH_2O$ to yield a product which could not be purified. The complex $[RhCl_3(MeC(CH_2SEt)_3)]$ was also synthesised. The 'H n.m.r. spectra of the complexes $[RhCl_3(PhSR)_3]$ provided an unequivocal assignment of fac and mer isomers because the mer isomer contains one unique sulphide whereas the fac isomer has all three equivalent. The far-i.r. spectra of $[RhCl_3(PhSR)_3]$ are generally consistent with the assigned fac and mer isomers. The mer isomers generally have three bands assignable to ν(Rh-Cl) and the fac isomers only two.

Rhodium (I) sulphide complexes are much more difficult to characterise and only polymeric substances were isolated, e.g. $[RhCl(CO)(MeSCH_2CH_2SMe)]_n$, $[RhCl(CO)(EtSCH_2CH_2SEt)]_n$. The reactions of sodium chloroiridate with sulphide do not occur as readily as the rhodium reactions. No products were isolated using isopropyl phenyl sulphide or diphenylsulphide and methylphenyl sulphide gave $[IrCl_3(PhSMe)_3]$ in only 20% yield.

The assignment of the configuration of the complexes $[MX_3(Et_2S)_3]$; [M = Rh, Ir,; X = Cl,Br] was a matter of controversy for some time. Earlier discussion (35,32) about the structure was based on a fac configuration for $[IrCl_3(SEt_2)_3]$ which later proved to have a mer configuration. Allen and Wilkinson have prepared the complexes of rhodium and iridium by using simple sulphides; Me_2S, Et_2S, C_4H_8S or $C_5H_{10}S$ which resulted in the formation of stable crystalline solids of the type MX_3L_3(28). They have shown clearly by using I.R, U.V. and ^1H n.m.r. and dipole moments measurements that all the complexes have a common octahedral meridianal configuration.

Substitution reactions of n-alkylphenyl sulphide complexes of ruthenium $[RuCl_3(PhSPr^n)_3]$ werefound to occur quite readily(36). Thus $[RuCl_3(PhSPr^n)_3]$ with aniline and pyridine (Py) in benzene solution yields $[RuCl_3(PhNH_2)_3]\ 0.5C_6H_6$ and $[RuCl_3(Py)_3]0.5C_6H_6$, all the organic sulphide having been displaced in contrast to the situation in the tertiary phosphine and arsine ruthenium complexes. It was not possible to isolate products from the reactions of

$[RuCl_3(PhSPr^n)_3]$ with p-toluidine, ethylamine, diethylamine, ethanediol or benzenethiol. The ease of the substitution of these n-alkylphenyl sulphide complexes was explained mainly due to the considerable degree of dissociation indicated in the molecular weight measurement in benzene e.g. 495 for $[RuCl_3(PhSEt)_3]$ compared with the theoretical value of 621.

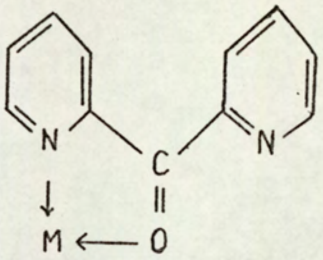
Further evidence of the weakness of the bond between rhodium and sulphur in complexes of the type RhX_3L_3; [X = Cl, L = Et_2S] was demonstrated by its catalytic activity as indicated earlier(29,30). The complexes also dissociate in hot acidified alcoholic solution, molecular weight measurement also showed some dissociation. While diethyl sulphide failed to react with pure rhodium triiodide the addition of potassium iodide to the chloride complex caused nearly 90% of rhodium to precipitate as rhodium triiodide. The iodide complexes were obtained by this reaction only in the presence of excess diethylsulphide. It was also noted that diethylsulphide failed to react at all with potassium hexakis (isothiocyanato) rhodium(III) in which the metal is present as the stable red $[Rh(NCS)]_6^{III}$ ion(27).

As a diaryl telluride is a potentially Π-acceptor ligand and pleasant to handle in comparison with alkyltellurides, alkyl selenides or alkyl sulphides the complexes of the type $RhX_3(R_2Te)_3$; [X = Cl, Br, R = Ph_2Te] should be quite useful as synthetic intermediates in preparing some other rhodium(III) complexes e.g. $Rh[chelate]LX_3$; [Chelate = 2,2' bipyridyl, 1,10' phenanthroline, di-2-pyridylamine, di-2-pyridylketone] or other types as will be described elsewhere in this work.

The possible routes and mechanism for the formation of some rhodium(III) complexes have been studied by some workers. Under various sets of reducing conditions rhodium(I)-bipy species are formed, e.g. in the presence of (a) BH_4^-(37) (b) H_2/EtOH-OH^-(38), and it seemed generally accepted that species such as $Rh[bipy]_2^+$ can exist(39). Recent evidence suggests that an active $Rh[bipy]^+$ species can react with RX(40) or with H_2(38,40). A complex such as $[Rh(bipy)(H)_2(PPh_3)_2]^+$ can be isolated as a stable compound. It might be of interest to use a weaker Π-acid than PPh_3e.g. Ph_2Te in the hope that a compound such as "$Rh(bipy)(Ph_2Te)_2(H_2)^+$" may be more reactive.

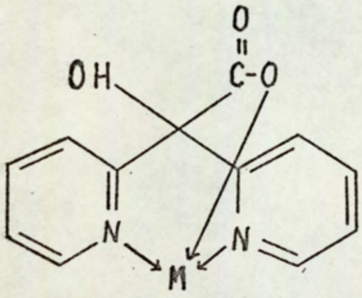
From the above consideration of the complex of the type $RhLL'X_3$; (L = Ph_2Te, L' = Di-2-pyridylketone, X = Cl) it is found that the chemistry of di-2-pyridyl ketone complexes was still in an unsatisfactory state(41,42).

The insertion of a carbonyl group between the two pyridyl-rings of 2,2'-bipyridyl will increase the flexibility of the chelate ring. Di-2-pyridyl ketone is potentially an ambidendate ligand. The ligand may potentially coordinate through both nitrogen atoms [N,N] or through one pyridyl group and together with the carbonyl group [N,O].



N,O coordination in Di-2-pyridyl ketone

The possibility of coordination through the carbonyl oxygen atom for di-2-pyridyl ketone exists since complexes of other ketones are known(43). Such coordination is accompanied by a characteristic shift in the carbonyl stretching frequency to a lower wave number in the infra-red spectrum. Complexes of 2-Benzoylpyridine have been reported(44) other ligands of the type X-CO-R e.g. β-diketones have been widely studied(43a). 2.2'-pyridil [pyCOCOpy] is known to react with hydrated nickel(II) and cobalt(II) acetate in methanol forming inner complexes of 2.2'-pyridilic acid of the type ML_2 where M = Co(II), Ni(II) and L = 2.2'-pyridilic acid(45)



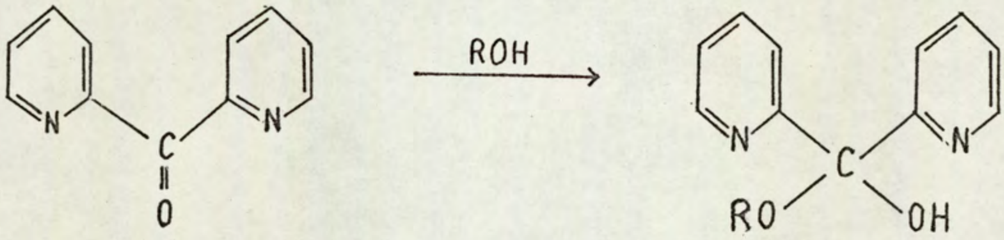
Di-2-pyridyl ketone forms a wide range of complexes with metal salts including Mn Fe Co Ni Rh Pd and Pt(42,41,46).

McWhinnie and Osborne(41) have prepared some compounds of copper which were considered to represent two modes of coordination. The pairs of compound $[Cu(pyCOpy)_2(ClO_4)_2]$ (N,N) and $[Cu(pyCOpy)_2(H_2O)_2](ClO_4)_2$(N,O) together with $[Cu(pyCOpy)\ Cl_2]$(N,N) and $[Cu(pyCOpy)Cl_2\text{-}EtOH]$(N,O) were considered to represent examples. The above pairs of compounds are readily interconverted and the observations could be explained in terms of the lower basicity of the carbonyl group compared with the 2-pyridyl group. This would in turn increase the affinity of copper(II) for solvent molecules when the ligand was N,O coordinated. However the assignment of 1445-1448 cm^{-1} to $\nu[CO]$ in the hydrated complexes of copper as an evidence of N,O coordination was not substantiated by Feller and Robson(42). They showed that the complex $Cu(pyCOpy)_2(H_2O)_2SO_4$ gave an e.s.r. spectrum which clearly indicated a copper environment of four equivalent nitrogen atoms each with a nuclear spin 1 and like McWhinnie's solvated pyCOpy cupric complexes has a strong bond at 1445 cm^{-1} in its i.r. spectrum. They suggested all the complexes to be N,N coordinated, the disappearance of $\nu[CO]$ in these compounds was then attributed to hydration or alcoholation across the ketone double bond.

$$>C=O + ROH \longrightarrow >C(OH)(OR)$$

Steric effects were invoked to explain the hydration reactions; thus when the trigonal carbon atom is replaced by a tetrahedral carbon atom this will allow the ligand to adopt a more deformed but nevertheless angle strain free configuration in which the α-hydrogen atoms are raised more above the CuN_2 plane than is possible in the ketonic ligand.

The compound Co(pyCOpy)Br_2 (green) will react with ethanol to give Co(pyCOpy)Br_2-EtOH. The spectroscopic and magnetic properties indicated the complexes to be pseudotetrahedral(47). The possibility of ligand re-arrangement might occur was considered by Osborne(47),

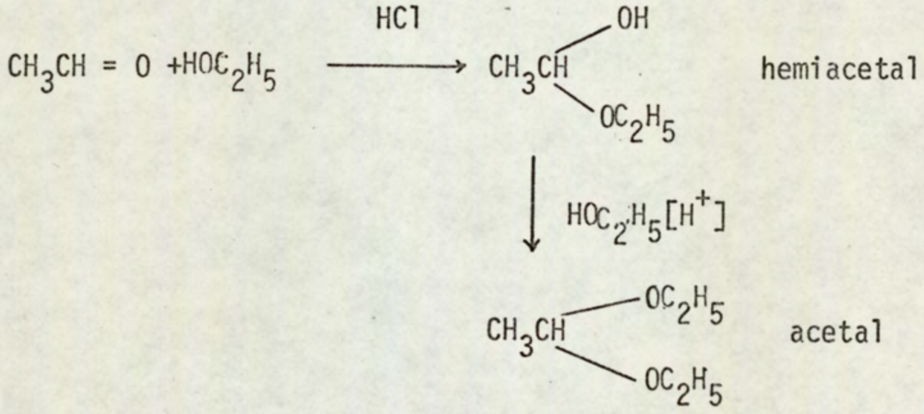


but the band at 1445 cm^{-1} could not be assigned. The anomalous magnetic moments found for some complexes of cobalt was explained in terms of spin paired complexes forming. This seemed to be odd since di-2-pyridyl ketone was considered to be a weak ligand [$\Delta < 11700$ cm^{-1}] and would form spin free complexes with transition metals such as Iron(II), Ni(II) and Co(II). The ligand field strength Δ [w.r.tCo(II)] necessary for spin pairing in Co(II) has been estimated as $\geq$ 15000cm^{-1} while the complexes of di-2-pyridyl ketone with cobalt perchlorate prepared by Osborne(47) showed magnetic moment of 1.9 B.M.

From the above consideration about Di-2-pyridyl ketone, it is clearly seen that much work remains to be done. The argument by Feller and Robson(42) about the steric effect that leads to the formation of a hemiacetal does not seem to be absolutely positive, since molecular models showed that the chelating di-2-pyridylketone has a large degree of flexibility in the six-membered ring which does not make it necessary for the ring to be planar. The effect of acidity seemed to be one of the main factors in the mechanism of acetal and hemiacetal formation. Under the catalytic influence of dry hydrogen chloride a typical aldehyde adds a molecule of ethyl alcohol to form a moderately stable hemiacetal, which combines with a second molecule of alcohol and yields a stable acetal$^{(48)}$.

$$RCHO + 2R^1OH \longrightarrow R.CH[OR^1]_2 + H_2O$$

e.g.



$$CH_3CH=O + HOC_2H_5 \xrightarrow{HCl} CH_3CH(OH)(OC_2H_5) \xrightarrow{HOC_2H_5[H^+]} CH_3CH(OC_2H_5)_2$$

From the above mechanism about acetal and hemiacetal formations it is clearly seen that pH of the solution is an important factor in addition to (if there is any) the effect of steric strain in the Di-2-pyridyl ketone rings showed by Feller and Robson$^{(42)}$. There is not much positive information about the stereochemistry of compounds such as $M[pyCOpy]_2Cl_2$ which are considered to be <u>cis</u> by Morgan$^{(46)}$ but not by others. The ligand field parameters of the ligand are not accurately known and some anomalous magnetic moments of some cobalt complexes mentioned earlier are not well understood.

CHAPTER TWO

EXPERIMENTAL

(A) CHEMICALS

All chemicals were obtained commercially and Analar grades were used whenever possible. Organic tellurides were prepared by the literature methods(3).

(B) SOLVENTS

Analar solvents were used when possible, otherwise reagent grades were used after distillation. Solvents used for some physical measurements e.g. conductivity measurements were purified by literature methods e.g. nitromethane(49) methylcyanide(50), dimethylformamide(49).

(C) ANALYSIS

Microanalyses for carbon, hydrogen and nitrogen were carried out by Mrs. B. Taylor, Microanalytical Laboratory, Chemistry Department, Aston University; Dr. A. Bernhardt, 5251 Elbach Uber Engelskirchen, West Germany; Dr. F. Strauss, Microanalytical Laboratory, 10 Carlton Road, Oxford, U.K. Some analyses of copper in copper(I) compounds were also done by Dr. Bernhardt, Germany. The analyses of carbon, hydrogen and nitrogen carried out in this department were done on F & M Scientific Instrument, Model "185" C, H, N analyser. Metals were determined by atomic absorption spectroscopy using spectroscopic grade metals dissolved in minimum volumes of analar concentrated nitric acid and diluted to the required volume as a stock solution. The stock solution was kept in polythene bottles to avoid changes in concentrations. The calibration graphs were obtained by appropriate dilution of the stock solutions to the working range of 5 - 25 μg/ml. In the latter part of this work metal analyses were read out automatically by the equipment, and these results could be compared and checked with the values obtained from the standard graphs. The atomic absorption spectrometer is of the type Perkin-Elmer Model 303.

(D) INFRA-RED SPECTRA

For the region 4000 - 250 cm^{-1} the spectra were obtained from a model 457 Perkin Elmer spectrophotometer. Solid samples were examined as Nujol mulls supported between KBr or CsI plates. Some specimens were examined as KBr discs.

For the region 410 - 200 cm^{-1} the spectra were recorded by a model 225 Perkin Elmer spectrophotometer. The solid samples were examined as Nujol mulls supported between CsI or polythene plates.

Far infra-red spectra in the region of 400 - 60 cm^{-1} were obtained from a R.I.I.C. FS 720 Fourier spectrophotometer. The spectra were not recorded instantly as with a double-beam spectrophotometer. The transmitted intensity of an interfering beam of radiation was recorded for a total of 1024 positions of a moving mirror using a Golay detector. The form of the resulting interferrogram is a function of the spectral distribution of the radiation entering the detector. A Fourier cosine transform was computed by the University ICL 1605 computer to give spectra. The solid specimens were samples as Nujol mulls in polythene vacuum tight cells. A different thickness of sample could be obtained by using a different type of spacer. Each sample was run at least twice to check the reproducibility of the print-out spectra. In some cases different physical conditions i. e. thickness of samples are varied to get satisfactory spectra.

(E) ELECTRONIC SPECTRA

Electronic absorption spectra in the U.V. and visible region 50000 cm^{-1} - 6000 cm^{-1} were obtained from a Unicam SP 700 spectrometer using matched silica cells.

The diffuse reflectance spectra were recorded using the SP 735 attachment unit. Magnesium oxide was used as a reference and also as a diluent wherever necessary.

(F) X-RAY POWDER PHOTOGRAPHS

X-ray powder photographs were taken using Cuk_{α} radiation. An exposure time of 2-3 hours was used.

(G) CONDUCTIVITY

Molar conductivities were measured with a "Mullard" conductivity bridge, using a standard conductivity cell type E7591/B and cell constant 1.36.

(H) MASS SPECTRA

The mass spectra were obtained with AE 1 MS 9 spectrometer at 70 eV.

(I) ELECTRON SPIN RESONANCE SPECTRA

The Hilger and Watts microspin instrument was used. The instrument is operated on the X-band frequency.

(J) MOLECULAR WEIGHT DETERMINATION

The molecular weights were determined using Mechrolab model 301A.

(K) NUCLEAR MAGNETIC RESONANCE SPECTRA

'H n.m.r. spectra were recorded on a Perkin-Elmer R10 operating at 60 MHz and Perkin-Elmer R14 for 100 MHz.

(L) MAGNETIC SUSCEPTIBILITIES MEASUREMENTS

Magnetic susceptibilities were determined by the Gouy method at room temperature. The Gouy tube was calibrated with $Hg[Co(NCS)_4]$; (taking $X_g = 16.44 \times 10^{-6}$ c.g.s. units at 20°C). The tube calibration was checked by measuring the magnetic susceptibility of $[Ni(en)_2S_2O_3]$ for which a value of X_g equal to 10.70×10^{-6} c.g.s. unit at 17°C was obtained. This agrees well with the literature value $X_g = 10.60\times10^{-6}$ c.g.s unit$^{(51)}$. The balance was the semi-micro type SM 12 (Stanton Instruments Ltd.) used in conjunction with an electromagnet. A current of 10 amperes was used for all measurements.

Diamagnetic corrections and the calculation of magnetic susceptibilities follow the book by Figgis and Lewis(52).

(M) MÖSSBAUER SPECTRA

The Mössbauer spectra were obtained with the Centronic Mössbauer spectrometer. Details of the apparatus and operations have been given by M. Fernandopulle(53).

(N) GAS-LIQUID CHROMATOGRAPHY

The chromatograms were obtained from the Pye 104 Gas chromatograph.

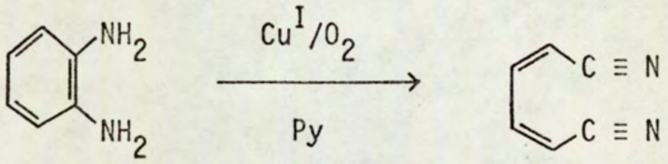
CHAPTER THREE

REACTIONS BETWEEN DIARYL TELLURIDES AND COPPER(I)HALIDES

(A) INTRODUCTION

Copper is one of the elements in the transition metal group which has been most widely studied. Copper compounds are effective catalysts in numerous chemical processes e.g. organic and inorganic redox reactions, photochemical reactions(54) copper-promoted reactions of aromatic compounds(55) and also copper is active biochemically(56).

In comparison with copper(II) the amount of literature concerned with copper(I) is very slight. It is only recently that interest in the chemistry of copper(I) has begun to grow fairly rapidly. Lappert et al.(57) recently prepared the stable alkyl complex of copper(I), trimethylsilylmethyl copper $(Me_3SiCH_2Cu)_n$; ($n = 4$ in C_6H_6, $= 6$ in C_6H_{14}) which proved to be an alkylating agent, its reactions with Me_3SiCl, $CH_2 = CHCH_2Br$ or PhI gave $(Me_3Si)_2CH_2$, $Me_3SiCH_2CH_2CH{=}CH_2$ or $PhCH_2SiMe_2$ respectively. Some organometallic complexes of copper(I) have been found to catalyse various kinds of organic reactions(57-64). Takahashi et al.(65) found the following reaction to be catalysed by copper(I)



which might be very valuable in industry for the production of nylon intermediates.

Thus, increasing interest in the chemistry of copper(I) along with the consideration of copper(I) as a softish or class (b) cation(6) led to this study of some complexes of copper(I) with organic tellurides which are classified as softish ligands.

Complexes of copper(I) with ligand to metal ratio 4:1, 3:1, 2:1 and 1:1 are known. Nyholm(66) has shown that the ligand methyldiphenylarsine forms all four types of complexes formulated as $[Cu(AsMePh_2)_4]X$, $[CuX(AsMePh_2)_3]$, $[Cu(AsMePh_2)_4][CuX_2]$ and $[CuCl(AsMePh_2)]_4$. Tertiary phosphine arsine and stibine form complexes with copper(I) with different ligand to metal ratio depending on the method of preparation and the amount of ligand used(67,68).

Most of the 1:1 complexes with softish ligands e.g. $[CuI(MR_3)]_4$(69), $[CuX(AsPh_3)]_4$ [X = Br,I](68a), $[CuX(PPh_3)]_4$(68b) are shown to be tetrameric. The X-ray analysis of $[CuI(AsEt_3)]_4$(70) showed it to have a structure with four copper atoms, each four coordinate at the apices of regular tetrahedron. The 2:1 complexes of many tertiary phosphine complexes of the type $(R_3P)_2CuX$; [R = aryl group e.g. phenyl or p-tolyl, X = halides thiocyanate etc.] achieve four coordinations by bridging the anionic ligands(71,72). The X-ray analysis of the 2:1 complex $((C_6H_5)(CH_3)_2As)_2Cu\,Cl$(73) showed that the complex is a chloro-bridged dimer, each copper atom being tetra-coordinated.

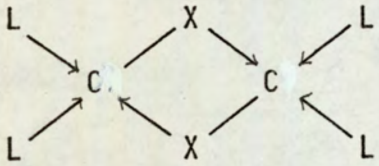
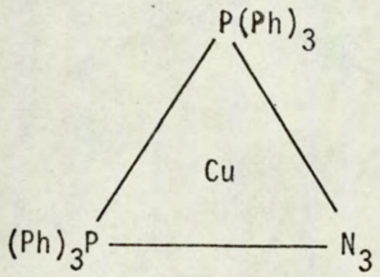
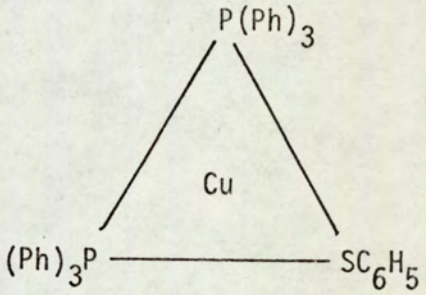


Fig.3.1 A bridging 2:1 copper(I) complex.

Tri-coordination in copper(I) complexes with softish ligands was thought to be rare but recently it has been shown to occur in many cases. X-ray analysis of the complex tris-(2-picoline)copper(I) perchlorate(74) showed it to have trigonal hybridisation about the copper atom. Tris (trimethylphosphine sulphide) copper(I) perchlorate was also shown by X-ray study to be a monomeric, trigonally coordinated cation, very recently X-ray analysis of the complex $[Cu((CH_3)_3PS)Cl]_3$ showed that copper(I) is three coordinate with phosphine sulphide act as a bridging ligand(75). The structures of $Cu(PPh_3)_2N_3$ and $Cu(PPh_3)_2SC_6H_5$(54) were suggested by the evidence of molecular weight measurement to be trigonal planar. The following probable structures were proposed:





Also it was suggested, but without evidence, that the complex $CuBr(SbPh_3)_2$(68a) is a monomer with a three coordinated copper(I) The explanation of molecular weight and n.m.r. data obtained from solutions of $(R_3P)_2CuX$ and $(R_3P)_3CuX$ were based on the three coordinated copper(I)(72,76). Recently(77) it has been shown that copper(I) prefers to form trigonal planar three coordinated complexes with ligands of group VA chalcogenides $(CuL_3)X$; ($X = ClO_4^-$ BF_4^-, $L = Ph_3PSe, R_3PS$; R = Me, Et, $^{iso}Pr.$; $PhMe_2PS$ and Ph_3AsS) rather than two or four coordinations.

The 3:1 complexes for example $Cu(PPh_3)_3X$; (X = Cl Br I) are well known and were found to dissociate in solution$^{(68b)}$. $CuF(PPh_3)_3$ was also made recently by Jardine et al.$^{(78)}$. The isolation of 4:1 complexes was aided by the use of poor coordinating anions e.g. $[Cu(PPh_3)_4]ClO_4$$^{(79)}$.

Some complexes of organic tellurides with copper(I) were synthesised. Their preparations, properties and structures are discussed in the following pages.

(B) PREPARATION OF THE COMPLEXES

Diphenyltelluride ($C_6H_5TeC_6H_5$) was prepared by the literature method$^{(3)}$. Further purification of the product was achieved by distilling under vacuum. (0.3 - 0.5 mm Hg).

Found: C = 50.8%; H = 3.48%

Calc.for $C_{12}H_{10}Te$,C = 51.0%; H = 3.82%

Di-p-tolyltelluride was prepared by the literature method$^{(3)}$, Di-p-ethoxyphenyltelluride was prepared by the same method used for the preparation of di-p-methoxyphenyltelluride$^{(3)}$ by using phenetole instead of anisole as a starting material for reaction with tellurium tetrachloride. The crude telluride was recrystallised from methanol.

Copper(I) chloride and copper(I) bromide were obtained commercially and further treatment to minimise the contamination of copper(II) was carried out by grinding the material in a mortar with enough 1N sulphuric acid and stirring the paste into a large quantity of dilute sulphurous acid, the washing and drying was done according to the method given in the literature$^{(80)}$ Copper(I) iodide was used without further purification.

(a) Copper(I) halides of diphenyltelluride

1. Chlorotris(diphenyltelluride)copper(I)

Diphenyltelluride (0.85 gm, 3mM) was dissolved in ethanol (20 ml) and added to the hot solution of copper(I) chloride (0.1 gm, 1 mM) in dilute hydrochloric acid (1N) (20 ml), the resulting solution was heated and stirred for 5 min. The white compound formed was filtered through sintered glass crucible and washed thoroughly with ethanol and dried under vacuum in the desiccator over P_2O_5.

Found: C,45.6%; H,3.30%; Cu,6.18%

$C_{36}H_{30}ClCuTe_3$

Requires: C,45.7%; H,3.18%; Cu,6.73%.

2. Di-μ-bromotetrakis(diphenyltelluride)dicopper(I).

Diphenyltelluride (0.6 gm, 2mM) was dissolved in ethanol (20 ml) and this solution was mixed with a hot solution of copper(I) bromide (0.14 gm, 1 mM) in dilute (1N) HBr (20 ml). The resulting solution was heated and stirred for 5 minutes, the yellowish-white solid was filtered through the sintered glass crucible, the solid was washed thoroughly with ethanol to afford a white solid which was dried under vacuum over P_2O_5.

Found: C,40.1%; H.2.85%; Cu,8.16%

$C_{48}H_{40}Br_2Cu_2Te_4$

Requires: C,40.7%; H,2.83%; Cu,8.99%.

3. Di-μ-iodo bis (diphenyltelluride)dicopper(I)

Diphenyltelluride (0.6 gm, 2 mM) in ethanol (20 ml) was added to copper(I) iodide (0.38 gm, 2mM) in water saturated potassium iodide. The resulting solution was heated and stirred for 5 minutes. The white solid was filtered through a sintered glass crucible and was washed thoroughly with ethanol to afford a white crystalline compound. The solid was dried under vacuum in a desiccator.

Found: C,30.9%; H,2.22%: Cu,13.7%

$C_{24}H_{20}Cu_2I_2Te_2$

Requires: C,30.5%; H,2.12%; Cu,13.5%

b) Copper(I) halides of di-p-tolyltelluride

1. Di-μ-chloro tetrakis(di-p-tolyltelluride)dicopper(I)

Di-p-tolyltelluride (1.24 gm,4mM) in ethanol (20ml) was mixed with a solution of copper(I) chloride (0.2 gm, 2 mM) in dilute HCl (20 ml), the resulting solution was heated and stirred for 5 minutes. The white solid formed was filtered through a sintered glass crucible and washed thoroughly with ethanol and water. The solid was dried under vacuum in a desiccator.

Found: C,46.8%; H,4.02%; Cu,8.17%

$C_{56}H_{56}Cl_2Cu_2Te_4$

Requires: C,46.8%; H,3.90%; Cu,8.84%.

2. Di-μ-bromotetrakis(di-p-tolyltelluride)dicopper(I)

Copper(I) bromide (0.28 gm, 2 mM) in dilute HBr (20 ml) was heated until all copper(I) bromide dissolved and then mixed with a solution of di-p-tolyltelluride (1.24 gm, 4 mM) in ethanol (20 ml), the resulting solution was heated and stirred for 5 minutes. The white solid obtained was filtered through sintered glass crucible and washed thoroughly with ethanol and water. The solid was dried under vacuum.

Found: C,44.2%; H,3.75%; Cu,8.25%

$C_{56}H_{56}Br_2Cu_2Te_4$

Requires: C,44.1%; H,3.67%; Cu,8.33%

3. Iodo bis (di-p-tolyltelluride)copper(I)

Di-p-tolyltelluride (1.24 gm, 4 mM) in ethanol (20 ml) was mixed with hot solution of copper(I) iodide (0.38 gm, 2 mM) in aqueous saturated KI (20 ml), the resulting solution was heated and stirred for 5 minutes. The white solid obtained was filtered through a sintered glass crucible and washed thoroughly with ethanol and water. The solid was dried under vacuum.

Found: C,41.8%; H,3.52%; Cu,7.44%

$C_{28}H_{28}CuITe_2$

Requires: C,41.5%; H,3.46%: Cu,7.84%.

c) Copper(I) halides of di-p-ethoxyphenyltelluride

1. Di-μ-chlorotetrakis(di-p-ethoxyphenyltelluride)dicopper(I)

Di-p-ethoxyphenyltelluride (0.75 gm, 2 mM) in ethanol (20 ml) was mixed with a hot solution of copper(I) chloride in dilute HCl (20 ml), the resulting solution was heated and stirred for 5 minutes, the white compound was filtered through a sintered glass crucible and washed thoroughly with ethanol.

Found: C,46.0%; H,4.29%; Cu,7.50%

$C_{64}H_{72}Cl_2Cu_2O_8Te_4$

Requires: C,45.8%; H,4.33%; Cu,7.56%

2. Di-μ-bromotetrakis(di-p-ethoxyphenyltelluride)dicopper(I)

Di-p-ethoxyphenyltelluride (0.75 gm, 2 mM) in ethanol (20 ml) was mixed with a hot solution of copper(I) bromide (0.14 gm, 1 mM) in dilute HBr (20 ml), the resulting solution was heated and stirred for 5 minutes, the white solid obtained was filtered through sintered glass crucible and washed many times with ethanol and water. The compound was dried under vacuum over P_2O_5.

Found: C,44.1%; H,4.39%; Cu,7.20%

$C_{64}H_{72}Br_2Cu_2O_8Te_4$

Requires: C,43.5%; H,4.08%; Cu,7.19%.

3. Di-μ-iodo bis(di-p-ethoxyphenyltelluride)dicopper(I)

Di-p-ethoxyphenyltelluride (0.4 gm, 1mM) in ethanol (20 ml) was mixed with a hot solution of copper(I) iodide (0.19 gm, 1 mM) in aqueous saturated KI (20 ml), the resulting solid was filtered through sintered glass crucible and washed many times with ethanol and water. The compound was dried under vacuum over P_2O_5.

Found: C,34.1%; H,3.32%; Cu,10.7%

$C_{32}H_{36}Cu_2I_2O_4Te_2$

Requires: C,34.3%; H,3.21%; Cu,11.3%.

d) Comment on the experiments

The above reactions were repeated with a range of metal to ligand ratios but only the products described were produced in a given case as proved by elemental analysis and vibrational spectroscopy. Thus under the experimental conditions used here, the stoichiometry of the product is a function of the nature of the copper(I) halide and of the telluride and not, apparently, a function of the mole ratio of the reactants.

(C) RESULTS

The analytical data of copper(I) halide-telluride complexes are presented in Table 3.1. The far-infrared spectra data of the complexes are gathered in Table 3.2.

The 'd' spacing of the complexes measured from the X-ray powder photographs are given in Table 3.3.

The plot of conductivity at various concentrations are shown in Fig. 3.2 - 3.4.

TABLE 3.1

Analytical Data of Some Copper(I) Halide-Telluride Complexes

Complexes	Found%			Required%		
	Cu	C	H	Cu	C	H
$[Cu(Ph_2Te)_3Cl]$	6.18	45.6	3.30	6.73	45.7	3.13
$[Cu(Ph_2Te)_2Br]_2$	8.16	40.1	2.85	8.99	40.7	2.83
$[Cu(Ph_2Te)I]_2$	13.7	30.9	2.22	13.5	30.5	2.12
$[Cu((p\text{-tolyl})_2Te)_2Cl]_2$	8.17	46.8	4.02	8.84	46.8	3.90
$[Cu((p\text{-tolyl})_2Te)_2Br]_2$	8.25	44.2	3.75	8.33	44.1	3.67
$[Cu((p\text{-tolyl})_2Te)_2I]$	7.44	41.8	3.52	7.84	41.5	3.46
$[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_2Cl]_2$	7.50	46.0	4.29	7.56	45.8	4.33
$[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_2Br]_2$	7.20	44.1	4.39	7.19	43.5	4.08
$[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)I]_2$	10.7	34.1	3.32	11.3	34.3	3.21

TABLE 3.2

Low-frequency Infrared Spectra of Copper(I)Halide-Telluride Complexes

$[Cu(Ph_2Te)_3Cl]$	$[Cu(Ph_2Te)_2Br]_2$	$[Cu(Ph_2Te)I]_2$
382 m	383 m	390 s
270	270 s	308 s
265 s,br		270 s
260	262 s	261 s
217 m	218 m	229 m
190 m	201 vw	197 m
168 m	182 m, br	181 w
146 w	155 m	173 m
121 m	133 sh	161 s
93 s	109 w	111 s

$[Cu((p-CH_3C_6H_4)_2Te)_2Cl]_2$;	$[Cu((p-CH_3C_6H_4)_2Te)_2Br]_2$;	$[Cu((p-CH_3C_6H_4)_2Te)I]_2$
382 s	382 s	382 s
312 s	315 m	308 m
276 w	274 w	243 s
258 w	238 s	237 m
240 s	182 w	193 m
213 m	164 s	163 s
183 s	142 m	146 m
147 sh	92 m	125 m
117s		107 s
87 w		

continued..

TABLE 3.2 continued

$[Cu((p.EtOC_6H_4)_2Te)_2Cl]_2$	$[Cu((p.EtOC_6H_4)_2Te)Br]_2$	$[Cu((p.EtOC_3H_4)_2Te)I]_2$
381 s	382 s	383 s
349 m	345 m	345 s
331 m	329 m	308 m
313 m	305 m	
302 m	205 m	235 w
210 m	181 w, br	210 m
$\underline{185}$ s	$\underline{163}$ m	182 w
148 sh	143 m	134 w
$\underline{128}$ m	$\underline{100}$ w	89 m

Bands assigned to copper-halogen stretching vibrations are underlined.

TABLE 3.3

'd' Spacing for Copper(I) Halide-Telluride Complexes

$[Cu((p\text{-tolyl})_2Te)_2Cl]$	$[Cu((p\text{-tolyl})_2Te)_2Br]_2$	$[Cu((p\text{-tolyl})_2Te)_2I]$
13.50(s), 10.05(m), 5.7(m)	13.50(s), 10.02(m), 5.75(w)	12.20(s), 10.00(s), 8.75(m)
4.72(m), 4.15(m), 3.9(w)	4.75(w), 4.18(m), 3.35(m)	4.15(s), 3.60(w), 3.35(m)
3.63(w), 3.35(m), 2.8(m)	3.15(w), 2.80(w), 2.10(vw)	3.11(vw), 2.92(vw), 2.82(vw)
2.45(m), 2.23(w), 2.17(w)	2.00(vw), 1.87(w)	2.32(w), 2.20(w), 2.10(w)
2.09(w), 2.00(w). 1.87(w)		1.93(w), 1.78(vw), 1.69(vw)
$[Cu((p\text{-EtO-}C_6H_4)_2Te)_2Cl]_2$	$[Cu((p\text{-EtOC}_6H_4)_2Te)_2Br]_2$	$[Cu((p\text{-EtOC}_6H_4)_2Te)_2I]_2$
15.0(s), 12.0(s), 6.25(s), 5.5(s)	13.8(s), 9.5(m), 5.5(m)	
5.0(s), 4.50(s), 4.10(s), 3.80(s)	4.45(w), 4.15(w), 3.65(m)	The photograph is very poor
3.62(s), 3.35(m), 3.20(s), 2.74(m)	3.2(m), 2.75(w), 2.2(w)	
2.49(s), 2.40(m), 2.25(w), 2.11(w)	1.94(m), 1.9(m)	
2.02(w), 1.38(m), 1.32(w)		

CONTINUED...

TABLE 3.3 continued

$[Cu(Ph_2Te)_3Cl]$	$[Cu(Ph_2Te)_2Br]_2$	$[Cu(Ph_2Te)I]_2$
10.35(s), 6.10(m), 5.70(m)	11.5(s), 6.8(m), 4.8(m)	12.0(s), 8.5(s), 4.28(m)
5.25(m), 5.10(m), 4.55(w)	4.3(m), 3.6(m), 3.4(m)	3.7(m), 3.5(w), 3.12(m)
4.25(w), 4.00(w), 3.70(s)	3.2(m), 2.92(w), 2.75(w)	2.32(m), 2.19(m), 1.97(w)
3.48(s), 3.35(w), 3.07(w)	2.40(w), 2.22(m), 2.12(w)	1.87(w), 1.75(vw)
2.92(m), 2.73(m), 2.65(w)	2.10(w), 1.97(m), 1.92(w)	
2.57(w), 2.50(w), 2.45(m)	1.84(m), 1.78(w), 1.72(w)	
2.36(vw), 2.33(w), 2.28(w)		
2.18(w), 2.15(w), 2.02(m)		
1.94(m), 1.85(w), 1.81(vw)		
1.76(vw), 1.72(vw), 1.70(vw)		
1.61(vw)		

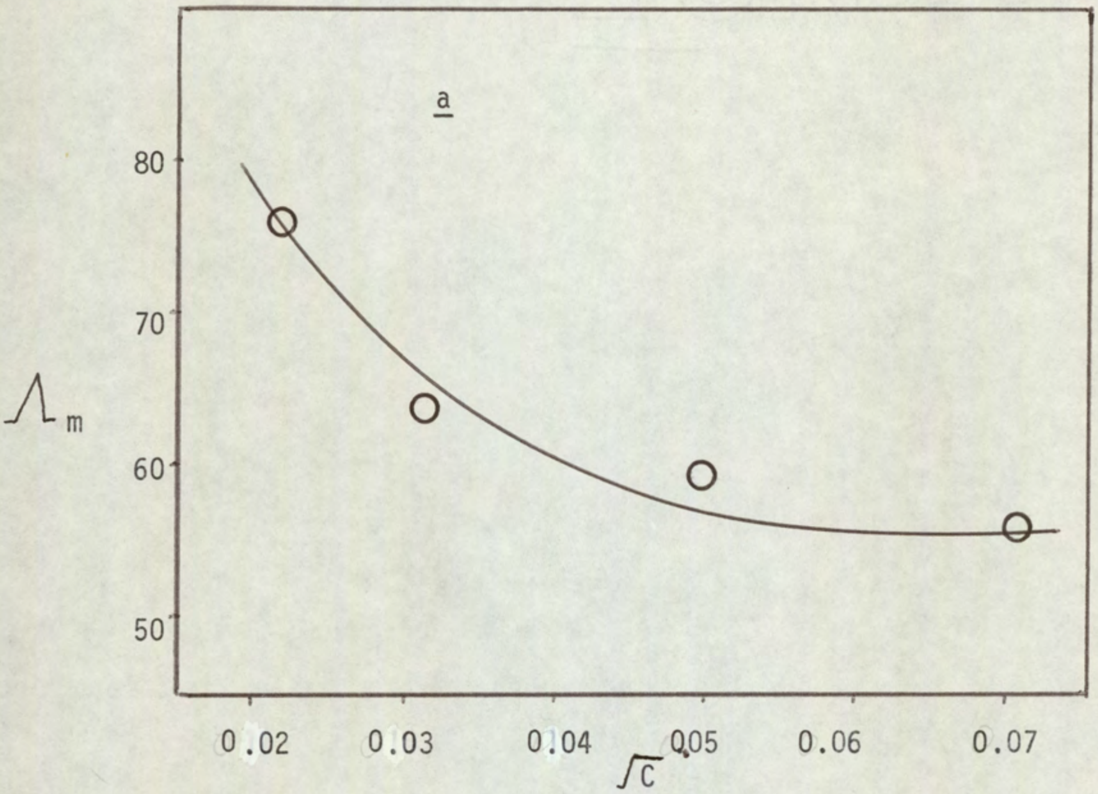


Fig. 3.2

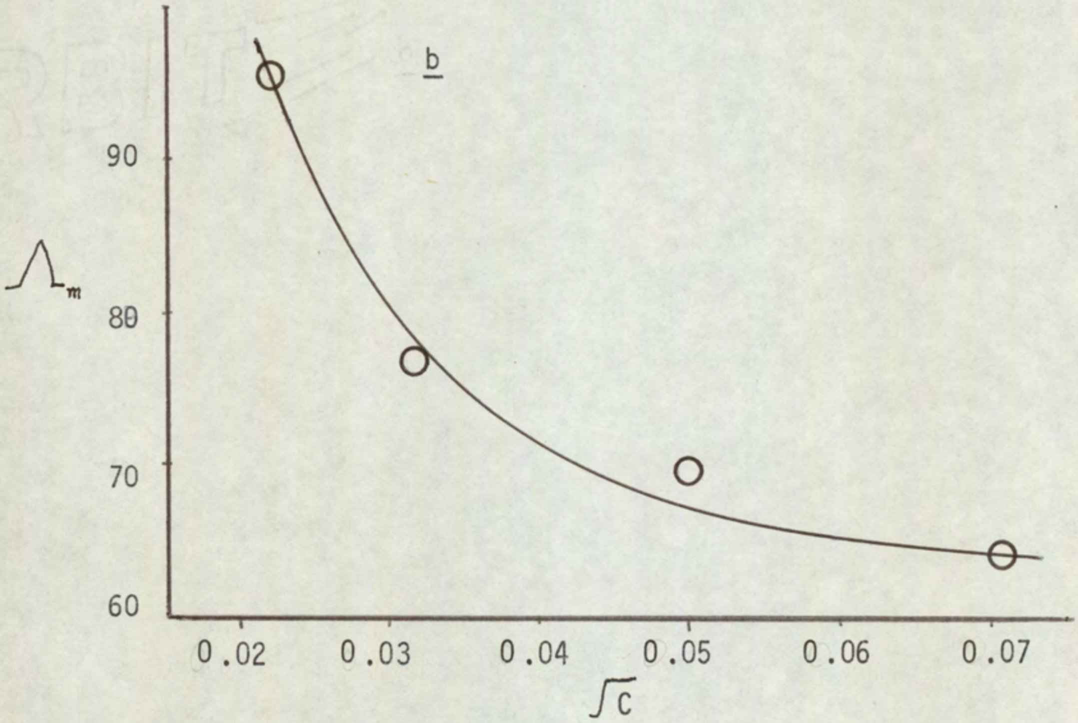


Fig. 3.2

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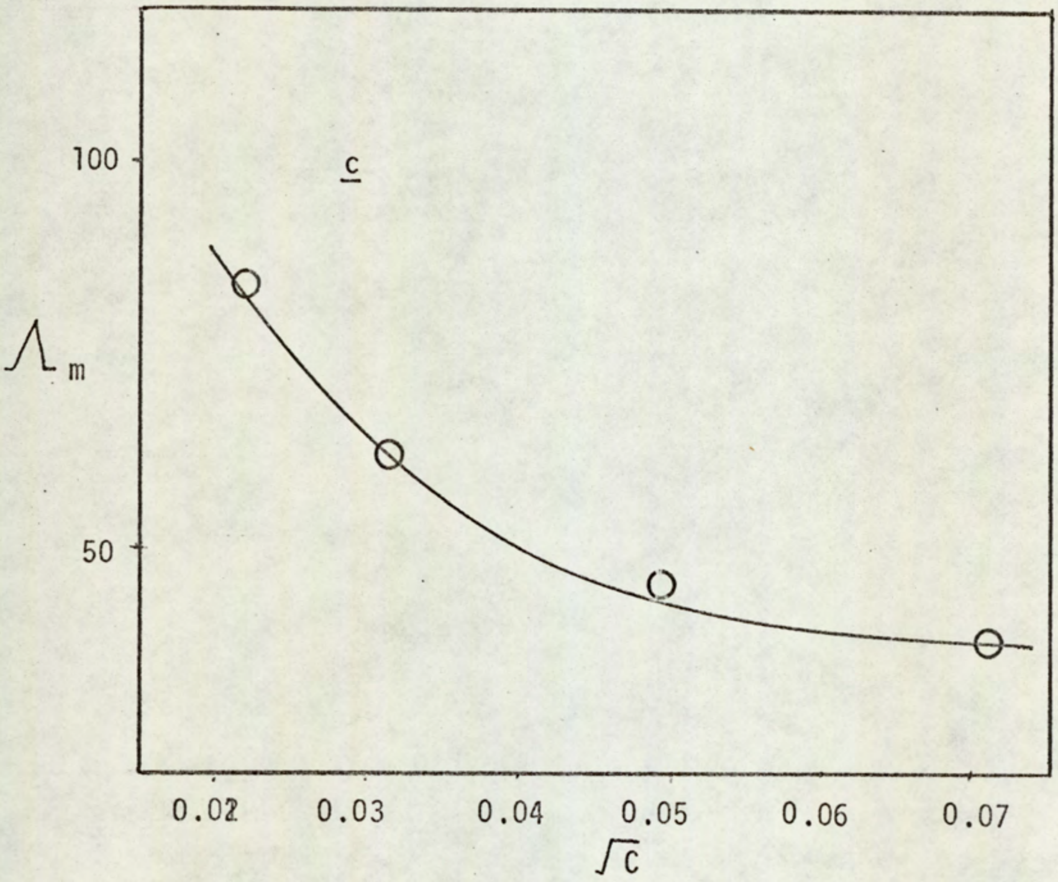

Fig. 3.2 Plot of molar conductivity (Λ_m) against (concentration)$^{\frac{1}{2}}$ for copper(I)-telluride complexes.

a. $[Cu(Ph_2Te)_3Cl]$

b. $[Cu(Ph_2Te)_2Br]$

c. $[Cu(Ph_2Te)I]$

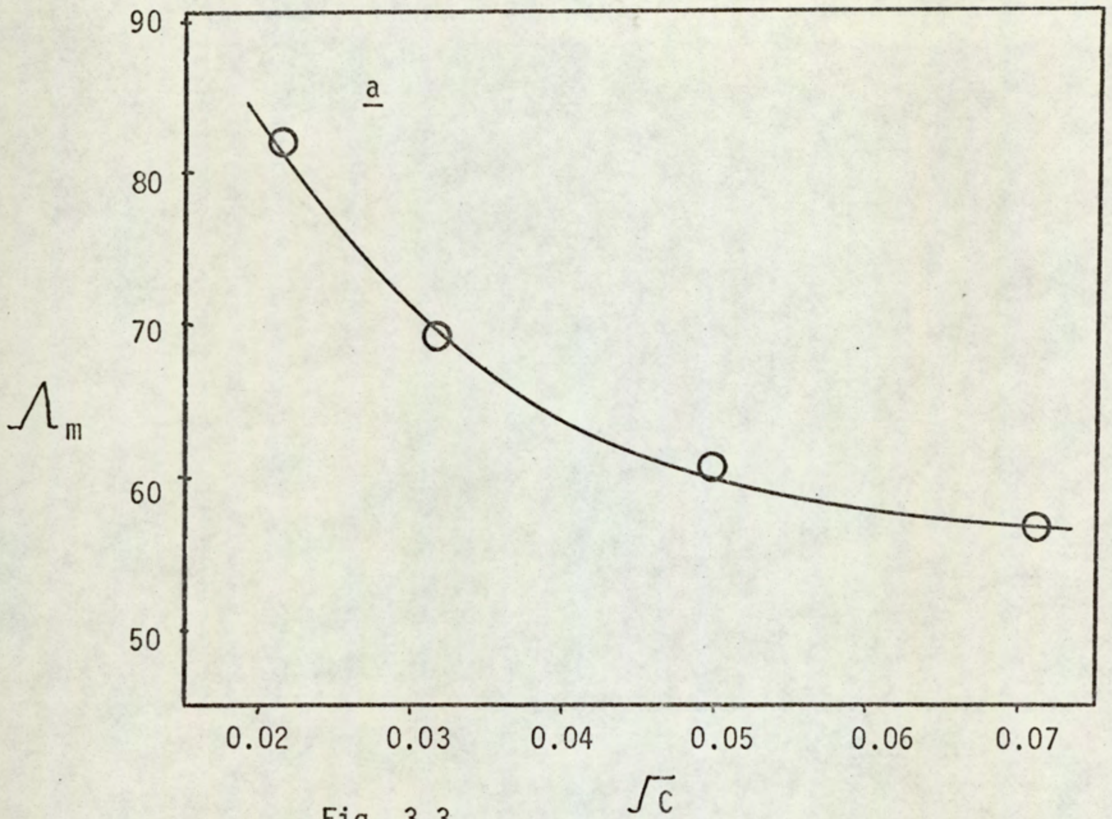

Fig. 3.3

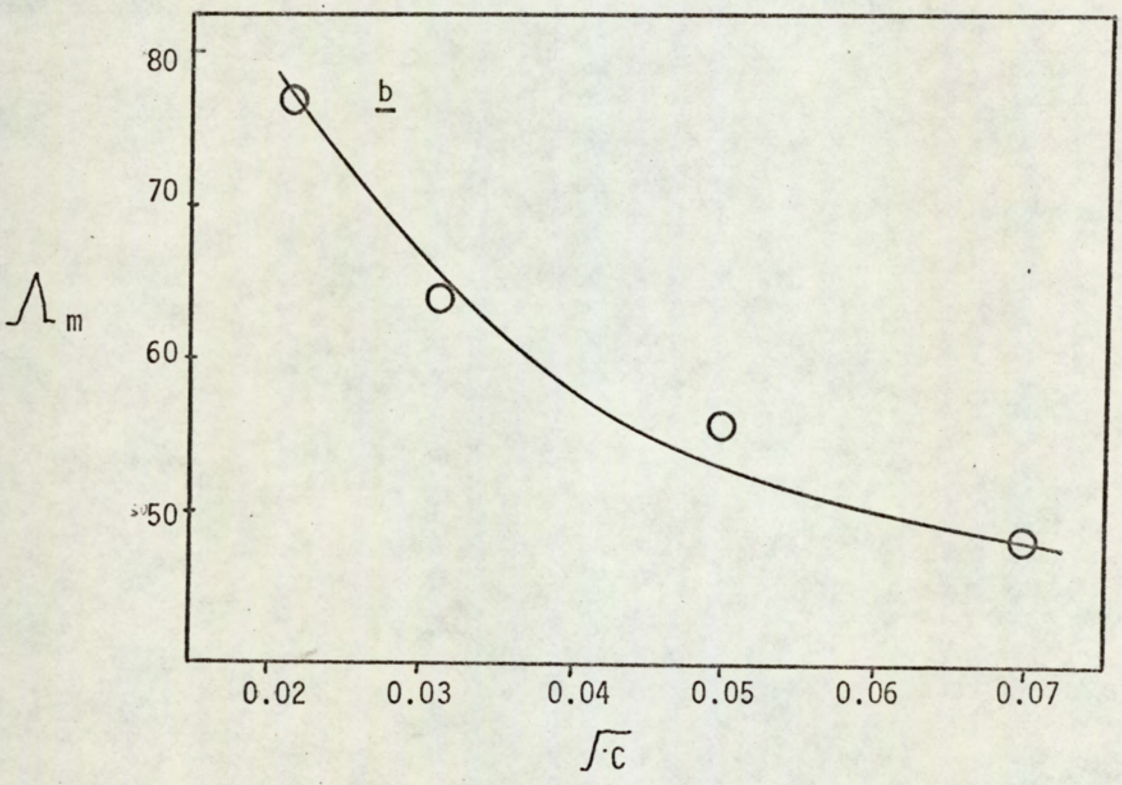

Fig.3.3

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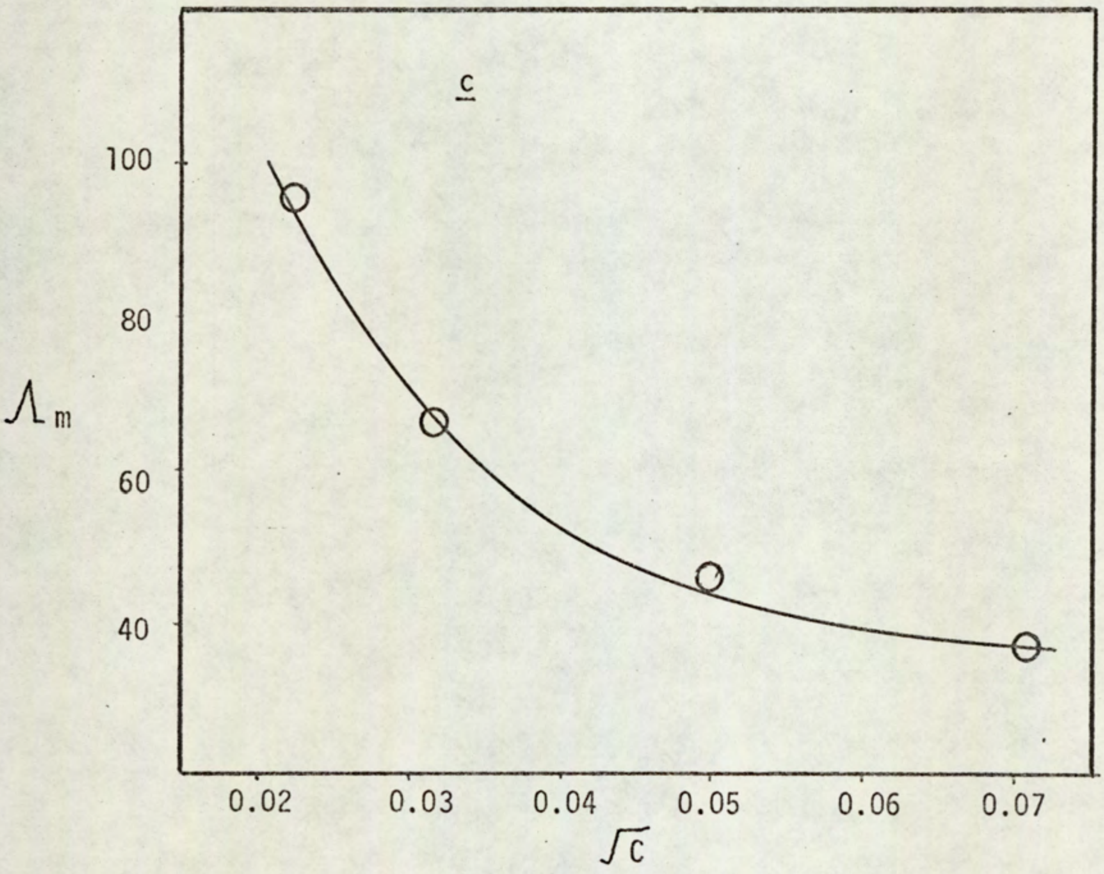


Fig. 3.3 Plot of molar conductivity (Λ_m) against (concentration)$^{\frac{1}{2}}$ for copper(I)-telluride complexes.

a. $[Cu((p\text{-tolyl})_2Te)_2Cl]$

b. $[Cu((p\text{-tolyl})_2Te)_2Br]$

c. $[Cu((p\text{-tolyl})_2Te)_2I]$

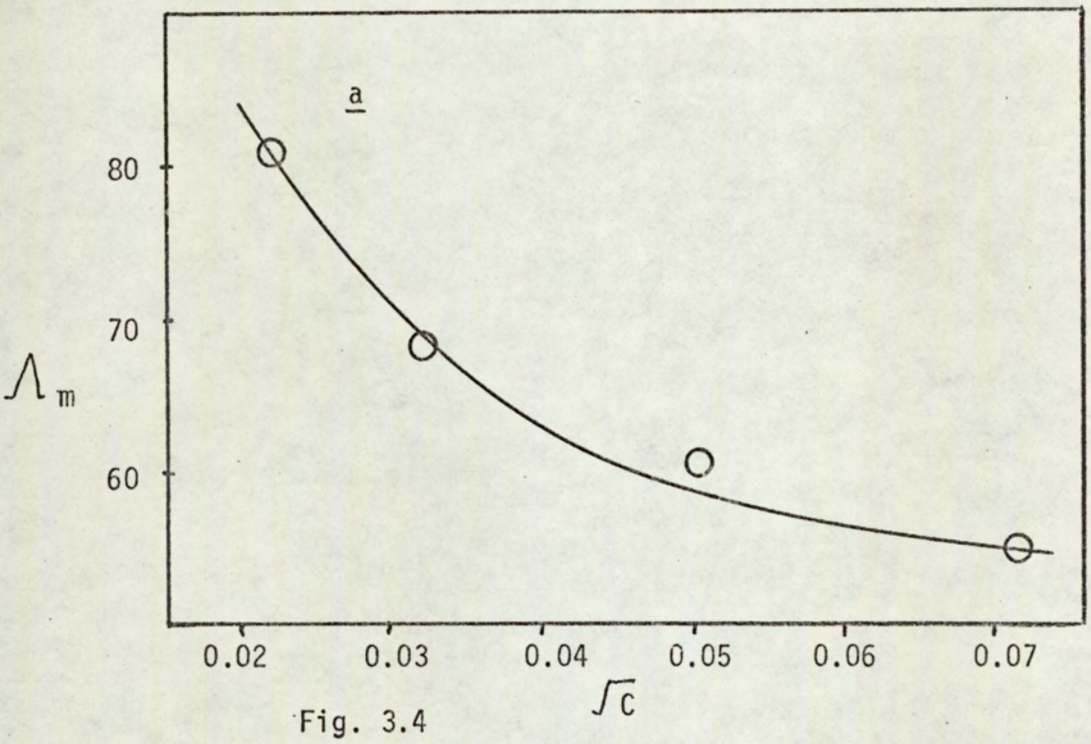


Fig. 3.4

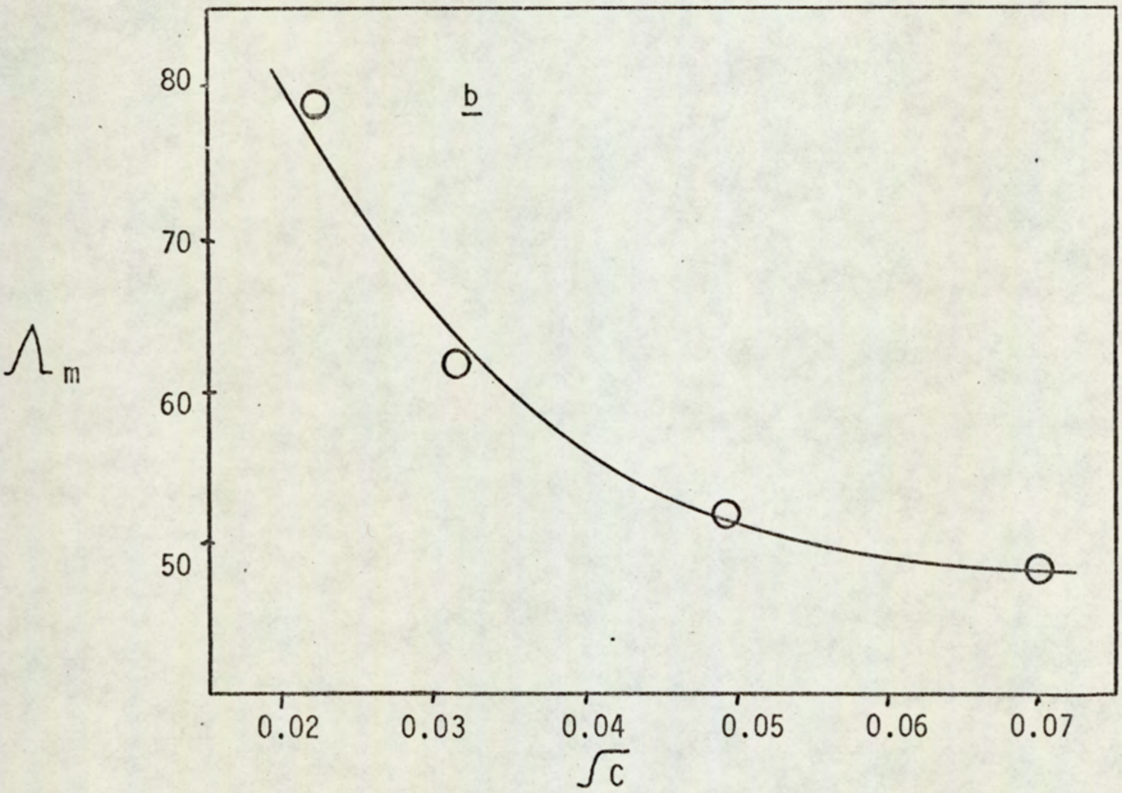


Fig. 3.4 continued

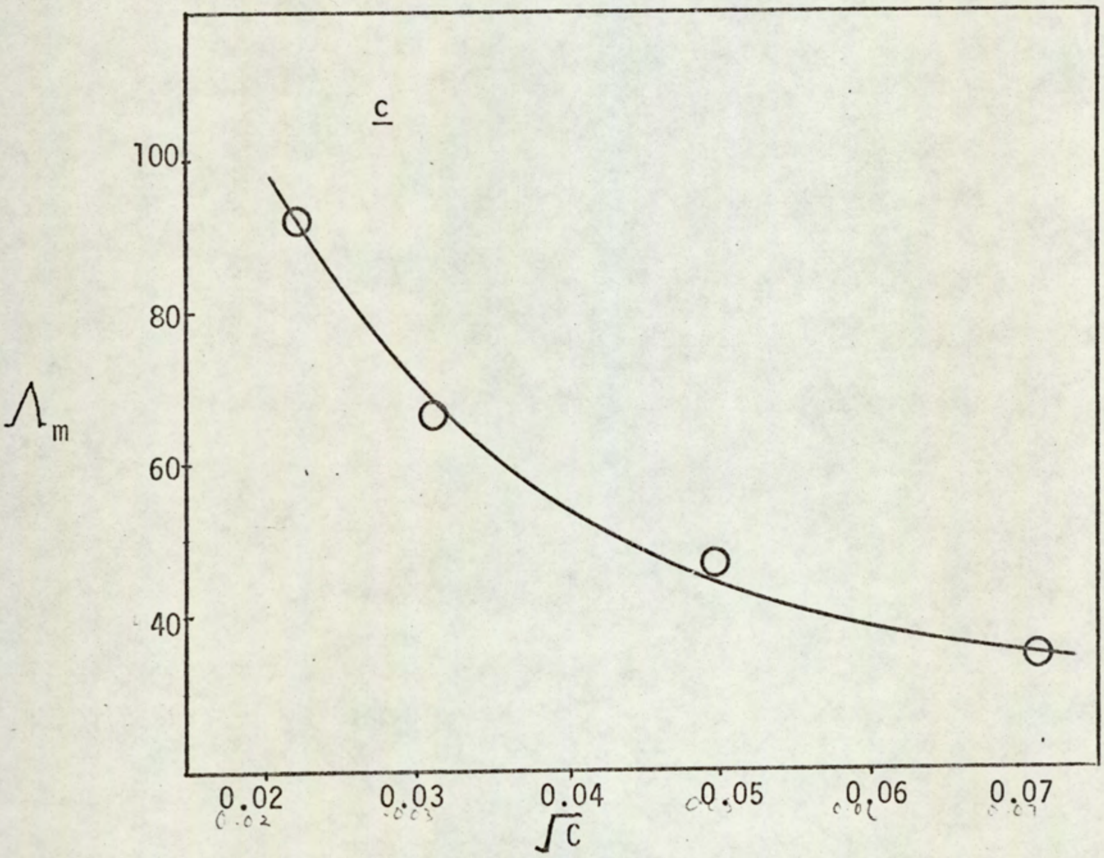


Fig. 3.4 Plot of molar conductivity (Λ_m) against (concentration)$^{\frac{1}{2}}$ for copper(I)-telluride complexes.

a. $[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_2Cl]$

b. $[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_2Br]$

c. $[Cu((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)I]$

(D) DISCUSSION

From the data of the analysis of the complexes shown in Table 3.1 it is indicated that complexes with different ratios of ligand: metal are formed. 2:1 complexes are preferentially formed by most of the halides as shown by the behaviour of copper(I) bromide with all the ligands, and copper(I) chloride with di-p-tolyltelluride and di-p-ethoxyphenyltelluride and of copper(I) iodide of di-p-tolyltelluride. 1:1 complexes were found for copper(I) iodide of diphenyltelluride or di-p-ethoxyphenyltelluride. One 3:1 complex was formed i.e. copper(I) chloride with diphenyltelluride.

Reactions using varying ligand: metal ratios, e.g. 4:1, 3:1, 2:1, 1:1 and excess: 1 were carried out but only the complexes with the stoichiometrics described above were obtained. This was confirmed by the analysis and identical i.r. spectra of the complexes prepared from different ligand: metal ratios. This type of behaviour of the copper(I) halide telluride in forming only certain types of complex irrespective of the amount of ligand used seemed to be different from copper(I) complexes of other ligands e.g. triphenylphosphine(68b) or methyldiphenylarsine(66) which are capable of forming complexes with different ligand: metal ratios. This might be due to the solubility properties, which favour the only precipitation of the complexes with a definite ratio in the case of diaryltelluride compounds of copper(I).

Due to the limited solubilities, molecular weight determinations by the Mechrolab vapor pressure osmometer could not be performed.

Attempts to obtain molecular weights by mass spectrometry were not informative, only peaks at m/e values corresponding to the free ligand and its fragmentations were observed.

The conductivities of the complexes in methylcyanide of 10^{-3} molar concentration gave a value of Λ_m about 60 - 70 $ohm^{-1}cm^2mole^{-1}$, these figures are too low for 1:1 electrolytes (about 120 - 160 ohm^{-1} cm^2 $mole^{-1}$) as suggested by Walton(81). It should be noted that if the values of the measured molar conductivities were doubled, the values obtained will fit reasonably well with 1:1 electrolyte e.g. CuL_4^+ CuX_2^- for 2:1 complexes. The molar conductivities at various concentrations were measured for each compound. From the graph obtained (Figures 3.2 - 3.4) it is clear that all the complexes behave as weak electrolytes. This will imply that salt-like structures such as $CuL_4^+X^-$ and $CuL_4^+CuX_2^-$ could probably be excluded. The likely nature of the mechanism that accounts for the conductivity behaviour is of the type

$$ML_nX + CH_3CN \rightleftharpoons ML_n.CH_3CN^+ + X^-$$

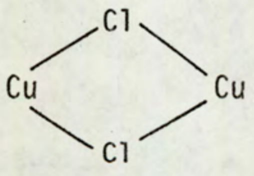
(M = Cu, L = diaryltelluride)

The above type of the equilibrium was invoked to explain some conductivity values ($\Lambda_m \approx 30$ ohm^{-1} cm^2) of other metal compounds(82).

The X-ray powder data of the compounds showed that copper(I) chloride and bromide of di-p-tolyltelluride are isomorphous. Closer examination of the `d´ values of the compounds showed that for the other 2:1 complexes i.e. copper(I) bromide with di-p-ethoxyphenyltelluride and diphenyltelluride and copper(I) chloride of di-p-ethoxyphenyltelluride are sufficiently similar to the copper(I) chloride and bromide of di-p-tolyltelluride to be reasonably considered as isomorphous. This X-ray data must be treated with caution since by changing the anionic ligand e.g. from chloride to iodide the size was increased and this might affect the distance in the lattice although the compounds may have similar structures.

The high-frequency i.r.spectra (4000 cm^{-1} - 400 cm^{-1}) of the complexes were quite similar to the spectra of the uncomplexed ligands. The only noteworthy observations are the similarity of the spectra of CuL_2X; [$L=(p\text{-}CH_3C_6H_4)_2Te,(p\text{-}OC_2H_5C_6H_4)_2Te, X = Cl,Br$]. These spectra were different from the case when X = I. This observation corresponds with the X-ray data which suggests the isomorphism of chloride and bromide copper(I) complexes of di-p-tolyltelluride, di-p-ethoxyphenyltelluride but not with iodide.

The low-frequency i.r.spectra are quite useful as an aid to determine the stereochemistry of the metal complexes$^{(83)}$. Copper-halogen stretching frequencies extend over a wide range. It was shown by Adams and Lock$^{(84)}$ that $\nu(Cu^{II} - Cl)$ is located within the range 320 - 220 cm^{-1} and that $\nu(Cu^{II} - Cl)$ for bridging halogen occurred



at about 230 cm^{-1}. The corresponding $\nu(Cu^{II} - Br)$ was quoted as 278 - 168 cm^{-1}. For the copper(I) compounds the i.r.spectrum of $(CuCl)_n$ showed a broad band with a maximum at 170 cm^{-1} (85) which is quite low for metal halogen stretching vibrations as compared with $CuCl_2$(84) which gives an absorption maximum at 290 cm^{-1}. Copper(I) halide stretching frequencies both terminal and bridged were assigned by a number of workers(85-89). Carthy and Efraty(86) assigned one strong bond at 267 cm^{-1} as $\nu_+(Cu - Cl)$ in the complex $(CuCl)_2(DPPA)_3$; (DPPA = bis (diphenylphosphine acetylene) which agrees well with a tetrahedral C_{3v} configuration of three phosphorous atoms and one halide around each copper atom where a single $\nu(Cu - X)$ is expected. The corresponding bromide $\nu(Cu - Br)$ was assigned at 202 cm^{-1}. Moers and Op Het Veld(87) assigned the strong bond at 255 cm^{-1} as a $\nu(Cu - Cl)$ stretching vibration in the trigonal-coordinated complex $Cu(PCy_3)_2Cl$. Cook et al.(90) suggested the range 220 cm^{-1} - 110 cm^{-1} to copper-chlorine vibration frequency and 200 cm^{-1} - 100 cm^{-1} to the corresponding copper-bromide vibrations. Two bands due to stretching of Cu - X bond in the halo-bridged complexes $(O - NMe_2.C_6H_4.AsMe_2)CuX$; (X = Cl, Br, I) were given as 232 cm^{-1}, 162 cm^{-1} for X = Cl, 202 cm^{-1}, 145 cm^{-1} for X = Br and 175 cm^{-1}, 128 cm^{-1} for X = iodine(89).

In the case of the complexes of the type CuL_2X; (L = di-p-tolyltelluride and X = Cl, Br) the bands observed at 183 cm^{-1} and 117 cm^{-1} are assigned as $\nu(Cu - Cl)$ stretching vibrations and the bands at 164 cm^{-1} and 92 cm^{-1} as $\nu(Cu - Br)$ stretching vibrations for the analogous bromo complex. The band at 183 cm^{-1} assigned as ν(Cu - Cl) probably has some enhancement from an internal mode of ligand vibration. For the iodo complex, since the structure of the compounds might be different from the chloro and bromo complexes as indicated by X-ray 'd' values and near i.r.spectra, the position and number of the bands expected will not follow the pattern of those of chloro and bromo complexes. The strong band at 163 cm^{-1} was tentatively assigned as ν(Cu - I) stretching vibration. Volponi et al.$^{(89)}$ assigned ν(Cu - I) stretching vibration in the iodobridged complex $CuI(O\text{-}NMe_2C_6H_4.As.Me_2)$ at 175 cm^{-1} and 128 cm^{-1}, no terminal copper(I) - iodine stretching vibration frequencies are known to help in the above assignment.

Copper(I) chloride and bromide of di-p-ethoxyphenyltelluride have similar far-infra-red spectra to that of di-p-tolyltelluride except only the bands due to ligand modes. The bands at 185 cm^{-1} and 128 cm^{-1} were assigned as ν(Cu - Cl) stretching vibrations and the bands at 163 cm^{-1} and 100 cm^{-1} as ν(Cu - Br) for the analogous bromo complex. In the case of diphenyltelluride complexes of copper(I) since different types of complexes were formed, the comparison of the spectra of chloro-, bromo- and iodo- complexes to aid in assigning ν(Cu - Cl), ν(Cu - Br), ν(Cu - I), which will decrease as the mass of halide increases, will not be useful since it is known that the ν(Cu - X) stretching vibrations changed with the stereochemistry and coordination number of the complexes$^{(83)}$. The band observed at 265 cm^{-1} was assigned as the ν(Cu - Cl) stretching vibration for the compound $Cu(Ph_2Te)_3Cl$. The terminal

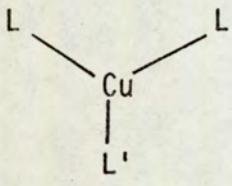
ν(Cu - Cl) stretching frequency in $(CuCl_2)(DPPA)_3$ has been reported by Carty and Effraty(86) at 267 cm^{-1}. The bands at 155 cm^{-1} and 109 cm^{-1} were assigned as ν(Cu - Br) stretching frequencies. In the case of 1:1 complexes Cu(Ph_2Te)I and [Cu((p-C_2H_5-C_6H_4)$_2$Te)I], the assignments of ν(Cu - I) proves to be difficult. In [Cu(Ph_2Te)I] two strong bands at 161 cm^{-1} and 111 cm^{-1} are observed and will be tentatively assigned as ν(Cu - I) stretching vibrations A satisfactory far i.r.spectrum of the compound [Cu((p-C_2H_5O-C_4H_4)$_2$Te)I] could not be obtained although many attempts have been made.

The bands around 380 cm^{-1} to 390 cm^{-1} observed in all complexes are due to vibrations of the phenyl ring of the ligands. McWhinnie and Patel(3) have assigned some low frequency spectra of Ph_2Te, the band at 386 cm^{-1} was due to phenyl group vibration and the bands at 271 cm^{-1}, 261 cm^{-1} and 256 cm^{-1} were assigned as tellurium-phenyl stretching frequencies ν(Te - Ph) which occurred in all complexes of copper(I) diphenyltelluride around 260 cm^{-1} to 270 cm^{-1}. In the case of di-p-tolyltelluride this ν(Te - R) occurred around 240 cm^{-1}.

Metal-tellurium vibrations have received very little attention. Hendra(91) showed that the symmetrical vibration of ν_{Pt-Te} is located in Raman at 169 cm^{-1}, while the asymmetric ν_{Pt-Te} is at 245 cm^{-1}. The IR active band at 227 cm^{-1} in $PtX_2(Me_2Te)_2$ was assigned as ν_{asym}(Pt - Te). It was observed that the bands around 142 cm^{-1} to 148 cm^{-1} occurred in all 2:1 complexes of copper(I) telluride, apparently independent of halogen, this will be assigned as ν(Cu-Te) stretching vibrations (in the case of $Cu(Ph_2Te)_2Br$, the broad band at 155 cm^{-1} due to $\nu(Cu - Br)$ obscured the band assigned as $\nu(Cu - Te)$).

The absence of the bands around 300 cm^{-1} and 200 cm^{-1} in the chloro and bromo copper(I) 2:1 complexes could possibly eliminate the structure $CuL_4^+CuX_2^-$; (X = Cl, Br) since CuX_2^- vibrations were observed at 296 cm^{-1} for X = Cl and 190 cm^{-1} for X = Br respectively(92). Also the presence of the bands assignable to Cu-X stretching vibrations can exclude the structure $CuL_2^+X^-$ since this type of complex will not have any band due to copper-halogen stretching vibrations. These agree with the results from the conductivities which exclude the possibility of the salt-like structures.

From the above evidence the structure of the complexes could be deduced, the 3:1 complex $Cu(Ph_2Te)_3Cl$ could possibly be tetrahedral since the coordinate number 4 for copper(I) (SP^3, tetrahedral) is very common(93). From this structure the band at 265 cm^{-1} was assigned as $\nu(Cu - Cl)$ stretching vibration. The 2:1 complexes could have the structure as bridged complexes(71,72) in which copper has coordination number 4 by bridging the anionic ligands (see Figure 3.1). Another possibility for the structure of the complexes is of three coordinated trigonal planar. These three-coordinated complexes were found in many cases e.g. $[Cu(Me_3PS)_3]ClO_4$(94), $[Cu(PCy_3)_2X]$(87), $Cu(PPh_3)_2N_3$, $Cu(PPh_3)_2OC_6H_5$(54) and many more(74,72). The structure could be written as



(L' = ClO_4^-, halide, etc.)

Fig. 3.5 - A trigonal planar structure copper(I) complex

The number of bands due to ν(Cu - X) stretching vibrations in the case of bridged complexes is expected to be two(89). The bands due to this bridged stretching would be located lower in frequency than the terminal stretching(83). From the spectra obtained in the case of 2:1 complexes of copper(I) telluride two bands due to copper-halogen stretching vibration could be assigned. The position of the bands (180 cm^{-1} - 100 cm^{-1}) are too low to be classified as terminal copper-halogen stretching vibration [ν(Cu - Cl) = 267 (86)]. From the above evidence it seems more likely that the structure of the 2:1 complexes of copper(I) telluride will be dimers with halogen bridging (see Figure 3.1). For [Cu((di-ptolyl)$_2$Te)$_2$I] the structure seemed to be different from other 2:1 complexes, the bands around 100 cm^{-1} to 163 cm^{-1} would be too high for ν(Cu - I) if the comparison was taken with ν(Cu - Cl) and ν(Cu - Br) in the bridged structure. Trigonal planar structure will be more likely for the above compound (see Figure 3.5, L = di-p-tolyltelluride, L' = I). The 1:1 complexes could have the linear structure (sp linear) or tetrameric as in the case of [Cu(Et$_3$As)I]$_4$ which was indicated by X-ray study(70), or halogen bridged as found in [Cu(PCy)X]$_2$(87).

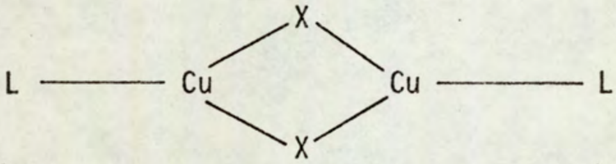
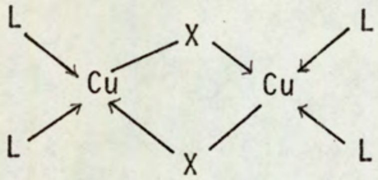


Fig. 3.6 A tricoordinated bridged structure copper(I) complex

The evidence obtained from this study was not enough for any conclusive characterisation of these 1:1 complexes. The complexes might have the three-coordinated bridged structure as Figure 3.6 above (L = Ph_2Te, di-p-ethoxyphenyltelluride, X = I) which two bands assigned as ν(Cu - I) were observed at 161 cm^{-1} and 111 cm^{-1} in $Cu(Ph_2Te)I$.

Raman studies are quite useful as a complementary tool to i.r.studies in the characterisation of these complexes, especially for 2:1 bridging complexes



which have a centre of symmetry. Two attempts have been made to get Raman spectra from Leicester University (coderg PH11) and Nottingham University (cary 81) were unsuccessful since it was not possible to get close enough to the exciting line end.

It is seen clearly that the positions of the bands (180-100 cm^{-1}) assigned as ν(Cu - X) stretching vibrations in these copper(I) telluride complexes were rather low compared with the available literature values 280 cm^{-1} - 180 cm^{-1}. This implies that the bonds between copper-halogen are rather weak or have low force constants. These observations agree well with ease of solvolysis of these compounds with methyl cyanide as indicated by the rather high value of Λ_m for the complexes (60 - 70 ohm^{-1} cm^2 $mole^{-1}$). This showed that the bond between copper and halogen is rather weak for this reaction to occur readily:

$$CuL_nX + CH_3CN \rightleftharpoons CuL_n.CH_3CN^+ + X^-$$

Another observation that should be mentioned is the ready surface oxidation of some of these compounds. When $Cu(Ph_2Te)_3Cl$ was left in the air for some time (a few weeks) some of the compound will change to light green, the product, which was not characterised, was probably a mixture of copper(I) and copper(II). The presence of copper(II) is confirmed by e.s.r. spectroscopy.

CHAPTER FOUR

THE REACTION OF TELLURIDE LIGANDS WITH RHODIUM(III), AND INVESTIGATION OF POSSIBLE USES OF THE RESULTING COMPLEXES

(A) INTRODUCTION

The researches into the chemistry of rhodium complexes are numerous as can be seen in the literature concerning inorganic, coordination and organometallic chemistry.

As rhodium could be classified as a class (b) metal and its sulphide complexes $Rh(R_2S)_3Cl_3$; (R = Et, $PhCH_2$) were successfully used by James et al.(29,30) as hydrogenation catalysts, the analogous telluride complexes of rhodium were investigated. The synthesis, chemistry, properties and potential uses of the telluride rhodium complexes are given in this chapter.

The far-infrared techniques have progressed quite rapidly so that it is now possible to get the spectra to the lower energy of 40 cm^{-1}. This is quite valuable since from this information, assignment of metal-ligand vibrations could be studied and will lead to more understanding of the structure of the compounds. Attempted assignments of $\nu(Rh-X)$; (X = Cl, Br) stretching vibrations have been made for some rhodium telluride complexes, their structure was also proposed with the help of other physical techniques.

It is also found that compared with phosphine, telluride is a poor Π acceptor ligand and not as good in stabilising lower oxidation states of rhodium.

(B) EXPERIMENTAL

In the preparation of the telluride complexes of rhodium by refluxing rhodium trichloride with diphenyltelluride, it was found that the yield of the product obtained from the reaction carried out under air is not satisfactory which restricted the further uses of the compound. It is also found that when the reaction was carried out under dinitrogen the yield was substantial and the reaction was clean. All the subsequent reactions in this chapter, unless otherwise stated, were carried out under dinitrogen.

(a) Preparation of Rhodium(III) complexes with organic tellurides

Reactions carried out under air

Trichloro*tris*(diphenyltelluride)rhodium(III)

Rhodium trichloride trihydrate (0.26 gm, 1mM) in ethanol(25ml) was added to diphenyltelluride (0.85 gm, 3mM) in ethanol (25 ml), a brown solid was formed immediately, the resulting solution was refluxed for 3 hours, it was observed that the originally brown solid formed dissolved while refluxing. The dark red solution was filtered off to remove some brownish-black solid left around the wall and the bottom of the flask. The clear solution was heated under vacuum by rotary evaporator to get rid of excess solvent. The orange solid precicipated while the solution was cooling. The product was filtered and washed thoroughly with ethanol and ether and recrystallised from ethanol.

Found: C,41.2%; H,2.97%

$C_{36}H_{30}Cl_3RhTe_3$

Requires: C,41.0%; H,2.85%.

In an attempt to improve the yield of the above product the following method was carried out.

When rhodium trichloride in ethanolic solution and diphenyltelluride in ethanol were mixed, a brown solid precipitated. The brown solid was filtered and the filtrate retained. The brown solid was extracted with ethanol and mixed with the first retained filtrate. The volume of the filtrate was reduced to afford the orange solid. The solid was filtered and washed with ethanol and ether and finally recrystallised with ethanol. The analysis of the complex conformed to the above formula $Rh(Ph_2Te)_3Cl_3$ and the i.r. spectrum was identical to the complex $Rh(Ph_2Te)_3Cl_3$ described above. The yield of the compound was still not satisfactory.

Reactions carried out under nitrogen

Trichloro*tris*(diphenyltelluride)rhodium(III)

Rhodium trichloride hydrate($RhCl_3$.x H_2O)(0.26 gm, 1 mM) in dinitrogen saturated alcohol (25 ml) was added to diphenyltelluride (0.85 gm, 3mM) in dinitrogen saturated ethanol (25 ml), the resulting solution was refluxed and stirred under the atmosphere of dinitrogen for 3 hours; an orange solid was precipitated while refluxing. The product was filtered through a sintered glass crucible and washed thoroughly first with hot and then cold ethanol.

Found: C,41.1%; H,2.89%; Cl,9.57%

$C_{36}H_{30}Cl_3RhTe_3$

Requires: C,41.0%; H,2.85%; Cl,10.1%.

Trichloro*tris*(di-p-tolyltelluride)rhodium(III)

The method for the preparation is similar to the one used for $Rh(Ph_2Te)_3Cl_3$. Di-p-tolyltelluride was used instead of diphenyltelluride.

Found: C,44.7%; H,4.02%

$C_{42}H_{42}Cl_3RhTe_3$

Requires: C,44.3%; H,3.69%

Trichloro*tris*(di-p-ethoxyphenyltelluride)rhodium(III)

The procedure for this preparation is similar to the one used for $Rh(Ph_2Te)_3Cl_3$. Di-p-ethoxytelluride was used instead of diphenyltelluride.

Found: C,43.3%; H,4.13%

$C_{48}H_{54}Cl_3O_6RhTe_3$

Requires: C,43.7%; H,4.09%

Tribromo*tris*(diphenyltelluride)rhodium(III)

Rhodium trichloride hydrated ($RhCl_3 \cdot x\ H_2O$) (0.26 gm, 1 mM) in dinitrogen saturated absolute alcohol (25 ml) was mixed with diphenyltelluride (0.85 gm, 3 mM) in dinitrogen saturated absolute alcohol (25 ml), the resulting solution was heated and stirred for 3 minutes then sodium bromide (1 gm) in a mixture of water (5 ml) and ethanol (5 ml) was added. The solution was refluxed and stirred under a dinitrogen atmosphere for 2 hours. The orange-brown solid was filtered off and washed thoroughly with hot and cold ethanol.

Found: C,36.9%; H,2.55%; Br,19.9%

$C_{36}H_{30}Br_3RhTe_3$

Requires: C,36.4%; H,2.53%; Br,20.2%

(b) Iridium complexes of diphenyl telluride

Trichlorotris(diphenyltelluride)iridium(III)

Hydrated sodiumchloroiridite ($Na_3Ir_2Cl_6.12H_2O$)(0.69 gm, 1 mM) in a mixture of water (10 ml) and absolute alcohol (15 ml) was mixed with diphenyltelluride (1.2 gm 4 mM) in absolute alcohol (25 ml) the resulting solution was refluxed for 3 hours. When the solution cooled down, the solution was decanted and an oily liquid was left in the flask. Petroleum ether (b.p.30° - 40°) was added to the oily liquid and the solution was stirred, the oily liquid crystallised affording an orange solid. The product was filtered off and washed thoroughly with ethanol and ether.

Found: C,37.9%; H,2.84%; Cl,9.28%

$C_{36}H_{30}Cl_3IrTe_3$

Requires: C,37.8%; H,2.62%; Cl,9.30%

Dichlorohydridotris(diphenyltelluride)iridium(III)

Sodiumchloroiridatehexahydrate ($Na_2IrCl_6.6H_2O$)(0.55 gm, 1mM) in absolute alcohol (25 ml) was added to diphenyltelluride (0.85 gm, 3 mM) in absolute alcohol (25 ml). The resulting solution was refluxed and stirred for 6 hours. It was observed that the orange-yellowish precipitate deposited while refluxing. The solid was filtered and washed thoroughly with hot and cold ethanol.

Found: C,38.6%; H,2.82%

$C_{36}H_{31}Cl_2IrTe_3$

Requires: C,38.9%; H,2.70%

(c) Complexes from the reaction of $Rh(Ph_2Te)_3Cl_3$ + ligands

(ligands = 2,2'bipyridyl, Di-2-pyridylamine, Di-2-pyridylketone, 1,10'phenanthroline, triphenylphosphine)

Trichloromono(2.2'bipyridyl)mono(diphenyltelluride)rhodium(III)

Trichlorotris(diphenyltelluride)rhodium(III) (0.52 gm, 0.5 mM) in benzene (20 ml) was added to 2,2'bipyridyl (0.08 gm 0.5 mM) in benzene (20 ml). The resulting solution was refluxed while stirring for 2 hours. A yellowish-orange solid precipitated while refluxing and this was filtered while the solution was hot. The solid was washed thoroughly with ethanol and benzene.

Found: C,41.0%; H,2.91%; N,4.37%

$C_{22}H_{18}Cl_3N_2RhTe$

Requires: C,40.8%; H,2.78%; N,4.33%

Trichloromono(diphenyltelluride)mono(1.10'phenanthroline)rhodium(III)

1,10'phenanthrolinehydrate (0.1 gm, 0.5 mM) in benzene (20 ml) was added to trichlorotris(diphenyltelluride)rhodium(III) (0.52 gm, 0.5 mM) in benzene (20 ml). The resulting solution was refluxed while stirring for 2 hours. The yellow-orange product precipitated in the course of refluxing and was filtered while the solution was hot through a sintered glass crucible. The solid was washed thoroughly with benzene and ethanol and dried under vacuum.

Found: C,43.3%; H,3.12%; N,4.23%

$C_{24}H_{18}Cl_3N_2RhTe$

Requires: C,42.9%; H,2.68%; N,4.17%

Trichloromono(diphenyltelluride)mono(di-2-pyridylamine)rhodium(III)

Trichlorotris(diphenyltelluride)rhodium(III) (0.52 gm, 0.5 mM) in benzene (20 ml) was mixed with di-2-pyridylamine(0.085 gm, 0.5 mM) in benzene (20 ml). The resulting solution was refluxed while stirring for 2 hours. The orange-yellow solid which precipitated during refluxing was filtered while the solution was hot. The solid was washed thoroughly with benzene and alcohol.;

Found: C,40.1%; H,3.27%; N,7.08%

$C_{22}H_{19}Cl_3N_3RhTe$

Requires: C,39.9%; H,2.87%; N,6.34%

Trichloromono(diphenyltelluride)mono(di-2-pyridylketone)rhodium(III)

Di-2-pyridylketone (0.09 gm, 0.5 mM) in benzene (20 ml) was added to trichlorotris(diphenyltelluride)rhodium(III) (0.52 gm, 0.5 mM) in benzene (20 ml). The resulting solution was stirred and refluxed for 2 hours. The yellowish-orange solid which precipitated during refluxing was filtered while the solution was still hot. The solid was washed thoroughly with benzene and ethanol.

Found: C,41.4%; H,2.94%; N,4.02%; Cl,15.3%

$C_{23}H_{18}Cl_3N_2ORhTe$

Requires: C,40.9%; H,2.66%; N,4.15%; Cl,15.7%

Reaction between $Rh(Ph_2Te)_3Cl_3$ and triphenylphosphine

Trichloro<u>tris</u>(diphenyltelluride)rhodium(III) (1.05 gm, 1 mM) in benzene (20 ml) was mixed with triphenylphosphine (0.26 gm, 1 mM) in benzene (20 ml). The resulting solution was refluxed while stirring for 2 hours. The excess solvent was evaporated using rotary film evaporator, then petroleum ether (30^0 - 40^0) was added which caused an orange solid to precipitate. The solid was washed thoroughly with petroleum ether and ethanol. Analysis showed that the product could be formulated as $Rh(Ph_2Te)(PPh_3)Cl_2$.

Found: C,50.5%; H,3.84%; Cl,10.2%; P,4.16%

$C_{30}H_{25}Cl_2PRhTe$

Requires: C,50.2%; H,3.48%; Cl,9.88%; P, 4.32%.

Reaction between $[Rh((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_3Cl_3]$ and triphenylphosphine

The preparation of this complex is similar to the one used for $Rh(Ph_2Te)(PPh_3)Cl_2$ but di-p-ethoxyphenyltelluride was used instead of diphenyltelluride.

Found: C,51.4%; H,4.25%

$C_{34}H_{33}Cl_2O_2PRhTe$

Requires: C,50.7%; H,4.10%

(d) Attempted reactions of rhodium trichloride with diphenyltelluride under reducing conditions

(1) Reaction of rhodium trichloride ($RhCl_3.xH_2O$) with diphenyltelluride and sodiumborohydride

Rhodium trichloride hydrate (0.263 gm, 1 mM) in dinitrogen saturated alcohol (25 ml) was added to excess diphenyltelluride (3 gm) in nitrogen saturated alcohol (25 ml). The resulting solution was heated and stirred for 5 minutes then sodium borohydride (0.05 gm) in ethanol (15 ml) was added. The colour of the solution changed immediately from red-orange to dark brown, a dark brown solid was deposited. The solution was further refluxed for another 1 hour. The dark brown solid was filtered off and washed with ethanol. The i.r. spectrum of the product contained no rhodium-hydride band and the analysis of the product obtained did not conform to any proposed formula. The product was not investigated further.

Also some variations were made in the preparation by using di-p-tolyltelluride in place of diphenyltelluride but this again afforded a dark brown solid which has a similar i.r. spectrum to the material from the diphenyltelluride reaction. When formadehyde or acetadehyde was added to the reaction mixture (1) above, it was found that instead of getting rhodium carbonyl complexes as in the case of triphenylphosphine reported by Robinson et al.(122) only dark brown solids were formed showing no carbonyl absorption or metal-hydride bands.

(2) Reaction of rhodiumtrichloride hydrate ($RhCl_3.xH_2O$) with diphenyltelluride and ethanolic potassium hydroxide

This reaction was carried out similarly to reaction (1) above. The change of reducing agent from $NaBH_4$ to ethanolic KOH did not make any difference to the observed reaction. Only a dark brown solid similar in i.r. spectrum and appearance to dark brown solid in (1) was formed.

(e) Attempted reactions of Dichlorobis(2.2'bipyridyl)rhodium(III) chloride with diphenyltelluride under reducing conditions

Dichlorobis(2,2'bipyridyl)rhodium(III)chloride dihydrate $[Rh(bipy)_2Cl_2]^+ Cl^-.2H_2O$ (0.56 gm, 1 mM) in ethanol (25 ml) was stirred magnetically, then sodium borohydride in ethanol was gradually added. A colour change of the solution from purple to dark brown was observed and during the colour change excess diphenyltelluride in ethanol was added to the above solution. The dark brown solution was refluxed for 1 hour. The dark brown solid obtained from this reaction showed no metal-hydride band in its i.r. spectrum and was not characterised further.

The change of reducing agent from BH_4^- to ethanolic KOH did not change the reaction, a similar dark brown solid was obtained.

(f) Attempted reactions of trichloromono(2.2'bipyridyl)mono (diphenyltelluride)rhodium(III),$[Rh(2,2'bipy)(Ph_2Te)Cl_3]$, with L(L = Ph_2Te,PPh_3) and benzylbromide under reduced conditions

(I) Reaction of $Rh(Ph_2Te)(2,2'bipy)Cl_3$ with benzyl bromide and borohydride

Trichloromono(2,2'bipyridyl)mono(diphenyltelluride)rhodium (III) (0.65 gm, 1 mM) in absolute alcohol (25 ml) was heated and stirred while sodium borohydride in absolute alcohol was added slowly. Then excess benzylbromide was added slowly to the reaction mixture. The solution was refluxed for 1 hour after which a dark brown solid was filtered off. This dark brown solid was similar to the one formed from the attempted reaction to stabilise rhodium(I) complex with diphenyltelluride. The dark brown product was not characterised further.

The variation in the condition of the reaction by adding excess Ph_2Te to the above reaction mixture before starting to reflux the solid recovered from the reaction mixture after refluxing 1 hour has the same i.r. spectrum as the starting material $[Rh(Ph_2Te)(2,2'bipy)Cl_3]$

(2) Reaction of $Rh(bipy)(Ph_2Te)Cl_3$ with triphenylphosphine and benzylbromide in the presence of borohydride

The reaction was carried out the same as in the case of f(1) by using triphenylphosphine instead of Ph_2Te, a yellow solid was obtained which was checked by mass-spectrometry and i.r. to contain triphenylphosphine. This reaction was repeated many times, the product was not reproducible; sometimes a dark brown solid was obtained and in the case of the yellow product, only a sufficient solid for i.r. study was obtained, the complex was not investigated further due to the unreproducibility of the reaction.

(g) Ionic complex of rhodium(III)chloride

Dichloromono(2,2'bipyridyl)bis(triphenylphosphine)rhodium(III) chloride dihydrate

Trichloromono(2,2'bipyridyl)mono(diphenyltelluride)rhodium(III) (0.32 gm,0.5 mM) in nitrogen saturated absolute alcohol (30 ml) was mixed with triphenylphosphine (0.26 gm, 1 mM) in nitrogen saturated absolute alcohol (25 ml), the resulting solution was refluxed for 2 hours, it was observed that the starting complex Rh(bipy)(Ph_2Te)Cl_3 which was not very soluble in ethanol dissolved during reflux. The clear solution was filtered and the filtrate was evaporated to remove excess solvent. The solution was cooled in the refrigerator. The yellow solid was filtered off and washed thoroughly with ethanol and ether.

Found: C,59.5%; H,4.57%; N,3.35%

$C_{46}H_{42}Cl_3N_2O_2P_2Rh$

Requires: C,59.7%; H,4.11%; N,3.03%

(h) Preparation of rhodium(I) complex of organic telluride

Since attempts to synthesise rhodium(I) complexes or organic tellurides by using rhodium(III) as a starting compound failed, preparations using a rhodium(I) compound $Rh_2(CO)_4Cl_2$ as a starting material were attempted.

Chloromono(carbonyl)bis(diphenyltelluride)rhodium(I)

Di-μ-chlorotetracarbonyldirhodium, $Rh_2(CO)_4Cl_2$(0.38 gm, 1 mM) in nitrogen saturated ethanol (25 ml) was mixed with diphenyltelluride (1 gm 3.6 mM) in nitrogen saturated absolute alcohol(25 ml) the resulting solution was refluxed and stirred for 2 hours, the solution was left to cool down, and the orange-brown solid was filtered off under N_2 atmosphere, and washed thoroughly with ethanol and ether.

Found: C,41.5%; H,3.02%

$C_{25}H_{20}ClORhTe_2$

Requires: C,41.1%; H,2.74%

(i) Attempted experiments to use $Rh(Ph_2Te)_3Cl_3$ as a hydrogenation catalyst

(a) Identification of product

Gas-liquid chromatography (GLC) was used for identification of products obtained from the hydrogenation reaction. The G.L.C. used was of the type Pye-Unicam series 104 using a silver chloride and a silicone gum SE 30 as columns with helium as a carrier gas at a flow rate of 50 ml/min and using a Katharometer detector. The substrate and the expected product were checked that they could be separated, for example when 1-decene was used as a substrate in the hydrogenation reaction, n-decane would be the expected product, n-Decane and 1-decene were checked that they could be efficiently separated as shown in Figure 4.1.

(b) Experiment

Trichlorotris(diphenyltelluride)rhodium(III) [$Rh(Ph_2Te)_3Cl_3$] 10^{-2}M in benzene (10 ml) was stirred while 1-decene (5 ml) was added to the solution, dihydrogen gas was bubbled through the resulting solution which was stirred at room temperature for 3 hours. The final solution

(5 ml) was taken out and sent for analysis by gas liquid chromatography. It was observed that no peak corresponding to n-decane in the chromatogram was obtained.

Then the above reaction was repeated, but this time the reaction was carried out at refluxing temperature. Again no peak corresponding to n-decane in the chromatogram of the product was observed. Reactions carried out by using the gas burette(Figure. 4.2) showed no appreciable amount of change in the volume of H_2 and no peak corresponding to n-decane was observed in the G.L.C. chromatogram of the product.

For the sake of the simplicity in comparison of the chromatogram the following solutions were run at the same time with the product on the gas-liquid chromatography, (1) benzene (2) $Ph(Ph_2Te)_3Cl_3$ in benzene, (3) Ph_2Te in benzene, (4) 1-decene, (5) n-decane, (6) mixture of 1-decene and n-decane, (7) $Rh(Ph_2Te)_3Cl_3$ in benzene and 1-decene, (8) $Rh(Ph_2Te)_3Cl_3$ in benzene and 1-decene and n-decane.

When the substrate was changed from 1-decene to 1-pentene, maleic acid or varying the solvent from benzene to methylcyanide and dimethylacetamide or changing the conditions of the reaction e.g. by heating the solution. It is apparently seen that no hydrogenation occurred in the reaction which was checked by no change in the volume of H_2 in the gas burette and no G.L.C. peaks that correspond to the expected product.

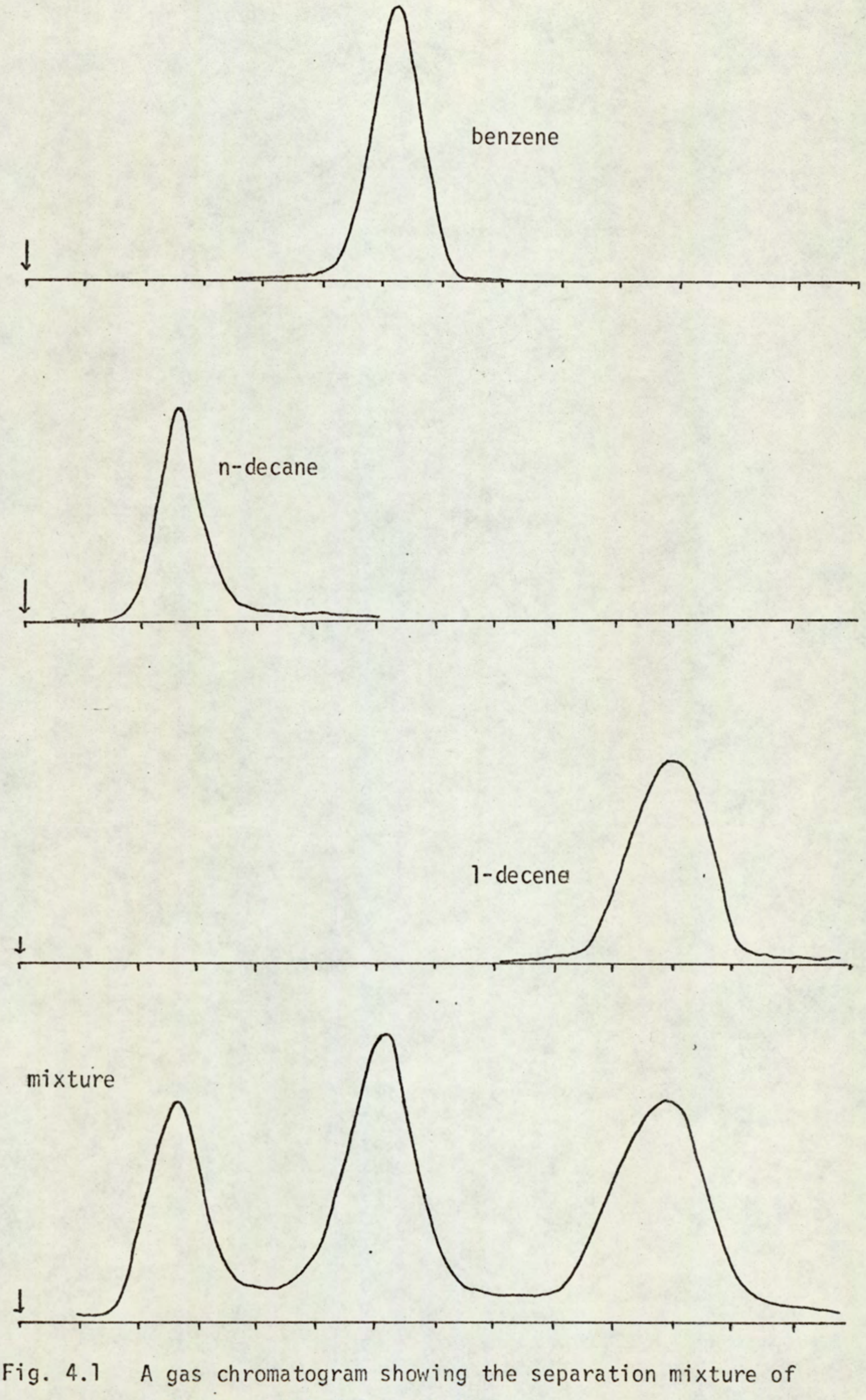


Fig. 4.1 A gas chromatogram showing the separation mixture of n-decane and 1-decene in benzene

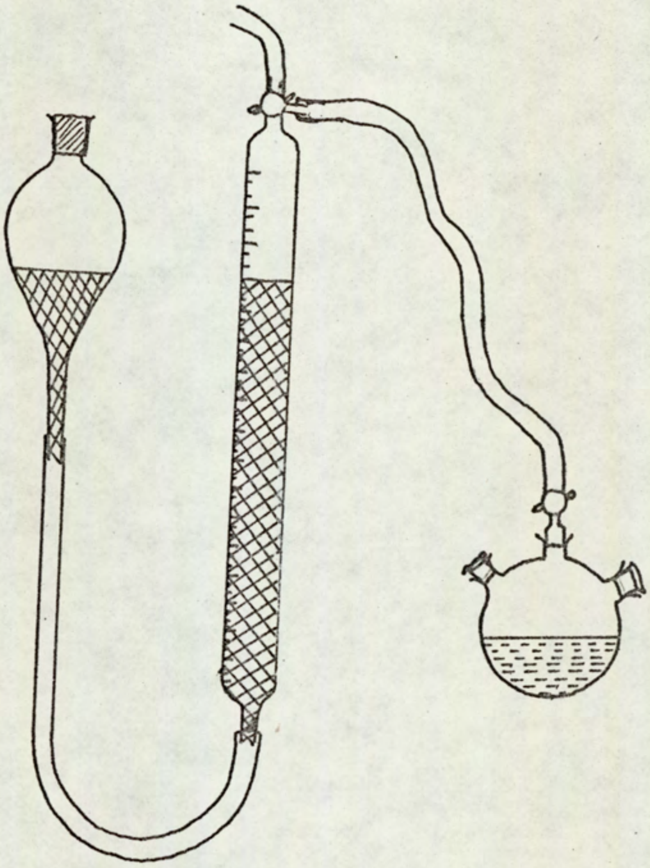


Fig. 4.2 A gas burette apparatus used for carrying out hydrogenation reactions.

(C) RESULTS

Analytical data for some telluride complexes of rhodium and iridium are presented in Table 4.1. The infra-red spectra in the region of 4000 - 400 cm^{-1} shows similar absorption patterns and therefore are not tabulated. The far infra-red spectra in the region 400 - 40 cm^{-1} of all the complexes are given in Table 4.2.

The molecular weight, conductivity and electronic spectral data are gathered in Table 4.3. The 'd' spacings of some complexes from the X-ray powder photographs are given in Table 4.4.

TABLE 4.1

Analytical data for Rhodium telluride complexes

Complexes	Found %				Required %			
	C	H	N	X(X=Cl,Br)	C	H	N	X(C=Cl,Br)
mer$[Rh(Ph_2Te)_3Cl_3]$	41.1	2.89		9.57	41.0	2.85		10.1
cis$[Rh(Ph_2Te)_3Cl_3]$	41.2	2.97			41.0	2.85		
$[Rh(Ph_2Te)_3Br_3]$	36.9	2.55		19.9	36.4	2.53		20.2
$[Rh((C_2H_5O\text{-}C_6H_4)_2Te)_3Cl_3]$	43.3	4.13			43.7	4.09		
$[Rh((CH_3C_6H_4)_2Te)_3Cl_3]$	44.7	4.02			44.3	3.69		
$[Ir(Ph_2Te)_3Cl_3]$	37.9	2.84		9.28	37.8	2.62		9.30
$[IrHCl_2(Ph_2Te)_3]$	38.6	2.82			38.9	2.70		
$[Rh(Ph_2Te)_2(CO)Cl]$	41.5	3.02			41.1	2.74		

continued...

TABLE 4.1 continued

Complexes	Found %					Required %				
	C	H	N	Cl	P	C	H	N	Cl	P
$[Rh(bipy)(Ph_2Te)Cl_3]$	41.0	2.91	4.37			40.8	2.78	4.33		
$[Rh(phen)(Ph_2Te)Cl_3]$	43.3	3.12	4.23			42.9	2.68	4.17		
$[Rh(dpm)(Ph_2Te)Cl_3]$	40.1	3.27	7.08			39.9	2.87	6.34		
$[Rh(pyCOpy)(Ph_2Te)Cl_3]$	41.4	2.94	4.02	15.3		41.0	2.66	4.15	15.7	
$Rh((C_6H_5)_3P)(Ph_2Te)Cl_2$	50.5	3.84		10.2	4.16	50.2	3.48		9.88	4.32
$Rh((C_6H_5)_3P)((C_2H_5OC_6H_4)_2Te)Cl_2$	51.4	4.25				50.7	4.10			
$[Rh(bipy)(Ph_3P)_2Cl_2]^+Cl^-\cdot 2H_2O$	59.5	4.57	3.35			59.7	4.11	3.03		

TABLE 4.2

I.R. Low-frequency vibration maxima(400-40cm^{-1}) of some Rhodium complexes

Complexes	I.R. absorption maxima (400 - 40 cm^{-1})					
mer[Rh(Ph$_2$Te)$_3$Cl$_3$]	383(s),	$\underline{333}$(vs),	$\underline{308}$(s),	$\underline{293}$(m),	289(m),	271(s)
	263(s),	246(s),	237(sh),	220(m),	216(s),	211(s)
	195(s),	180(sh),	143(m),	122(m)		
*$\underline{\text{cis}}$[Rh(Ph$_2$Te)$_3$Cl$_3$]	$\underline{342}$(vs),	$\underline{300}$(m),	$\underline{285}$(m),	273(s),	261(s),	236(w)
	224(w)					
[Rh(Ph$_2$Te)$_3$Br$_3$]	332(vw),	317(vw),	286(w,sh),	272(s)	$\underline{260}$(vs),	247(w)
	$\underline{239}$(w,m),	214(m),	207(s),	202(s),	198(s),	191(s)
	187(s),	185(s),	182(s)			
[Rh(p-C$_2$H$_5$OC$_6$H$_4$)$_2$Te)$_3$Cl$_3$]	383(s),	$\underline{338}$(s),	335(s),	330(m),	325(w),	$\underline{314}$(m)
	$\underline{288}$(s),	255(s,m),	217(s),	205(w),	201(w),	192(m)
[Rh((p-tolyl)$_2$Te)$_3$Cl$_3$]	360(vw),	$\underline{335}$(s),	$\underline{301}$(s),	$\underline{285}$(s),	255(sh)	
	242(s,br)					

continued...

TABLE 4.2 continued

Complexes	I.R. absorption maxima (400 - 40 cm^{-1})					
[Ir$(Ph_2Te)_3Cl_3$]	$\underline{320}$(vs),	315(s),	311(s),	$\underline{306}$(vs),	303(s),	273(s),	270(s)
	263(s),	259(sh),	249(m,s),	244(m),	234(m),	230(vw),	225(w)
	216(vw),	208(m),	200(vw),	183(sh),	178(m),	167(m),	153(vw)
	148(vw),	142(w),	107(m),	97(sh),	88(w)		
* [IrH$Cl_2(Ph_2Te)_3Cl_3$]	$\underline{309}$(vs),	259(vs),	242(s),	224(w),	206(w)		
[Rh(bipy)$(Ph_2Te)Cl_3$]	376(w),	$\underline{340}$(vs),	329(s),	$\underline{301}$(vs),	274(vs),	260(s),	253(sh)
	236(vs)						
[Rh(phen)$(Ph_2Te)Cl_3$]	384(s),	$\underline{346}$(vs),	$\underline{331}$(s,vs),	$\underline{310}$,308(vs),	289(sh),	297(vs),	294(sh)
	279(s),	264(s),	258(s),	249(s,vs),	240(s),	219(m),	181(m)
	161(m),	142(w)					
[Rh(dpm)$(Ph_2Te)Cl_3$]	381(s),	$\underline{332}$(s),	$\underline{304}$(m),	287(m),	281(w),	273(m,w)	
	261(m),	246(s),	180(br,m),	157(br,m)			

TABLE 4.2 continued

Complexes	I.R.absorption maxima (400 - 40 cm^{-1})
[Rh(pyCOpy)(Ph_2Te)Cl_3]	372(sh), $\underline{350}$(s), $\underline{328}$(s), 320(sh), $\underline{300}$(m), 274(m)
	261(s), 246(s), 226(s), 210(m) 196(s) 193(s)
	182(w), 169(m), 149(m), 142(m), 122(m).
Rh(Ph_3P)(Ph_2Te)Cl_2	382(s), $\underline{342}$(m), $\underline{303}$(br,m) 287(w), 268(m), 260(m,s)
	232(m), 194(br,m), 146(w)
*Rh(Ph_3P)((p-OC_2H_5)$_2$Te)Cl_2	380(s,m), $\underline{337}$(s), $\underline{300}$(br,m), 295(sh), 252(w,m) 230(br,w)
[Rh(bipy)(Ph_3P)$_2$$Cl_2$]$^+$$Cl^-$.2$H_2$O	383(s), 380(s), 377(s), 372(s), $\underline{349}$(s), 343(s), $\underline{337}$(s), 283(m), 275(s)
	262(w), 257(s), 234(m), 227(w), 225(m), 211(w,m), 207(m)
	189(w), 177(s)
[Rh(CO)(Ph_2Te)$_2$Cl]	$\underline{309}$(s,split), 274(s), 272(s), 260(vs), 251(w), 248(w), 231(m)
	215(w), 213(m), 198(m), 194(m), 186(m), 176(m), 145(br,w,m)
	110(w)

* 400 cm^{-1} - 200 cm^{-1} only

TABLE 4.3

Molecular weight, Conductivity and Electronic spectral Data of some Rhodium Telluride Complexes

Complexes	Molecular Weight		Molar Conductivity	Electronic spectra (kK)				
	Cal.	Found	(10^{-3}M)	Intra-ligand	Charge transfer	$^1A_1 \rightarrow {}^1T_2$	$^1A_1 \rightarrow {}^1T_1$	$^1A_1 \rightarrow {}^3T_1$
mer[Rh($Ph_2Te)_3Cl_3$]	1054	1050	3*	42.5	38.0, 29.5	24.5	20(sh)	
fac[Rh($Ph_2Te)_3Cl_3$]	1054	1010			36.0, 30.0	24.0		
[Rh($Ph_2Te)_3Br_3$]			10*	43.0	37.0, 27.5	23.2	19.5(sh)	
[Rh((p-$C_2H_5OC_6H_4)_2Te)_3Cl_3$]	1321	1318	5*	43.0	37.0, 29.0	23.5		
[Rh((p-$CH_3C_6H_4)_2Te)_3Cl_3$]			8*	40.0	35.6, 29.2	24.8		
[Ir($Ph_2Te)_3Cl_3$]			15*		39.5	30.5		
[IrH$Cl_2(Ph_2Te)_3Cl_3$]			6†	43.7	37.3	30.0		
[Rh($Ph_2Te)_2$(CO)Cl]			8+		34.8,31.5,27.0			
[Rh(bipy)($Ph_2Te)Cl_3$]			7+	43.5	37.1,30.7	23.8		
[Rh(phen)($Ph_2Te)Cl_3$]			30†	43.0	37.0,28.7	23.6		
[Rh(dpm)($Ph_2Te)Cl_3$]			12†	43.7	38.0,29.3	24.6		
[Rh(pyCOpy)($Ph_2Te)Cl_3$]			11+		29.6	23.1		

continued...

TABLE 4.3 continued-

Complexes	Molar conductivites (10^{-3} M)	Electronic spectra (kK)				
		Intra-ligand	Charge transfer	$^1A_1 \rightarrow {}^1T_2$	$^1A_1 \rightarrow {}^1T_1$	$^1A_1 \rightarrow {}^3T_1$
$Rh(Ph_3P)(Ph_2Te)Cl_2$	7*	43.2	30	25.0		
$Rh(Ph_3P)(p\text{-}C_2H_5OC_6H_4)_2TeCl_2$	12*					
$[Rh(bipy)(Ph_3P)_2Cl_2]^+Cl^-.2H_2O$	70+	45	40	30.2		

N.B. * Measured in methyl cyanide

\+ Measured in nitromethane

† Measured in DMF

TABLE 4.4

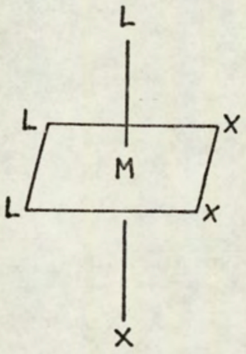
X-ray "d" Values of Some Telluride Complexes of Rhodium and Iridium

mer$[Rh(Ph_2Te)_3Cl_3]$	cis$[Rh(Ph_2Te)_3Cl_3]$	$[Rh(Ph_2Te)_3Br_3]$
8.2(s), 5.0(s)	3.80(s), 3.70(s)	12.0(s), 10.0(s)
4.3(m), 3.45(w)	3.60(s), 3.31(w)	8.55(s), 7.6(s)
3.2(w), 2.9(w)	3.10(w), 2.60(s)	5.9(w), 5.1(w)
2.8(w), 2.7(w)	2.17(m), 1.9(w)	4.7(w), 4.1(w)
2.4(w), 2.2(w)	1.87(w), 1.82(s)	3.4(w), 3.1(w)
1.82(w)	1.71(w), 1.69(m)	2.9(w), 2.5(w)
	1.64(s)	2.4(w), 2.2(w)
		1.8(w)
$[Rh(p\text{-}CH_3C_6H_4)_2Te)_3Cl_3]$	$[Rh((p\text{-}EtO.C_6H_4)_2Te)_3Cl_3]$	$[Ir(Ph_2Te)_3Cl_3]$
6.85(s), 6.0(w)	14.5(s), 13.0(s)	14.0(s), 12.5(s)
5.5(w), 4.8(m)	8.25(s), 6.5(s)	8.0(m), 6.75(s)
4.2(m), 4.1(m)	5.4(w), 4.4(w)	5.8(s), 5.25(m)
3.9(m), 3.3(w)	3.7(m), 3.2(m)	4.3(m), 4.1(w)
3.1(w), 2.5(w)	2.9(m), 2.6(w)	3.7(m), 3.45(w)
	2.5(w),	2.9(m), 2.79(m)
		2.64(m), 2.32(m)
		2.27(m)

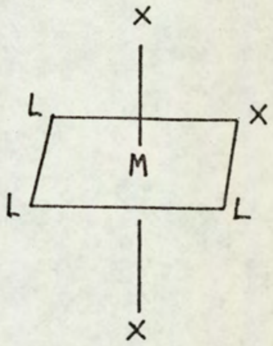
(D) DISCUSSION

(a) Rhodium(III) complexes of diaryltelluride

Reactions of diphenyltelluride with rhodium trichloride hydrated ($RhCl_3 \cdot xH_2O$) were carried out under two sets of conditions; one in air and the other under dinitrogen. It was found that both reactions yielded complexes with the empirical formula $Rh(Ph_2Te)_3Cl_3$ which were confirmed by analysis, conductivity measurement (non-electrolytes) and molecular weight determination in benzene. Rhodium(III) and iridium(III) are known to form a number of octahedral non-ionic complexes of the type MX_3L_3 where X is an anionic ligand and L is a mono-dentate tertiary phosphine or arsine(95-99) pyridine(105) or alkyl sulphide(28,32).



(a) fac = facial configuration

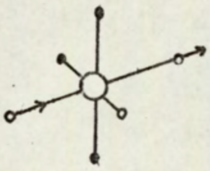


(b) mer = meridianal configuration

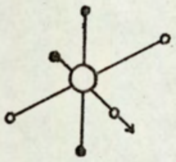
The configurations of the complexes ML_3X_3 have been assigned on the basis of dipole moment determination(95,100) far-i.r.spectra(96-98) and in some cases with a suitable choice of ligand, ^1H and ^{31}P n.m.r. spectroscopy(97,101). In this work the assignment of the configuration will be based on the evidence of i.r. and n.m.r. spectroscopy.

Some considerations on the application of these techniques to aid in the assignment will be appropriate. Low-frequency i.r. spectroscopy is one of the methods of distinguishing between mer and fac isomers for the complexes of the type MX_3L_3. The fac isomer which has C_{3v} symmetry is expected to have two i.r. active modes involving rhodium-chlorine stretching vibrations ($A_1 + E$) whereas for the mer (C_{2v} symmetry) is expected to have three ν(Rh-Cl) stretching vibrations in the i.r. ($2A_1 + B_1$). The form of these are presented below.

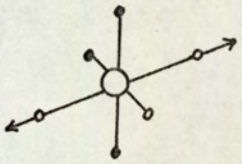
mer isomer



$\nu(M - X_3)B_1$

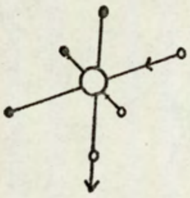


$\nu(M - X_3)A(1)$

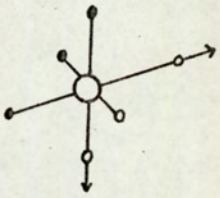


$\nu(M-X_3)A_1(2)$

fac-isomer



$\nu(M - X_3)E$



$\nu(M - X_3)A_1$

Generally for the isomers of rhodium complexes the number of bands assignable to ν(Rh-Cl) conform to the prediction, but in the iridium cases only two bands were observed for mer isomers and this was explained as being due to a low transition moment associated with the $A_1(2)$ vibration i.e. it might be due to the trans chlorine being collinear with the result that the symmetric stretching vibration causes hardly any change of dipole moment and hardly any absorption(98). The above explanation for the unobserved $A_1(2)$ vibration in iridium complexes was not favoured by Chatt et al.(102) who measured the Raman spectrum of mer $[IrCl_3(PEt_3)_3]$ which is almost identical to its i.r. spectrum. Accidental degeneracy of the two normal modes seemed to be more likely. It is seen that far i.r. spectroscopy is often not able to distinguish between the fac and mer isomers on the number of i.r. bands corresponding to metal-halogen stretching vibrations. For the iridium complexes of tertiary phosphines and arsines, it has been observed that mer isomers absorb at about 20 - 30 cm^{-1} higher frequency than fac isomers(102).

^1H n.m.r. should provide an unambiguous method for the assignment of the configuration of the complexes of the type MX_3L_3; (M = Rh, Ir, X = halogen, L = dialkylsulphide or substituted tertiaryphosphine, e.g. dimethylphenylphosphine). For example in the dialkylsulphide case, the fac isomer has all three equivalent dialkylsulphide groups whereas the mer contains dialkylsulphide molecules in two different environments, two equivalent dialkylsulphide molecules which are trans to each other and the one which is trans to chlorine. The complexes $M(Me_2S)_3X_3$; (M = Rh, Ir; X = halogen) have been shown to give two distinct peaks with intensity ratio 2:1 which is consistent with the mer configuration(28). Another example showing the applicability of the n.m.r. technique to differentiate between fac and mer isomers of the complex of the type ML_3X_3 (M = Rh, Ir; L = dimethylphenylphosphine, X = halogen), the methyl resonance of two dimethylphenylphosphine ligands in the mutual trans positions is usually 1:2:1 triplet which might be due to the virtual coupling of trans phosphines (97,104) i.e. the phosphorous atoms of trans phosphines couple with the α hydrogens with equal strength, thus an α hydrogen is split into a triplet rather than the expected doublet. For two phosphines in mutually cis positions a 1:1 doublet is obtained. It is observed that the methyl resonance of the compound mer-trichlorotris (dimethylphenylphosphine) iridium(III) or the analogous rhodium(III) consists of a 1:2:1 triplet of total relative intensity two and a 1:1 doublet of total relatively intensity one.

The complexes $Rh(Ph_2Te)_3Cl_3$ were prepared under two different conditions, the one prepared under dinitrogen gave a comparatively higher yield and was used for further investigations, this compound will be discussed first. The conductivity measurement showed that the complex is a non-electrolyte in methylcyanide. The molecular weight measurement in benzene indicated that the complex is a monomer conforming to the formula $Rh(Ph_2Te)_3Cl_3$ which is also supported by the analysis. The far infrared spectra of the compound could provide some information about the configuration. The corresponding bromide complex prepared by metathetical reaction using NaBr has the similar formula $Rh(Ph_2Te)_3Br_3$ and this will be helpful for comparison of the rhodium-halogen stretching vibrations. The complex $Rh(Ph_2Te)_3Br_3$ is also a non-electrolyte in methylcyanide and has similar electronic spectra (diffuse reflectance) and X-ray powder patterns to the complex $Rh(Ph_2Te)_3Cl_3$. This makes the comparison in the i.r. low frequency vibration useful. Two strong bands at 333 cm^{-1} and 308 cm^{-1} and another weak to medium band at 293 cm^{-1} could possibly be assigned as ν(Rh-Cl) stretching vibrations. The band at 333 cm^{-1} can be assigned as the antisymmetric B_1 of two trans chlorine atoms from the intensity of the band, the weak band at 293 cm^{-1} is very likely to be symmetric $A_1(2)$ vibration of the mutually trans chlorine atoms, since this vibration will produce only a small dipole moment hence a small absorption. The strong band at 308 cm^{-1} will be assigned as ν(Rh-Cl) stretching vibration $A_1(1)$ involving the chlorine trans to the telluride. The comparison with the dialkylsulphide complexes of the type $Rh(R_2S)_3Cl_3$ show a similar pattern, i.e.there are two bands about 350 cm^{-1} to 325 cm^{-1} and another one at 300 cm^{-1} assignable to ν(Rh-Cl)(28). The only difference is their assignment of the bands at 325 cm^{-1} to $A_1(2)$ and the one at 300 cm^{-1} to $A_1(2)$ modes. The metal-chlorine stretching vibration frequencies are known to depend markedly on the ligand trans to chlorine atom in the complexes(96). In the complex mer $[RhCl_3(PEt_3)_3]$ there are three bands at 323, 288, 256 cm^{-1} assignable to ν(Rh-Cl), the lowest frequency is assigned to motion involving chlorine atom trans to tertiary phosphine. This trans effect of ligand trans to chlorine atom in lowering the ν(M-Cl) was also observed by Jenkins and Shaw(98). They explained the weakening of bond to be caused by an inductive electron release mechanism by the weakly electronegative ligands e.g. hydride, phosphine. The trans effect of the telluride trans to chlorine in the complex $Rh(Ph_2Te)_3Cl_3$ and sulphide trans to chlorine in the complex $Rh(R_2S)_3Cl_3$ seemed to be small in comparison with the phosphine complex, a fact which is indicated in the higher frequency of the bands assigned as ν(Rh-Cl) (A_1(1) trans telluride or sulphide) than in the phosphine complexes. The comparison of the frequencies of the bands assigned as ν(Rh-Cl) in the telluride and sulphide complexes of the same type showed that the latter has slightly higher frequencies, this might indicate the better Π-acceptor properties of the telluride. The disappearance of the strong bands assigned as ν(Rh-Cl) in the complex $Rh(Ph_2Te)_3Br_3$ also confirmed the assignment of ν(Rh-Cl) stretching vibrations. Taking into consideration the useful formula $\nu(RhCl) \times 0.76 \approx \nu(RhBr)$, the bands expected to be ν(RhBr) stretching vibrations would be around 250, 236 and 222 cm^{-1}. The band at 260 cm^{-1} will be tentatively assigned as ν(Rh-Br) with the enhancement of coupling of ν(Te - Ph) stretching vibration which occurred around this number. The weak band at 239 cm^{-1} might be another ν(Rh-Br) that could be observed. The strong band located at 245 cm^{-1} present in $Rh(Ph_2Te)_3Cl_3$ could possibly be either the bending mode of the rhodium chlorine vibration , δ(Rh-Cl),or ligand mode of enhanced intensity, in the bromide case a very weak band at 245 cm^{-1} was also observed. Taking this formula $\delta(Rh\text{-}Cl) \times 0.76 = \delta(Rh\text{-}Br)$ it is found that the band at 182 cm^{-1} was observed in $Rh(Ph_2Te)_3Br_3$ but not in the chloride, so this might be δ(Rh-Br) bending vibration. From the evidence of the i.r. alone it is suggested that the complex $Rh(Ph_2Te)_3Cl_3$ prepared under dinitrogen might have the mer configuration.

The complex of rhodium trichloride with another telluride was also prepared namely trichlorotris(di-p-ethoxyphenyltelluride)rhodium(III), $[Rh((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_3Cl_3]$. The conductivity measurement in acetonitrile and molecular weight measurement in benzene indicated the complex to be a non-electrolyte and to be monomeric. Since di-p-ethoxyphenyltelluride also absorbs strongly in the region to be expected for ν(Rh-Cl) stretching vibrations (di-p-ethoxyphenyltelluride have bands at 335 cm^{-1} and 300 cm^{-1}), the assignment of ν(Rh-Cl) stretching vibration seemed to be a bit difficult. The band at 338 cm^{-1} seemed to be composite (not symmetric as in the ligand) so it was assigned as the B_1 ν(Rh-Cl) stretching vibration plus a ligand mode. The medium band at 314 and 288 cm^{-1} were assigned as $A_1(2)$ and $A_1(1)$ rhodium-chlorine stretching vibrations respectively. Also in the complex $Rh((p\text{-}tolyl)_2Te)Cl_3$ three bands assignable to ν(Rh-Cl) stretching vibrations were observed at 335 cm^{-1}, 301 cm^{-1} and 285 cm^{-1}. It was observed that the position of the band assignable as ν(Rh-Cl) in all complexes considered seemed to be insensitive to the nature of diaryltelluride.

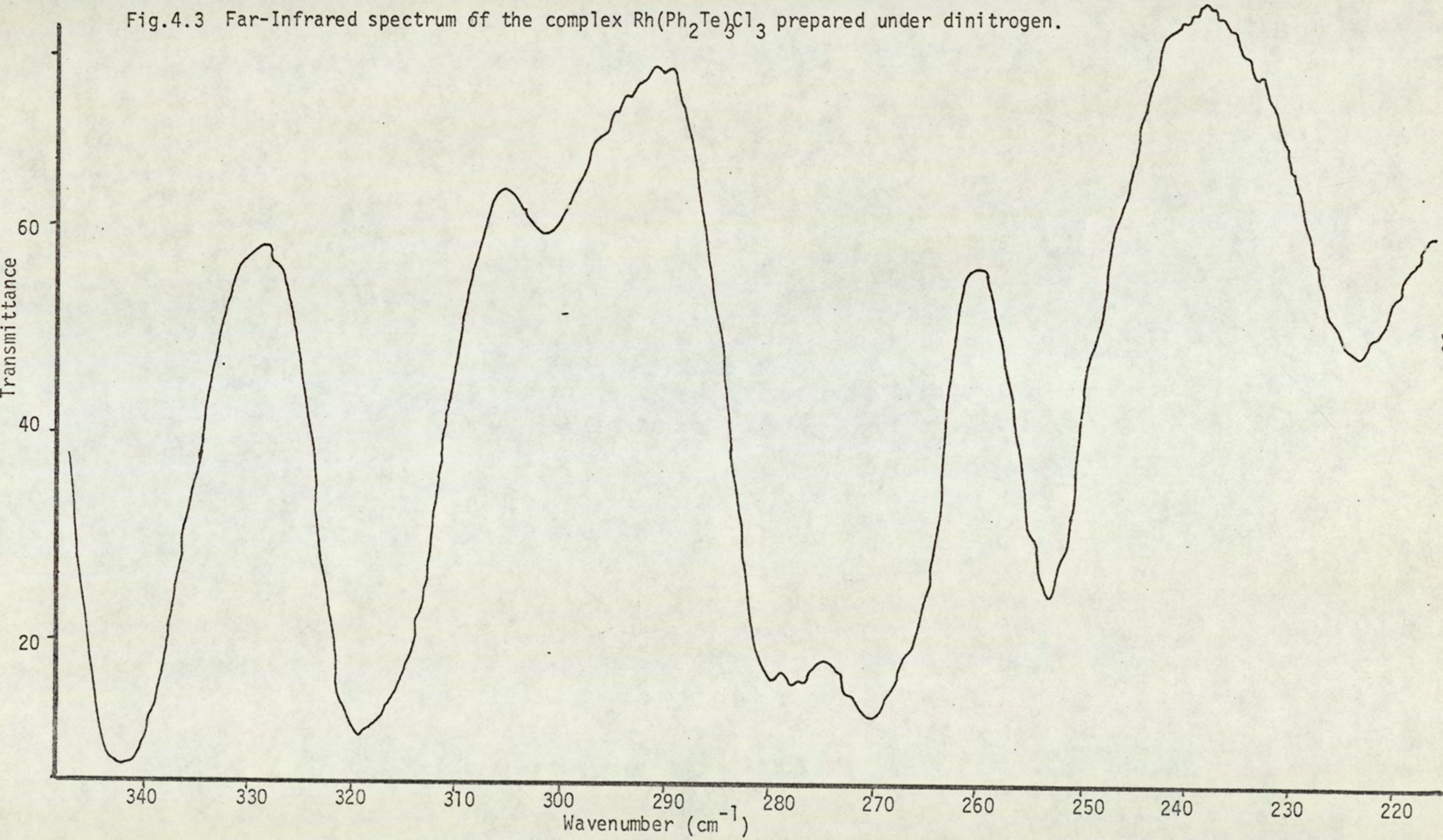
Another physical method that has been used to help in assigning the configuration of this octahedral rhodium telluride complex is ^1H n.m.r. The n.m.r. spectrum of the complex as shown in Figure 4.5 showed that the resonances centred around τ 2.56 and τ 3.30 could be analysed in terms of equivalent mutually trans-telluride groups and a further contribution from the other telluride trans- to chloride, the intensity ratio of the two sets of signals being 2:1. For the sake of comparison the n.m.r. spectrum of p-ethoxyphenyltelluride is also included in Figure 4.6. A closer look at the resonances due to methyl protons in the complex at around τ 8.62 showed that there is some complexity in the peaks. This would imply that ligands might be located in different environments. Another thing that could explain the complexity of the peaks is the coupling with $^{103}Rh(I=\frac{1}{2})$ nucleus, but this seemed to be unlikely since the p-ethoxy group is situated quite far apart from the rhodium nucleus. From the consideration of n.m.r. data it is probable that the complex $[Rh((p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)_3Cl_3]$ has a mer configuration, since $Rh(Ph_2Te)_3Cl_3$ was also prepared by the same method and both complexes have many similar properties e.g. monomeric, non-conducting, also similar in i.r. spectra and electronic spectra and X-ray powder pattern. $Rh(Ph_2Te)_3Cl_3$ is also assigned to have the mer configuration.

The electronic spectra of the complexes were measured. It is observed that the spectra changed only slightly with the change of telluride ligand, this suggests that the complexes have a common configuration. The electronic spectra of the rhodium complexes (Table 4.3) consist of three bands in the U.V. region which were considered to be charge transfer bands and intraligand transition, the bands at about 24.5 kK and 20 kK in $Rh(Ph_2Te)_3Cl_3$ move to about 23.2 kK and 19.5 kK in $Rh(Ph_2Te)_3Br_3$ and these will be tentatively assigned as $^1A_1 \longrightarrow {}^1T_2$ and $^1A_1 \longrightarrow {}^1T_1$ transitions respectively. The electronic spectra of dialkylsulphide of rhodium complexes have been given(28,32) and the pattern seems to be similar to the telluride complexes of rhodium described above.

It was mentioned earlier in the discussion that the reaction carried out under air between rhodium trichloride and diphenyltelluride seemed to give different products from the one carried out under di-nitrogen. The X-ray powder photographs of the two products are different, also the far and near infra-red spectra of the two complexes showed distinct differences. The analysis, conductivity and molecular weight measurementsconform to the formula $Rh(Ph_2Te)_3Cl_3$ the same as the one under N_2 discussed above. Another point that is worth mentioning is the very similar electronic spectra of the two products $[Rh(Ph_2Te)_3Cl_3]$ (air), $[Rh(Ph_2Te)_3Cl_3]$(dinitrogen). This suggested that the compound prepared under N_2 either might be the same or have changed into the compound prepared under air. When the complex mer $Rh(Ph_2Te)Cl_3$ (prepared under N_2) was recrystallised in ethanol or reprecipitated by dissolving the compound in the minimum amount of benzene and adding n-hexane to get the precipitate, the compound obtained after recrystallisation or reprecipitation gave a different far-i.r.spectrum from the one before recrystallisation and now seemed to be a mixture of the complexes prepared under N_2 and air. This suggests that there might be some change in the configuration of the complex $Rh(Ph_2Te)_3Cl_3$ when it goes into solution.

The complex $Rh(Ph_2Te)_3Cl_3$ (air) has the far infra-red spectrum (400 - 200 cm^{-1}) different from the one prepared under N_2, the band at 333 cm^{-1} assigned as B_1 ν(Rh-Cl) in mer $Rh(Ph_2Te)_3Cl_3$ seemed to move up to 342 cm^{-1}, the band at 308 cm^{-1} $A_1(1)$ seemed to disappear and the band at 293 cm^{-1} $A_1(2)$ seemed to move up to 300 cm^{-1}, the band at 285 cm^{-1} probably occurred from the splitting of the E mode because of the lower site symmetry in the crystal (E ⟶ 2 bands). It is seen that the assignment of the configuration on i.r. basis alone sometimes is not conclusive. Since the complex $Rh(Ph_2Te)_3Cl_3$, prepared under air (and is considered to be fac) does not give a good yield, it was not

Fig.4.3 Far-Infrared spectrum of the complex $Rh(Ph_2Te)_3Cl_3$ prepared under dinitrogen.



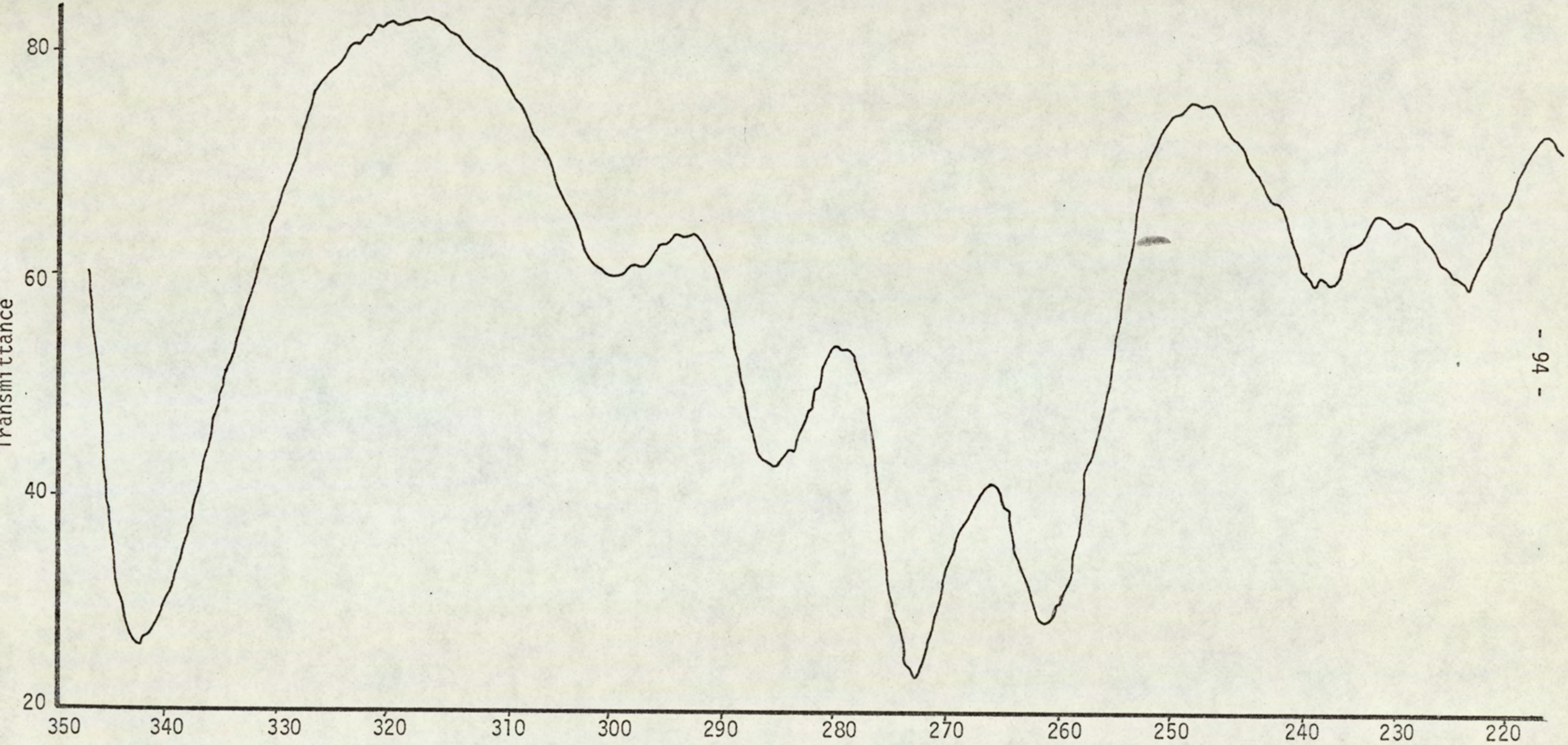


Fig.4.4 Far-Infrared spectrum of the complex $Rh(Ph_2Te)_3Cl_3$ prepared under air.

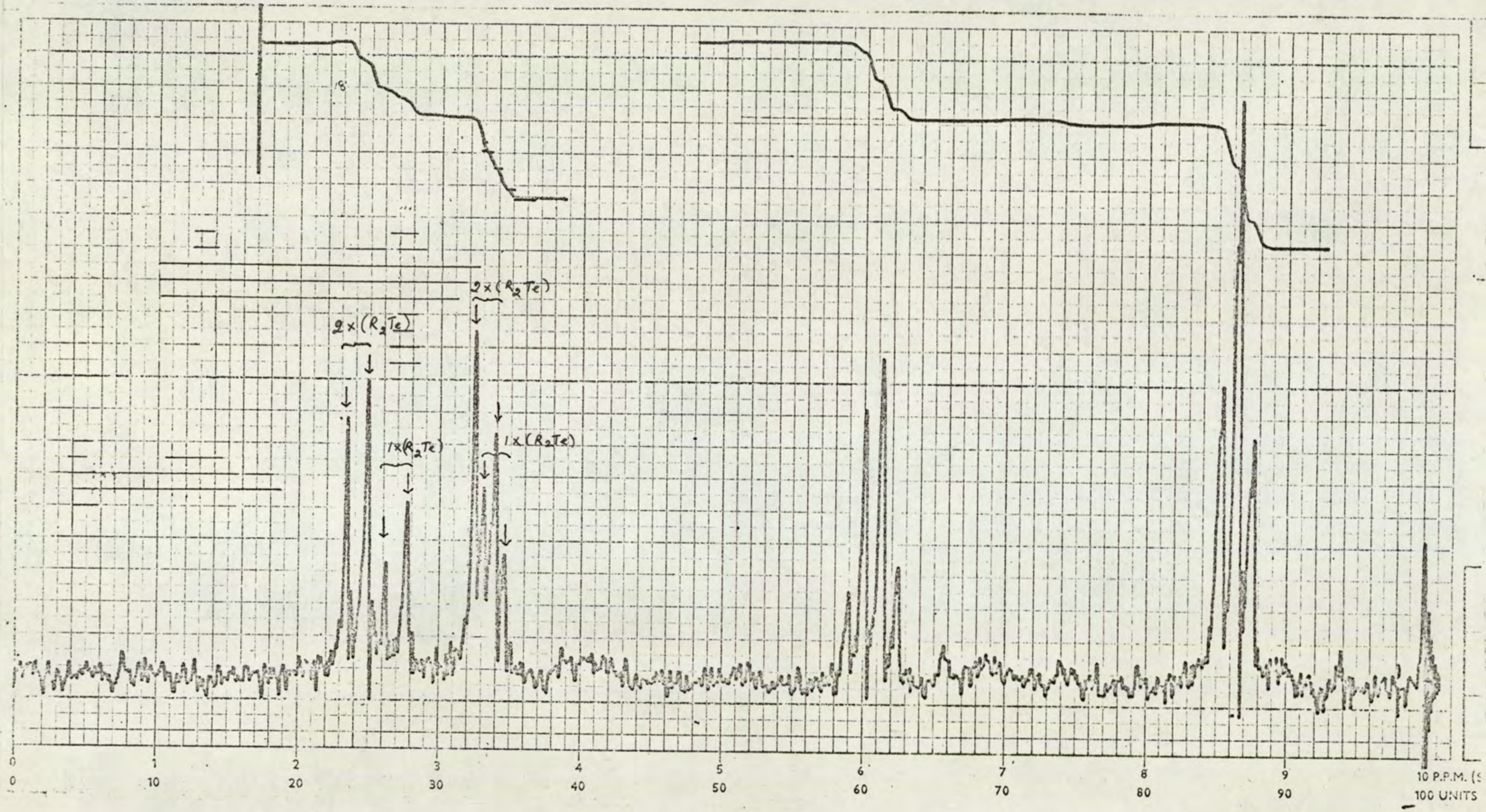


Fig. 4.5 'H n.m.r. spectrum of complex $[Rh((p\text{-}EtO\text{-}C_6H_4)_2Te)_3Cl_3]$

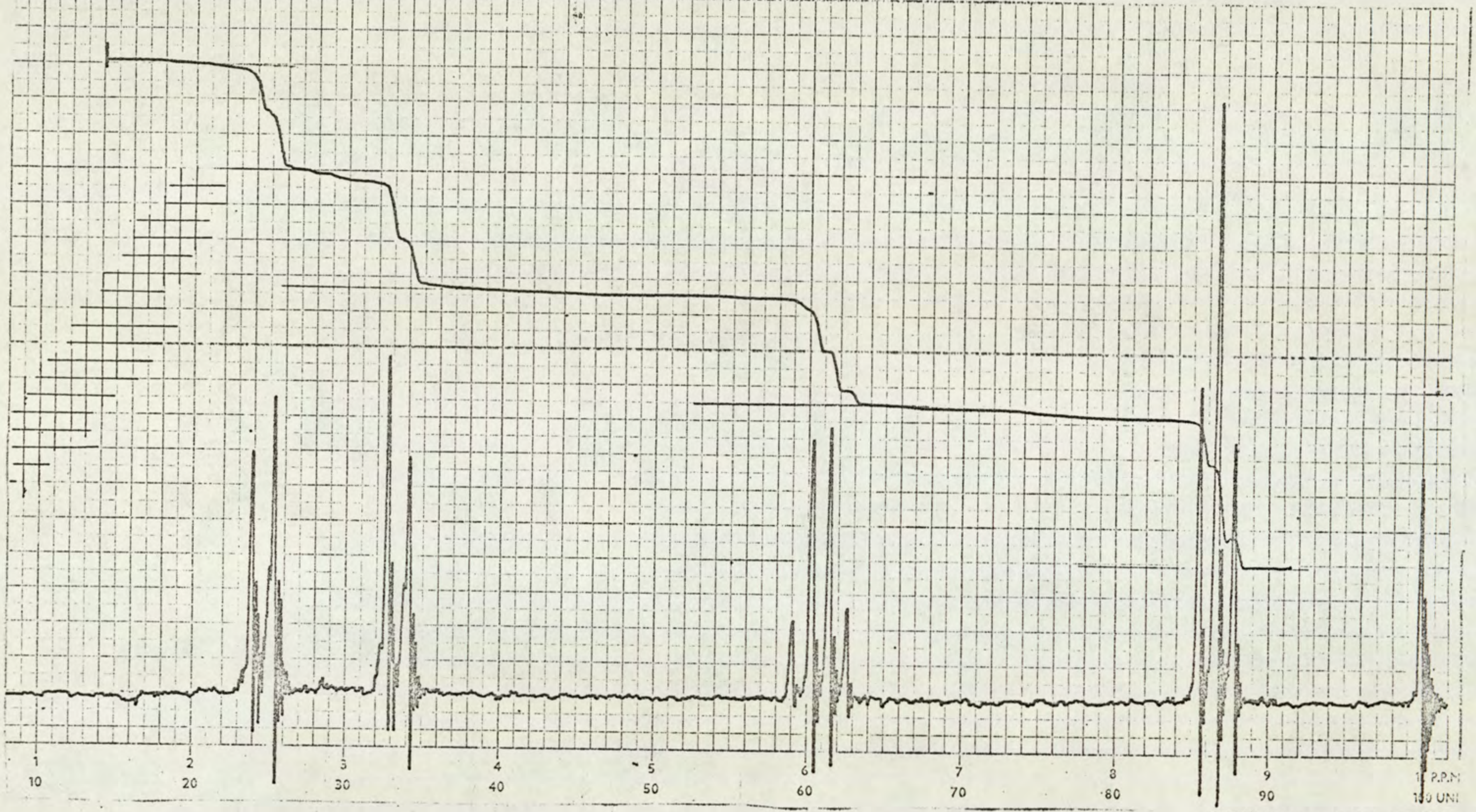


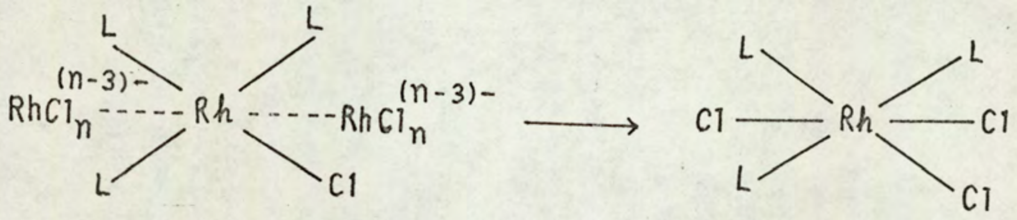
Fig. 4.6 'H n.m.r. spectrum of di-p-ethoxyphenyltelluride, $(p\text{-}C_2H_5O\text{-}C_6H_4)_2Te$

considered as a synthetic intermediate in the preparations of other complexes and in investigations of potential catalytic properties, instead the complex mer $Rh(Ph_2Te)_3Cl_3$,prepared under N_2,was used for the subsequent reactions.

The suggested explanation for the formation of mer $Rh(Ph_2Te)_3Cl_3$ in the case when dioxygen was excluded could be written as follows when a rhodium(I) intermediate is postulated

$$RhCl_3 + R_2Te \xrightarrow{N_2} RhCl + R_2TeCl_2$$

$$RhCl + 3L;(L{=}R_2Te) \longrightarrow RhL_3Cl$$



mer

In the case of preparing the compound under air only simple substitution reaction of rhodium chloride and diphenyltelluride occurred forming octahedral fac $Rh(Ph_2Te)_3Cl_3$, this explanation is only tentative.

(b) Rhodium(I) complex of diphenyltelluride

To support the point that rhodium(I) with a telluride ligand might exist, a complex of rhodium(I) with diphenyltelluride was synthesised. The complex with the formulation $[Rh(CO)(Ph_2Te)_2Cl]$ was obtained from the reaction of $[Rh_2(CO)_4Cl_2]$ with excess diphenyltelluride. The reaction seems to be similar to the well known reaction of rhodium carbonyl with triarylphosphine, triarylarsine and triarylstibine,when the bridged structure of the starting rhodium(I) compound was broken(106).

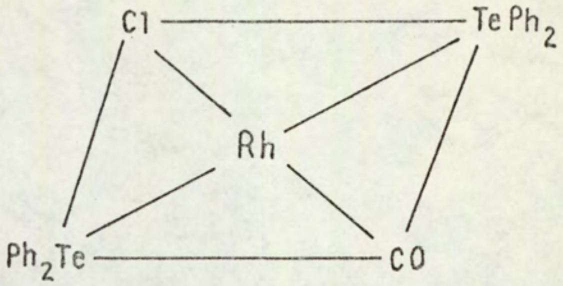
$$[Rh_2(CO)_4Cl_2] + 4L \longrightarrow 2[RhL_2(CO)Cl] + 2CO$$

$$(L = Ar_3P,\ Ar_3As \text{ or } Ar_3Sb)$$

The complex $Rh(Ph_2Te)_2(CO)Cl$ was found to be non-electrolyte. The far infra-red spectrum indicated that the complex might has a trans square planar structure (C_{2v} symmetry) with the band at 309 cm^{-1} assigned as ν(Rh-Cl) stretching vibration. The far i.r. spectra of the rhodium(I) tertiary phosphine or arsine of the type trans $[Rh(CO)L_2Cl]$ show a medium to strong band due to ν(Rh-Cl) stretching vibration in the range 295 - 311 cm^{-1} the position of the band varies very little with the nature of donor ligand (P or As) or with the substituents (ethyl or phenyl) in the ligand$^{(96)}$.

An X-ray study of the complex $[RhCl(CO)(P(C_6H_5)_3)_2]^{(107)}$ along with the low dipole moment (3.15 D)$^{(106)}$ proved that the compound has trans configuration.

The i.r. spectrum obtained from the interferrometer (400-40 cm^{-1}) showed that the band at 309 cm^{-1} assigned as ν(Rh-Cl) stretching vibration seemed to split (Ca. 5 cm^{-1} to low frequency). This extra band might be due to $\nu(Rh-{}^{37}Cl)$ stretching vibration with the main band associated with $\nu(Rh - {}^{35}Cl)$ stretching vibration. This splitting and assignment of the extra band were also observed in the rhodium(I) phosphine and arsine of the type $[Rh(CO)(L)_2Cl]$ studied by Bennett, Clark and Milner$^{(96)}$.



The carbonyl stretching vibration in the complex [Rh$(Ph_2Te)_2$(CO)Cl] was observed at 2035 cm^{-1}, which is seen to be higher than in the phosphine complex [Rh$(PPh_3)_2$(CO)Cl] where ν(C = 0) = 1961 cm^{-1}(108). This may be explained by assuming the poorer σ donor of the telluride compared with phosphine which in turn made the basicity of the metal in telluride complex less than in phosphine complex, thus the higher ν(C=0) in telluride complex than in phosphine complex.

Also the complexes <u>trans</u> [Rh(CO)$(L)_2$Cl]; (L = S(C_2H_5), Se$(C_2H_5)_2$ and Te$(C_2H_5)_2$) reported by Faraone et al.(20) have the ν(C = 0) stretching vibration in the range 1955 - 1965 cm^{-1} and one band ν(Rh - Cl) in the range 299 - 304 cm^{-1}. The lower carbonyl stretching vibration in the aliphatic telluride complex compared with the diphenyltelluride complex could also be explained in terms of better σ donor of $(C_2H_5)_2Te$ than $(C_6H_5)_2Te$.

(c) Iridium(III) complexes of diphenyltelluride

Some reactions of iridium salt with diphenyltelluride were also carried out. It was found that when sodium chloroiridite ($Na_3IrCl_6.12H_2O$) was refluxed with diphenyltelluride in ethanol, an analogous complex of rhodium with the formulation $Ir(Ph_2Te)_3Cl_3$ was obtained.

The X-ray "d" values of this $Ir(Ph_2Te)_3Cl_3$ was found to be similar to the mer $Rh(Ph_2Te)_3Cl_3$ to suggest the similar structure. The comlexes of the type mer MX_3L_3 with C_{2v} symmetry were expected to give three i.r. bands ($2A_1 + B_1$) corresponding to metal-halogen stretching vibrations. This was found to be the case in the rhodium complexes but not in iridium when only two bands were observed. The disappearance of the third band was explained in terms of the degeneracy of two of the vibrational modes(102,103). In the $Ir(Ph_2Te)_3Cl_3$ complex two bands assignable to ν(Ir-Cl) stretching vibrations were found at 320 cm^{-1} and 306 cm^{-1} respectively. Comparison of these figures to the corresponding sulphide complexes showed that ν(Ir-Cl) stretching vibrations in the telluride complexes are slightly lower than in the sulphide complexes, but higher than the phosphine complexes $[IrCl_3(Me_2S)_3]$; ν(Ir-Cl) = 334, 321 cm^{-1}, $[IrCl_3(Et_2S)_3]$; ν(Ir-Cl) = 324, 306 cm^{-1}(28) which was also found to be the case in the rhodium complexes.

From the comparison of ν(M-Cl) in complexes of the type MX_3Cl_3; (X = telluride, sulphide and phosphine) the Π-acceptor properties of the ligands could be arranged in the following order phosphine > telluride > sulphide.

The complex $Ir(Ph_2Te)_3Cl_3$ was also found to be a non-electrolyte, the U.V. and visible spectra (Table 4.3) of the complex was also recorded, the bands above 30 kK were assigned as the charge-transfer band, and the d-d transition band was observed at 30.5 kK. The assignment was similar to the rhodium complexes above.

From the evidence that have been discussed it could be possibly concluded that the complex $Ir(Ph_2Te)_3Cl_3$ has a similar structure and configuration with mer $Rh(Ph_2Te)_3Cl_3$ that was prepared under dinitrogen; so that mer configuration was assigned to this $Ir(Ph_2Te)_3Cl_3$ complex.

Another type of complex was formed when sodium chloroiridate ($Na_2Ir\ Cl_6.6H_2O$) was refluxed for a long time (6 hours) with diphenyltelluride in ethanol. From the analysis and the band at 2080 cm^{-1} in the infra-red spectrum the complex of the formula $IrHCl_2(Ph_2Te)_3$ was proposed. It has been known that when heating iridium salt with ligands e.g. tertiary phosphine, arsines and stibines in alcohol (or aqueous alcohol) or KOH-ethanol, hydride complexes of the formulation $[IrHCl_2(Ph_3X)_3]$; (X = P, As, Sb) occur(109,110). The complexes are air-stable, diamagnetic and non-electrolyte with ν(Ir-H) stretching vibrations around 2100 - 2200 cm^{-1}.

Metal hydride complexes usually have the ν(M-H) stretching frequency in the range 1700 - 2000 cm^{-1}(111). It is known that the M-H bond is sensitive to the nature of the ligand trans to hydride, i.e. substitution in the trans position with ligands of increasing trans effect causes a decrease in the M-H stretching vibration(110). For the monohydrides $IrHX_2L_3$; (L = tertiary phosphine, tertiary arsine X = Cl) ν(Ir-H) for the H trans to phosphine or arsine (Fig. 4.7a) is about 2000 - 2100 cm^{-1} and about 2195 - 2200 cm^{-1} for the H trans to chlorine (Fig. 4.7b).

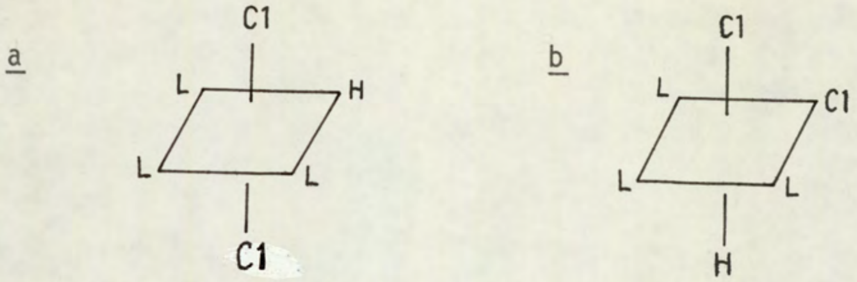


Fig.4.7 Configurations of the complexes of the type $IrHCl_2(L)_3$

The $IrHCl_2(Ph_2Te)_3$ complex has the band at 2080 cm^{-1} assigned as ν(Ir-H) stretching vibration this indicated that H is trans to telluride (Fig. 4.7a). In agreement with this the far-i.r. spectrum of the complex shows only one strong band assigned as ν(Ir-Cl) stretching vibration at 309 cm^{-1} (Cl trans to Cl). If the complex has the configuration of Fig. 4.7b two bands due to ν(Ir-Cl) stretching vibrations are expected(98). Another technique that is used to detect metal-hydride bond formation is n.m.r. The hydride resonance always occurred at very high field (τ = 15 - 40)(111, 112). No metal-hydride signal was found in this $IrHCl_2(Ph_2Te)_3$ complex; this might be due to some interaction between the complex and the solvent which led to the disappearance of the metal hydride bond.

Another possibility that the band observed at 2080 cm^{-1} in the i.r. spectrum of the complex might originate from ν(C = O) vibration should be considered, since it is known that in addition to hydride complexes, hydride-carbonyl and carbonyl complexes could also be formed in the reaction of iridium salts with tertiary phosphine or tertiary arsine in alcoholic solution depending on the conditions of the reaction. Complexes of the types $[IrCl(CO)L_2]$, $[IrHCl_2(CO)L_2]$ are known to have form from the above reactions(113). But from the analytical figures obtained it is very unlikely that carbonyl complex

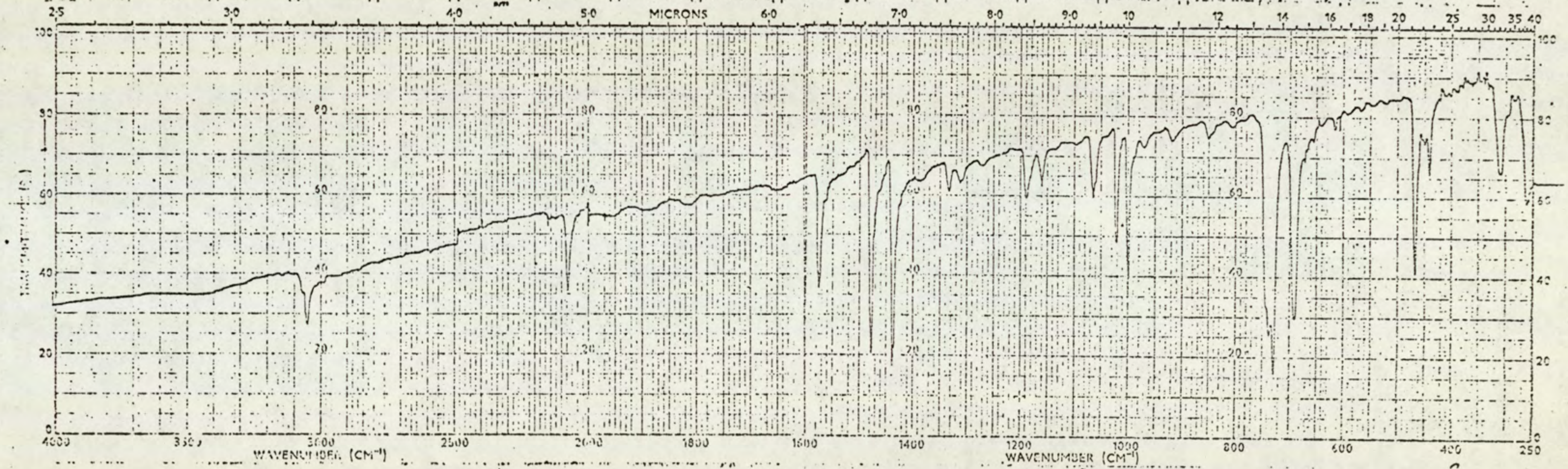


Fig. 4.8 Infrared spectrum of complex $\left[IrHCl_2(Ph_2Te)_3\right]$

was formed since this would require the loss of one diphenyltelluride group which could markedly affect the analytical figure.

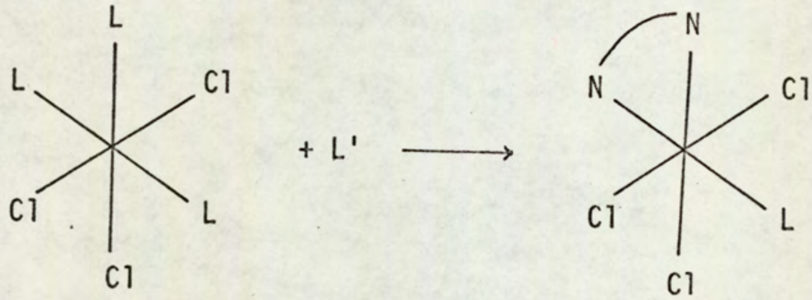
To conclude, it should be noted that hydride formation in this telluride system occurs less readily than in the phosphine or arsine complexes. The hydride formation depends markedly on the severity of the reaction i.e. refluxing the iridium salt (sodium chloroiridate) with diphenyltelluride in ethanol 3 hours or less yielded the <u>mer</u> $Ir(Ph_2Te)_3Cl_3$, it needs at least 6 hours of the refluxing time to obtain $IrHCL_2(Ph_2Te)_3$ complex.

(d) Complexes of the type $Rh(Ph_2Te)(L)Cl_3$; (L = chelate ligands)

Reactions using <u>mer</u> $Rh(Ph_2Te)_3Cl_3$ as synthetic intermediates were carried out. The benzene solutions of the complexes <u>mer</u> $Rh(Ph_2Te)_3Cl_3$ with an excess of chelates (chelate = 2,2'bipy, 1,10 phenanthroline, di-2-pyridylamine, di-2-pyridylketone) were refluxed for 2 - 3 hours to give the complexes of the type $Rh(Ph_2Te)(L)Cl_3$; (L = bidentate chelate). The formulation of the formula of the complexes obtained from the neutral ligand exchange reactions as $Rh(Ph_2Te)(L)Cl_3$ was confirmed by the evidence of the analysis i.r. and their non-conducting properties. The diffuse reflectance spectra of the four complexes $Rh(L)(Ph_2Te)Cl_3$; (L = 2,2'bipy, 1,10'-phenanthroline, di-2-pyridylamine, di-2-pyridylketone) are very similar to suggest that they all have a common structure.

As mentioned in the general introduction (Chapter One) rhodium-sulphide bonds are quite labile as indicated in the work of Dwyer and Nyholm$^{(27)}$ and in the use of such compounds as catalytic complexes, e.g. $Rh(Et_2S)_3Cl_3$ in the work of James and co-workers(29). Also the ruthenium-sulphide bond in the complexes $[RuCl_3(PhSP_r{}^n)_3]$ could be replaced in the substitution reaction with aniline and pyridine to give (36) $[RuCl_3(Ph.NH_2)_3]$ 0.5 C_6H_6 and $[RuCl_3(Py)_3]$ 0.5 C_6H_6 respectively. Another ligand exchange reaction of the complexes IrL_3Cl_3 (L = tertiary phosphine or arsine) with the ligand dimethylphenylphosphine was found to give the disubstituted complex $[IrCl_3(Ars)(PMe_2Ph)_2]$; (Ars = $AsEt_3$ or $AsEt_2Ph$) no matter how much ligand was used(114). This similar phenomenon seemed to occur in the reactions of $Rh(Ph_2Te)_3Cl_3$ with chelates where the complexes $Rh(L)(Ph_2Te)Cl_3$ were always formed irrespective of the amount of ligand used.

Considering the reaction of the mer $[RhCl_3(Ph_2Te)_3]$ with the chelate ligands, the product $Rh(L)(Ph_2Te)Cl_3$; (L = chelate ligand) formed from these reactions will have the symmetry of C_s, if no re-arrangement occurs during reaction:



(L' = 2.2'bipyridyl, 1,10 phenanthroline, di-2-pyridylamina, di-2-pyridylketone)

From the considerations of the close similar structure and the similar type of ligands in the complexes $Rh(Ph_2Te)(L\ )Cl_3$, the position of the bands assignable to ν(Rh-Cl) stretching vibrations should be quite near to each other, and this happened to be the case. The bands around 340 - 350 cm^{-1}, 320 - 330 cm^{-1} and 300 cm^{-1} appeared to be very strong in intensity will be tentatively assigned as ν(Rh-Cl) stretching vibration (Table 4.3).

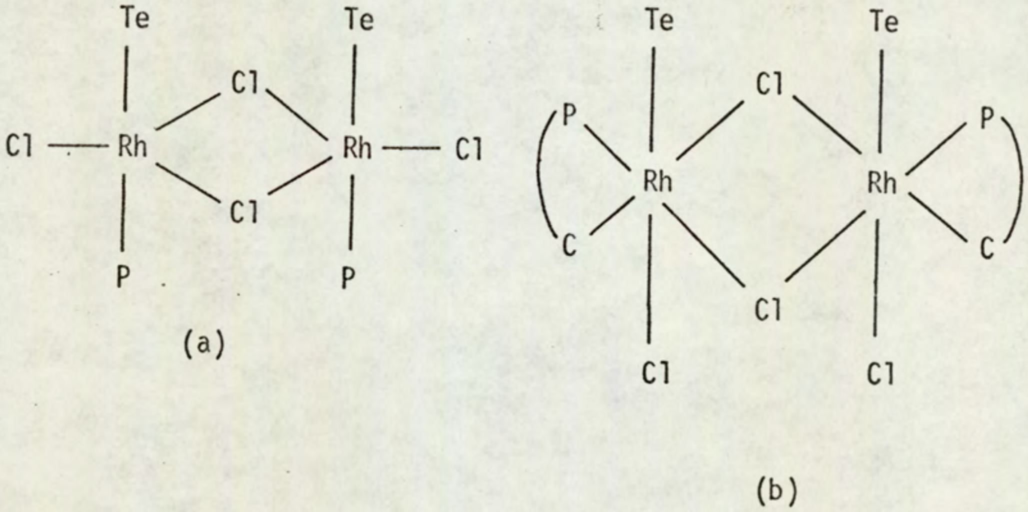
The diffuse reflectance spectra of the complexes show similar patterns, to suggest a common structure. The bands around and above 30 kK were assigned as charge-transfer and probably intraligand transitions ($\Pi \rightarrow \Pi^*$). The band around 23 - 24 kK might be due to the d-d transition $^1A_1 \longrightarrow {}^1T_2$, the assignments of the electronic spectra followed the pattern suggested by Fergusson et al.$^{(32)}$ and Allen and Wilkinson$^{(28)}$.

(e) Reaction of mer $RhCl_3L_3$;(L = Ph_2Te, $(p\text{-}C_2H_5O\text{-}C_6H_4)Te$) with triphenylphosphine

When the reaction of mer RhL_3Cl_3 with triphenylphosphine was carried out in benzene the product did not precipitate while the reaction was going on as was the case during reaction with chelate ligands. The complex was isolated by evaporating the excess solvent and adding n-hexane. The complex was found to be a non-electrolyte in methylcyanide and has the analysis corresponding to the formula $[Rh(Ph_2Te)((C_6H_5)_3P)Cl_2]$. The i.r. and mass spectrum indicated that the compound contained both diphenyltelluride and triphenylphosphine.

The diamagnetism of the complex suggests that the possibility of the compound to have the metal ion in the divalent oxidation state with a d^7-configuration as found in the case of $RhCl_2((o\text{-tolyl})_3P)_2$(115) or $[MX_2(PCy_3)_2]$; (M = Rh,Ir; X = Cl, Br)(116) can be excluded. These divalent rhodium complexes usually have the magnetic moment about 2.2 - 2.3 B.M. corresponding to one unpaired electron.

The complex $Rh(Ph_2Te)(TPP)Cl_2$; (TPP = triphenylphosphine) showed diamagnetism suggesting a low-spin d^6 configuration. The possibility of forming hydride complex $RhHCl_2(Ph_2Te)(TPP)$ is excluded since the reaction was carried out in benzene and no band corresponding to ν(Rh-H) (about 2000 cm^{-1}) was observed in the i.r. or metal-hydride signal was observed in the n.m.r. spectrum. The structure of the complex could then be either a bridging metallated complex by the formation of a metal-carbon bond by splitting of a hydrogen atom of a phenyl group in triphenylphosphine(Fig. 4.9b) or formation of five co-ordinated rhodium complex with a bridging chlorine atoms (Fig.4.9a)



(a)

(b)

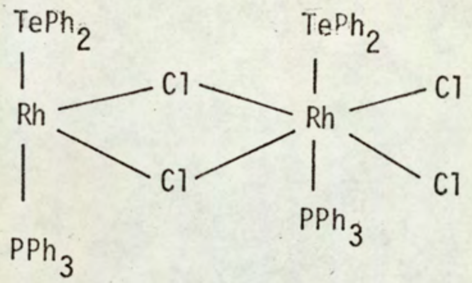
Fig. 4.9 A proposed possible structure for the complex $Rh(Ph_2Te)(Ph_3P)Cl_2$.

Formation of a metal-carbon bond by internal metallation of an alkyl or aryl group of a co-ordinated ligand is known(117). Different ligands including amines, Schiff bases, azo compounds, phosphites, and tertiary phosphines are known to form the metallated complexes with metals such as Pd, Rh, Ir, Ru etc. Internal metallations giving five-membered chelate rings occur most readily(117).

The far infra-red spectrum of the complex $Rh(Ph_2Te)(TPP)Cl_2$ has bands assigned as ν(Rh-Cl) stretching vibrations at 342 cm^{-1} and 303 cm^{-1} The strong band at higher frequency is quite reasonably associated with the terminal rhodium-chlorine stretching vibration while the medium one at lower frequency may possibly arise from the bridging ν(Rh-Cl) vibration. Clark(118) found that there was generally reduction of about 30 - 40 cm^{-1} in changing from terminal metal-chlorine stretching vibration to bridging vibration. An assignment of ν(Rh-Cl) stretching vibrations in the complex $[RhCl_3,dpte]_2$; dpte = 1,2 di(phenylthio)ethane which has both terminal and bridging rhodium-chlorine stretching vibrations has been made by Walton(119). Terminal ν(Rh-Cl) was assigned at about 330 cm^{-1} and the band around 280 cm^{-1} for the bridging ν(Rh-Cl) stretching vibration.

The evidences for the formation of metallated complex are generally obtained from the i.r., n.m.r., X-ray and deuteration studies. The i.r. technique was used to support the claim for the formation of Ru - C bond in the complex $RuX[P(OC_6H_4)(OPh)_2][P(OPh)_3]_3$(120). Since the ligands contained in the complex $Rh(Ph_2Te)(TPP)Cl_2$ absorb in the region which might be useful for the assignment of the vibrations of substituted aryl ring, the i.r. spectra seemed not to be very useful. The n.m.r. should prove quite useful by measuring the number of protons in the spectra of the complex. For the metallation to occur in the complex the number of protons will be one less than expected for the non-metallated complex (which is equal to the number of protons attached to the ligands in the complex). To aid in this n.m.r. study the corresponding complex formulated as $[Rh(p\text{-}C_2H_5O\text{-}C_6H_4)_2Te)(PPh_3)Cl_2]$ was synthsised and the n.m.r. of the complex was recorded. It was found that the spectrum obtained is rather complicated and not very informative. The proton counts obtained from the integration of the peaks are less than expected even for the ortho-metallated complex. The use of n.m.r. spectroscopy in proving the ortho-metallation of the complex sometimes proves to be difficult since it depends on the high accuracy of the integration of the spectrum to distinguish the difference of one proton. Without using the techniques of X-ray crystallography and deuteration studies, the metallation of the complex could not be conclusively proved.

The possibility for the complex $[Rh(L)(TPP)Cl_2]$; ($L = Ph_2Te$, $(p\text{-}C_2H_5O\text{-}C_6H_4)_2Te$) to have the structure similar to iridium complex $IrCl_2(PC_y)_2$ suggested by Moers et al.(116) could be excluded since this structure would have more than one terminal ν(Rh-Cl) stretching vibration:

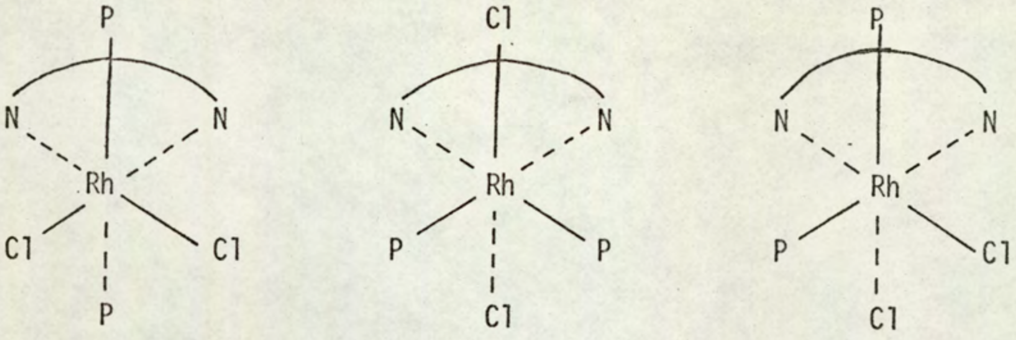


To conclude this discussion about the complex $Rh(Ph_2Te)(TPP)Cl_2$ two structures as shown in Fig. 4.9 were proposed.

(f) Ionic complex of rhodium(III) chloride

When the complex $Rh(Ph_2Te)(2,2'bipy)Cl_3$ was reacted with excess triphenylphosphine in ethanol, the yellow complex formulated by the analysis as $[Rh(PPh_3)_2(bipy)Cl_2]^+Cl^-.2H_2O$ was obtained. The presence of the water in the compound was confirmed by the presence of the broad band around 3500 cm^{-1} in the i.r. spectrum. The conductivity in nitromethane of 70 ohm^{-1} cm^2 $mole^{-1}$ is quite reasonably conformed to the 1:1 electrolyte.

The ionic complex of rhodium with the ligands such as 2,2'-bipy, 1,10'phenanthroline are well known(121). They are of the type $[Rh(AA')_2X_2]^+$; (AA' = 2,2'bipyridyl or 1,10'phenanthroline, X = Cl). All the complexes were shown to have the cis configuration by the evidences of far i.r., Raman and ^1H n.m.r. spectroscopy. The complex formulated as $[Rh(bipy)(PPh_3)_2H_2]^+ClO_4^-$ recently synthesised by Bhayat and Mcwhinnie(40) was shown by n.m.r. and i.r. spectroscopy to have cis configuration. There are three possibilities that the configuration of the complex $[Rh(PPh_3)_2(bipy)Cl_2]^+$ could have as presented below:



$C_{2\nu}$ $C_{2\nu}$ C_1

(a) (b) (c)

Fig. 4.10 Configurations of complex $[Rh(PPh_3)_2(bipy)Cl_2]^+$

The three structures shown above will have two bands due to rhodium-chlorine stretching vibrations in the infra-red spectra, but for the structure 4.10b one of the rhodium-chlorine vibrations will be less intense than the other. The presence of two strong bands at 349 cm^{-1} and 337 cm^{-1} assignable as ν(Rh-Cl) stretching vibrations in the complex $[Rh(bipy)(PPh_3)_2Cl_2]^+Cl^-.2H_2O$ suggests that the complex might have the structure 4.10a or 4.10c. In the complex $[Rh(bipy)(PPh_3)_2H_2]^+$, the cis configuration (structure a) has been proved(40), so by analogy this $[Rh(bipy)(PPh_3)_2Cl_2]^+$ complex might have the cis configuration (structure a).

(g) Reactions involving attempted stabilisation of rhodium(I) with telluride ligands and attempted preparation of the complex of the type $[Rh(chelate)(R_2Te)_2H_2]^+$

It is known that triphenylphosphine is a good ligand in stabilising lower oxidation states of rhodium e.g. a complex such as

$[RhH(PPh_3)_4]$ was successfully synthesised by a rapid and convenient method as reported by two groups of workers.(103 , 40).

The purpose of this experiment is trying to use the telluride ligand to prepare the rhodium(III) hydride complex of the formula $[Rh(chelate)(R_2Te)_2H_2]^+$ since it is reported that(40) the complex $[Rh(bipy)(PPh_3)_2H_2]^+$ was successfully prepared. It was hoped that using telluride instead of phosphine, the complex formed might be more reactive.

The details of the experiments given in the experimental section showed that when the reaction of rhodium trichloride with excess diphenyltelluride under reducing conditions, instead of obtaining the hydride complexes of rhodium(I) (as found in the case of the triphenylphosphine complex), only the unidentified products with no rhodium-hydride bond in the i.r. were obtained. This negative result implies that telluride is not as good as triphenylphosphine in stabilising rhodium(I) hydride complexes.

Also attempting reactions to prepare a complex of the type $[Rh(bipy)(Ph_2Te)_2H_2]^+$, using the similar route reported by Bhayat and McWhinnie(40) in preparing the complex $[Rh(bipy)(PPh_3)_2H_2]^+$ was not successful. Only dark brown unidentified products with no ν(Rh-H) stretching vibration were obtained. These experiments clearly indicate that telluride ligand when compared with triphenylphosphine is not as good in stabilising rhodium(I) complexes or rhodium(III) hydride complexes which might be inpart due to the lower Π acidity of telluride compared with triphenylphoshine.

(h) Attempted reactions using trichlorotrisdiphenyltelluride rhodium(III) as a homogeneous hydrogenation catalyst

It has been known that some complexes of co-ordinated ligands, particularly Π acceptors such as CO, PPh_3, SEt_2 have quite effective potential catalytic properties. Complexes such as $RhCl(PPh_3)_3$, $IrCl(CO)(PPh_3)_2$, $Rh_2Cl_2(SnCl_2.EtOH)_4$ have been used as catalysts in the hydrogenation and hydroformylation of alkene and alkynes(122).

As mentioned in the general introduction (Chapter One) James et al.(29) have successfully used the complex $Rh(Et_2S)_3Cl_3$ as a hydrogenation catalyst for the reaction of olefinic compounds such as maleic acid and ethylene. The kinetics have been interpreted as the initial reduction to a rhodium(I) species, which with olefin co-ordinated, then activates molecular hydrogen.

Attempts were made to study the possible catalytic properties of $RhCl_3(Ph_2Te)_3$ in the hydrogenation reactions of some olefins. The experimental details were given in the experimental section. Olefins used as substrate in this study are 1-decene, 1-pentene and maleic acid. 1-Decene being used because it has the advantage of being a liquid which is easy to handle and having low volatility, 1-Decene has been used successfully before by Kulasingam(123) in his studies of some catalytic properties of the complex $Rh(tripyam)Cl_3$. As shown in Fig. 4. 1 it was possible to separate the 1-decene and n-decane by gas-liquid chromatography; this will facilitate the identification of product since n-decane would be the likely product from the hydrogenation of 1-decene.

Maleic acid has been used successfully by James and his Associates (29) and was also used in this experiment. They showed that solvents play an important role in assisting the dissociation of the initial complex to produce the species which are active in the hydrogenation process. The polarity and co-ordinating ability of the solvent seems to be important for example $Rh(Et_2S)_3Cl_3$ does not catalyse the hydrogenation reaction in benzene but is active in the more polar solvents e.g. N,N'dimethylacetamide (DMA) (ε = 38) which assists in the dissociation of the initial complex. Solvent-assisted dissociation of Octahedral complexes is well-substantiated(124).

Although the molecular weight determination of the $RhCl_3(Ph_2Te)_3$ complex in benzene solution showed no dissociation, an experiment with a 10^{-2}M benzene solution of the complex was conducted to see whether it was possible for any hydrogenation to occur. It was found that, no peak in the chromatogram corresponding to n-decane was observed in the product. Also reaction carried out by using a gas burette to measure the amount of H_2 showed no appreciable amount of volume change. The explanation for the lack of activity of $Rh(Ph_2Te)_3Cl_3$ is possibly due to the non-dissociation of the complex in benzene as has been observed in the case of $Rh(Et_2S)_3Cl_3$ in benzene(29).

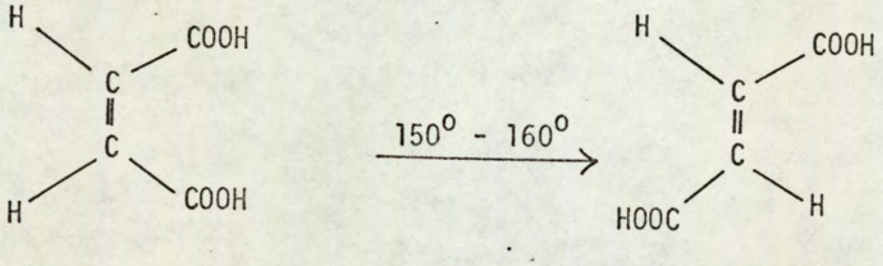
Similar experiments in DMA solution along the line of James and co-workers were carried out. Instead of observing the potential catalytic ability of the complex $Rh(Ph_2Te)_3Cl_3$ as James et al.(29) did in the rhodium sulphide complex, it was found that there was no appreciable H_2 uptake in the reaction, also gas-liquid chromatography showed no peaks corresponding to n-decane.

The inactivity of the complex $Rh(Ph_2Te)_3Cl_3$ in DMA seemed to be surprising since DMA is quite a good polar solvent in helping the dissociation of the complex. The tentative explanation for the lack of activity of this $Rh(Ph_2Te)_3Cl_3$ complex is that there might not be a reduction of the complex $Rh(Ph_2Te)_3Cl_3$ to rhodium(I) by dihydrogen so that no hydrogenation can occur, or the James et al.$^{(29)}$ mechanism proposed for $Rh(Et_2S)_3Cl_3$ might not work in this telluride complex, i.e. the reaction

$$\mathrm{RhL_2Cl_3 + H_2 \not\longrightarrow HRhCl_3L_2^- + H^+}$$

may not occur since the attempts to stabilise rhodium hydride complexes by telluride were not successful as discussed earlier.

When maleic acid was used instead of 1-Decene as a substrate, no hydrogenation product "succinic acid" was observed in the product. The reactions were carried out at room temperature and refluxing temperature,the product obtained from the refluxing mixture was shown to be similar to Fumaric acid by i.r. and melting point, (compared with authentic fumaric acid sample) this is not surprising since it is known that maleic acid could be converted to fumaric acid by heat



Maleic acid

Fumaric acid

CHAPTER FIVE

AN INVESTIGATION OF THE CO-ORDINATION BEHAVIOUR OF DI-2-PYRIDYLKETONE WITH SELECTED FIRST ROW TRANSITION METALS

(A) INTRODUCTION

In the previous chapter the synthesis of the complex $[Rh(Ph_2Te)(pyCOpy)Cl_3]$ was described. In the general introduction (Chapter 1) it is pointed out that the literature of the co-ordination chemistry of di-2-pyridylketone is in a state of some confusion, it was therefore considered worthwhile to take this opportunity to clarify some of the problems that have arisen in this area in the past. Accordingly, this chapter details the results of investigations of di-2-pyridylketone with various transition metal compounds.

(B) PREPARATION OF THE COMPLEXES

Di-2-pyridylketone was purchased from Phase Separation Ltd. Metal salts are available commercially.

(1) Cobalt(II) complexes of di-2-pyridylketone

(a) Mono(di-(2-pyridyl)ethoxymethanol)bis(di-2-pyridylketone)cobalt(II) perchlorate

Cobalt perchlorate hexahydrate (0.36 gm, 1 mM) was refluxed for 4 hours with triethylorthoformate (50 ml) to remove water. Di-2-pyridylketone (0.55 gm, 3 mM) in triethylorthoformate (10 ml) was added to the solution. The orange solid formed immediately, the resulting solution was refluxed for another hour, the solid was filtered through a sintered glass crucible (porosity 4) while a solution was still hot. The orange solid was washed with a small amount of hot triethylorthoformate and ether. The sample was dried over P_2O_5 under vacuum for one day.

Found: C,48.8%; H,3.60%; N,9.43%

$C_{35}H_{30}Cl_2CoN_6O_{12}$

Requires: C,49.0%; H,3.50%; N,9.88%

(b) Hydroxonitratobis(di-2-pyridylketone)cobalt(II)dihydrate

Cobalt nitrate hexahydrate (0.87 gm, 3 mM) was refluxed for 4 hours with triethylorthoformate (50 ml) to remove water. Di-2-pyridylketone (1.66 gm, 9 mM) was added to the solution, an orange solid was formed immediately, the reflux was continued for another hour. The solid was filtered through a sintered glass crucible while the solution was hot. The solid was washed with a small amount of hot triethylorthoformate and ether. The sample was dried over P_2O_5 under vacuum for one day.

Found: C,49.1%; H,3.57%; Co,11.1%; N,13.5%

$C_{22}H_{21}CoN_5O$

Requires: C,48.7%; H,3.87%; Co,10.8%; N, 12.9%

Halide complexes of ligand: metal ratio 2:1

(c) Bis(di-2-pyridylketone)cobalt(II)chloride

Di-2-pyridylketone (0.74 gm, 4 mM) was dissolved in cold EtOH (saturated with N_2) (20 ml) and this was added to a cold ethanolic solution of anhydrous cobalt chloride (0.26 gm, 2 mM). The resulting solution was refluxed for 1½ hours. A yellow solid precipitated down while refluxing. The solid was filtered through a sintered glass crucible and washed thoroughly with ethanol and ether.

Found: Co,11.4%; Cl,14.5%

$C_{22}H_{16}Cl_2CoN_4O_2$

Requires: Co,11.8%; Cl,14.2%

Halide complexes with ligand to metal ratio 1:1

(d) Dichloromono(di-(2-pyridyl) methoxymethanol) cobalt(II)methanol-solvates

Anhydrous cobalt chloride (0.26 gm, 2 mM) in 2,2'dimethoxypropane (25 ml) was refluxed for ½ hour then di-2-pyridylketone (0.37 gm, 2 mM) in 2,2'-dimethoxypropane (10 ml) was added to the above solution, the resulting solution was refluxed for 1½ hours. A violet solid formed during reflux and was filtered through a sintered glass crucible while hot. The compound was washed with 2,2'dimethoxypropane and ether several times. The analysis showed that samples obtained from different preparations contained from one to three moles of methanol.

Found: C,43.0%; H,3.42%; Co,15.2%; N,8.21%

$C_{13}H_{16}Cl_2CoN_2O_3$

Requires: C,41.3%; H,4.23%; Co,15.6%; N,7.41%

(e) Dibromomono(di-2-pyridylketone)cobalt(II)

Di-2-pyridylketone (0.37 gm, 2 mM) in cold ethanol (25 ml) was added to anhydrous cobalt(II) bromide (0.43 gm, 2 mM) in ethanolic solution (25 ml). The resulting solution was refluxed for 1½ hours. The excess solvent was evaporated off with a rotary film evaporator to a small volume. Addition of petroleum ether (b.p.100 - 120^0) to the solution while heating afforded a green solid. The solid was filtered off and washed thoroughly with ether.

Found: C,33.7%; H,2.16%; Co,13.7%; N,6.81%

$C_{11}H_8Br_2CoN_2O$

Requires: C,32.8%; H,1.99%; Co,13.7%; N,6.96%

Complex of cobalt(III)with di-2-pyridylketone

(f) Hydroxoperchloratobis(di-(2-pyridyl)ethoxymethanol)cobalt(III) perchlorate

Di-2-pyridylketone(0.55gm, 3 mM) in ethanol (25 ml) was added to cobalt(II) perchlorate hexahydrate (0.36 gm, 1 mM) in ethanol (25 ml). The resulting solution was refluxed for 2 minutes, then 20 vol. Hydrogen peroxide (10 ml) was added, the reflux was continued for another 2 hours. The pink solid was filtered and washed thoroughly with ethanol and ether.

Found: C,42.8%; H,3.85%; Co,8.22%

$C_{26}H_{29}Cl_2CoN_4O_{13}$

Requires: C,42.4%; H,3.81%; Co,8.01%

(2) Nickel(II) complexes of Di-2-pyridylketone

(a) Tris(di-2-pyridylketone)nickel(II)perchlorate dihydrate

Nickel(II) perchlorate hexahydrate (0.36 gm, 1 mM) was refluxed in triethylorthoformate (50 ml) for 4 hours to remove water. Di-2-pyridylketone (0.55 gm, 3 mM) in triethylorthoformate (10 ml) was added to the solution. The light brown solid was formed immediately, the resulting solution was refluxed for another 1 hour. The solid was filtered through a sintered glass crucible and washed thoroughly with triethylorthoformate and ether (if ethanol was added to the solid while suction being applied the compound will decompose).

Found: C,45.9%; H,3.29%; N,10.1%; Ni,7.16%

$C_{33}H_{28}Cl_2N_6NiO_{13}$

Requires: C, 46.7%; H,3.07%; N,9.91%; Ni,6.93%

(b) The complex between $Ni(NO_3)_2.6H_2O$ and di-2-pyridylketone was similarly prepared to that used in the case of $Ni(pyCOpy)_3(ClO_4)_2.2H_2O$ the analysis showed that the complex could be formulated as $Ni(pyCOpy)(pyCOpy.EtOH)(NO_3)_2$.

Found: C,44.2%; H,3.84%; N,12.3%

$C_{24}H_{22}N_6NiO_9$

Requires: C,44.2%; H,4.29%; N,12.8%

(3) Copper(II) complexes with Di-2-pyridylketone

(a) Diaquobis(di-2-pyridylketone)copper(II) perchlorate

Copper(II) perchlorate hexahydrate (0.37 gm, 1 mM) in absolute alcohol (20 ml) was added to di-2-pyridylketone(0.55 gm, 3 mM) in cold ethanol (20 ml). The immediately precipitated mauve complex was filtered off and washed thoroughly with ethanol and ether.

Found: Cu,8.16%

$C_{22}H_{18}Cl_2CuN_4O_{12}$

Requires: Cu,8.36%

(b) Bis(di-(2-pyridyl)ethoxymethanol)copper(II)nitrate hydrate

Di-2-pyridylketone (0.55 gm, 3 mM) in absolute alcohol (20 ml) was added to copper(II) nitrate trihydrate (0.24 gm, 1 mM) in absolute alcohol (20 ml), the resulting solution was stirred for 5 minutes then petroleum ether (b.p. 100 - 120^0) (30 ml) was added, the stirring was continued for another 30 minutes, the blue-violet solid precipitated while stirring, and was filtered off and washed thoroughly with ethanol and ether.

Found: C,46.4%; H,4.86%; Cu,8.90%; N,12.2%

$C_{26}H_{30}CuN_6O_{11}$

Requires: C,46.8%; H,4.50%; Cu,9.54%; N,12.6%

(4) Iron complexes of di-2-pyridylketone

(a) Bis(di-2-pyridylketone)Iron(II)chloride

Di-2-pyridylketone (0.37 gm, 2 mM) in nitrogen saturated absolute ethanol (25 ml) was added to the solution of iron(II)chloride tetrahydrate (0.2 gm, 1 mM), the resulting solution was refluxed for 1½ hours. The blue solid was filtered off and washed thoroughly with alcohol and ether.

Found: C,52.9%; H,3.44%; Cl,13.5%; Fe,11.5%; N,11.0%

$C_{22}H_{16}Cl_2FeN_4O_2$

Requires: C,53.3%; H,3.23%; Cl,14.3%; Fe,11.3%; N,11.3%

(b) Reaction between ferrous perchlorate and di-2-pyridylketone

Di-2-pyridylketone (0.55 gm, 3 mM) in nitrogen saturated absolute alcohol (25 ml) was added to the solution of iron(II) perchlorate hexahydrate (0.35 gm, 1 mM) in absolute alcohol (25 ml) the resulting solution was refluxed for 2 hours. The excess solvent was evaporated using a rotary film evaporator. The solution was cooled in the refrigerator and the precipitated green solid was filtered through a sintered glass crucible and washed thoroughly with ethanol and ether. Analysis showed that the product could be formulated. as $Fe(pyCOpy)(pyCOpy.EtOH)(ClO_4)_2$

Found: C,43.7%; H,3.31%; Fe,7.60%; N,8.82%

$C_{24}H_{22}Cl_2FeN_4O_{11}$

Requires: C,43.1%; H,3.29%; Fe,8.34%; N,8.37%

(c) Di-isothiocyanato *bis*(di-2-pyridylketone)iron(II)

Anhydrous iron(III)chloride (0.16 gm, 1 mM) in ethanol (25 ml) was mixed with potassium thiocyanate (1 gm) in ethanol (25 ml) and the whole solution was filtered into di-2-pyridylketone (0.55 gm, 3 mM) in ethanol (25 ml). The resulting solution was refluxed for 2 hours.

The dark red brown complex was filtered and washed thoroughly with ethanol and ether.

Found: C,52.8%; H,3.30%; Fe,9.42%; N,15.6%

$C_{24}H_{16}FeN_6O_2S_2$

Requires: C,53.1%; H,2.96%; Fe,10.2%; N,15.5%

(d) Bis(di-(2-pyridyl)ethoxymethanol)mono(di-2-pyridylketone)iron(III) perchlorate hydrate

Di-2-pyridylketone (0.55 gm, 3 mM) in absolute alcohol (25 ml) was added to iron(III) perchlorate hexahydrate (0.46 gm, 1 mM) in absolute alcohol (25 ml), the resulting solution was refluxed for 1½ hours. The solution was cooled in the refrigerator, the yellowish-white solid was filtered off and washed thoroughly with ethanol and ether.

Found: C,43.9%; H,4.13%; Fe,5.96%; N,7.62%

$C_{37}H_{38}Cl_3FeN_6O_{18}$

Requires: C,43.7%; H,3.74%; Fe,5.49%; N,8.26%

(e) Trichloromono(di-2-pyridylketone diethyl acetal)iron(III)

Di-2-pyridylketone (0.55 gm, 3 mM) in absolute alcohol (25 ml) was added to anhydrous iron(III)chloride (0.16 gm, 1 mM) in absolute alcohol (25 ml). The resulting solution was refluxed for 1½ hours. The solution was cooled in the refrigerator, the yellow solid was filtered off and washed thoroughly with ethanol and ether.

Found: C,42.2%; H,3.85%; Fe,13.6%

$C_{15}H_{18}Cl_3FeN_2O_2$

Requires: C,42.8%; H,4.28%; Fe,13.3%

RESULTS

Analytical data for some di-2-pyridylketone complexes of cobalt, nickel and iron are presented in Table 5.1. The magnetic moments and Mössbauer parameters are given in Table 5.2. Table 5.3 shows the conductivity and electronic spectral data of some di-2-pyridylketone complexes.

Tabulations of some infrared absorption vibrations of some complexes are given in Table 5.4.

TABLE 5.1

Analytical data for some di-2-pyridylketone complexes

Complexes	Found %					Required %				
	C	H	N	M	X	C	H	N	M	X
$Co(pyCOpy)_2(pyCOpy\text{-}EtOH)(ClO_4)_2$	48.8	3.60	9.43			49.0	3.50	9.88		
$Co(pyCOpy)_2(NO_3)(OH)\cdot 2H_2O$	49.1	3.57	13.5	11.1		48.7	3.87	12.9	10.8	
$Co(pyCOpy)Cl_2n.MeOH(n{:}1\text{-}3)$	43.0	3.42	8.21	15.2		41.3	4.23	7.41	15.6	
$Co(pyCOpy)Br_2$	33.7	2.16	6.81	13.7		32.8	1.99	6.96	13.7	
$Co(pyCOpy)_2Cl_2$				11.4	14.5				11.8	14.2
$Co(pyCOpy\text{-}EtOH)_2(OH)(ClO_4)_2$	42.8	3.85		8.22		42.4	3.81		8.01	
$Ni(pyCOpy)_3(ClO_4)_2\cdot 2H_2O$	45.9	3.29	10.1	7.16		46.7	3.07	9.91	6.93	
$Ni(pyCOpy)(pyCOpy\text{-}EtOH)(NO_3)_2$	44.2	3.84	12.3			44.2	4.29	12.8		
$Fe(pyCOpy)(pyCOpy\text{-}EtOH)(ClO_4)_2$	43.7	3.31	8.82	7.60		43.1	3.29	8.37	8.34	
$Fe(pyCOpy)_2Cl_2$	52.9	3.44	11.0	11.5	13.5	53.3	3.23	11.3	11.3	14.3
$Fe(pyCOpy)_2(NCS)_2$	52.8	3.30	15.6	9.42		53.1	2.96	15.5	10.2	

continued..

TABLE 5.1 continued

Complexes	Found					Required				
	C	H	N	M	X	C	H	N	M	X
$Fe(pyCOEt_2Opy)Cl_3$	42.2	3.85		13.6		42.8	4.28		13.3	
$Fe(pyCOpy\text{-}EtOH)_2(pyCOpy)(ClO_4)_3H_2O$	43.9	4.13	7.62	5.96		43.7	3.74	8.26	5.49	
$Cu(pyCOpy\text{-}EtOH)_2(NO_3)_2H_2O$	46.4	4.86	12.2	8.90		46.8	4.50	12.6	9.54	
$Cu(pyCOpy)_2(H_2O)_2(ClO_4)_2$				8.16					8.36	

TABLE 5.2

Magnetic moments and Mössbauer data for some di-2-pyridyl complexes

Complexes	Colour	Magnetic Moment μ_{eff} (B.M.)	Mössbauer paremeters mm/sec	
			I.S*(δ)	Q.S*
$Co(pyCOpy)_2(pyCOpy-EtOH)(ClO_4)_2$	Orange	5.30		
$Co(pyCOpy)_2(NO_3)(OH).2H_2O$	Orange	4.97		
$Co(pyCOpy)Cl_2n.MeOH(n:1-3)$	Violet	4.95		
$Co(pyCOpy)Br_2$	Green	4.23		
$Co(pyCOpy)_2Cl_2$	Yellow	4.85		
$Co(pyCOpy-EtOH)_2(OH)(ClO_4)_2$	Pink	0		
$Ni(pyCOpy)_3(ClO_4)_2.2H_2O$	Light brown	3.20		
$Ni(pyCOpy)(pyCOpy-EtOH)(NO_3)_2$	Green	4.17		
$Fe(ClO_4)_2 + pyCOpy \longrightarrow$ product	Green	5.25	0.55	0.87
$Fe(pyCOpy)_2Cl_2$	Blue	5.30	1.12	3.32
$Fe(pyCOpy)_2(NCS)_2$	Dark brown	0	0.50	0.22
$Fe(pyCOEt_2Opy)Cl_3$	Yellow	6.20	0.56	0.15
$Fe(pyCOpy-EtOH)_2(pyCOpy)(ClO_4)_3.H_2O$	White	5.70	0.45	-
$Cu(pyCOpy-EtOH)_2(NO_3)_2.H_2O$	Mauve	1.83		
$Cu(pyCOpy)_2(H_2O)_2(ClO_4)_2$	Mauve	1.78		

*I.S. = chemical isomer shift(with respect to stainless steel). Q.S. = Quadrupole splitting.

TABLE 5.3

Conductivity and electronicspectral data for some di-2-pyridylketone complexes

Complexes	Molar Conductivities Λ_m(10^{-3}M sol)	Diffuse reflectance maxima (kK)
$Co(pyCOpy)_2(pyCOpy\text{-}EtOH)(ClO_4)_2$	140	9.35, 19.8, 21.9
$Co(pyCOpy)_2(NO_3)(OH).2H_2O$	74	10.0, 19.7, 22.3
$Co(pyCOpy)Cl_2n.MeOH$	32	7.9, 14.9, 17.8, 19.3
$Co(pyCOpy)Br_2$	35	7.3, 10.0, 15.6, 16.9,(sh),18(sh)
$Co(pyCOpy)_2Cl_2$	48*	21.4, 27.4
$Co(pyCOpy\text{-}EtOH)_2OH(ClO_4)_2$	143*	18.1, 21.1, 25.9, 31.0
$Ni(pyCOpy)_3(ClO_4)_2.2H_2O$	170	11.0, 17.5, 23.5, 28.0
$Ni(pyCOpy)(pyCOpy\text{-}EtOH)(NO_3)_2$	65	9.2, 16.6
$Fe(ClO_4)_2 + pyCOpy \longrightarrow$ product	150	8.3, 13.2, 19(sh), 29
$Fe(pyCOpy)_2Cl_2$	30	16.0, 24.5
$Fe(pyCOpy)_2(NCS)_2$	-	16.3, 24.3, 30
$Fe(pyCOEt_2Opy)Cl_3$	4.2	10.0, 11.5, 17.2, 19.5
$Fe(pyCOpy\text{-}EtOH)_2(pyCOpy)(ClO_4)_3.H_2O$	220	9.0, 18.4, 21.2
$Cu(pyCOpy\text{-}EtOH)_2(NO_3)_2.H_2O$	72	18 (slight unsymmetric)
$Cu(pyCOpy)_2(H_2O)_2(ClO_4)_2$	134	19 (slight unsymmetric)

TABLE 5.3 continued

* measured in DMF, all the other conductivity measurements were carried out in nitromethane

\- not soluble

TABLE 5.4

Infra-red Spectral data of some di-2-pyridylketone complexes

Complexes	$\nu(C = O)$	$\nu(OH)$	$\nu(C = C)$and $\nu(C = N)$ring mode vibrations	$\nu(ClO_4)$ or $\nu(NO_3)$ or $\nu(NCS)$	$\nu(M - X)$
$Co(pyCOpy)_2(pyCOpy\text{-}EtOH)(ClO_4)_2$	$\overbrace{\text{1680, 1698s}}$ 1705(sh)	3500 w,br	1590s, 1605s	1100s	-
$Co(pyCOpy)_2(NO_3)(OH).2H_2O$	1690s	3400 br	1595s, 1605sh	1460s, 1290s, 1020s	-
$Co(pyCOpy)Cl_2.nMeOH$	-	3120 br	1609s	-	233 s, 249 s
$Co(pyCOpy)Br_2$	1675s	-	1590s	-	245 s, 268 s
$Co(pyCOpy)_2Cl_2$	1690s	-	1590s	-	254 s
$Co(pyCOpy\text{-}EtOH)_2OH(ClO_4)_2$	-	3585s, 3500s 3200s, 2800s,br	1610s	1090s, 1115s 1060sh	-
$Ni(pyCOpy)_3(ClO_4)_2.2H_2O$	1685s	3600m,br 3520m	1615(m) 1590(s)	1090s	-
$Ni(pyCOpy)(pyCOpy\text{-}EtOH)(NO_3)_2$	1690m	3400s,v. br	1605s	1455s, 1290s 1020s	

continued..

TABLE 5.4 continued

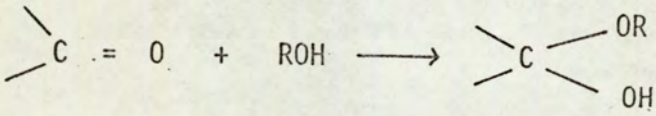
Complexes	ν(C = 0)	ν(OH)	ν(C = C) and ν(C = N) ring mode vibrations	ν(ClO_4)or ν(NO_3) or ν(NCS)	ν(M - X)
$Cu(pyCOpy)_2(H_2O)_2(ClO_4)_2$	-	3515s, 3490s 3200m,br	1610s	1090s,br	-
$Cu(pyCOpy\text{-}EtOH)_2(NO_3)_2.H_2O$	-	3400s	1610s	1370s	
$Fe(pyCOpy)_2Cl_2$	1680s	-	1590s	-	260s
$Fe(pyCOpy)_2(NCS)_2$	1680s	-	1590s	ν(CNS),2090s 805s, 480s	-
$Fe(ClO_4)_2$+pyCOpy ⟶ green solid	1695s, 1685s 1530br	3500m,br	1605s	1100 s	-
$Fe(pyCOpy\text{-}Et_2O)Cl_3$	-	-	1605s	-	347s, 326s 293s, 283s
$Fe(pyCOpy\text{-}EtOH)_2(pyCOpy)(ClO_4)_3.H_2O$	1530s	3500s, 3000s, v.br.,3400s	1618s, 1602s	1090 s	-

(D) DISCUSSION

(1) Cobalt complexes of di-2-pyridylketone

(a) Perchlorate and nitrate complexes

Cobalt complexes of di-2-pyridylketone were studied earlier by Osborne(47) who found that for one complex namely tris(di-2-pyridylketone)cobalt(II) perchlorate pentahydrate $Co(pyCOpy)_2(ClO_4)_2 5H_2O$, the magnetic moment was 1.9 B.M. The complex was claimed to be spin-paired and has $^2E_g(t_{2g}^6\ e_g^1)$ as a ground state. The ligand field strength which can cause a ^2E_g originating in the ^2G state of the free ion to become a ground state was estimated to be large ($\Delta_{oct} > 15000\ cm^{-1}$), the ligand field strength of di-2-pyridylketone was calculated to be around 11000 cm^{-1} which should give rise to spin free complexes in the cobalt case. The cobalt perchlorate complex of di-2-pyridylketone prepared by the same method used by Osborne i.e. refluxing $Co(ClO_4)_2.6H_2O$ with di-2-pyridylketone in ethanol under air was synthesised. It was observed that the pink compound originally formed in the solution turned to tan while the solution was left to cool down. The magnetic moment of the tan compound was found to be 2.22 B.M., this could indicate that the compound might be contaminated by the presence of some cobalt(III), also the analysis of the tan compound could not be interpreted by assuming a pure Co(II) complex. An attempt has been made to prepare a cobalt(II) complex under an atmosphere of dinitrogen to prevent possible oxidation by air. The light orange cobalt(II) perchlorate complex formulated as $Co(pyCOpy)_2(pyCOpy.EtOH)(ClO_4)_2$ was formed. The complex was found to be genuine cobalt(II) complex by the evidence of magnetic moment of 5.3 B.M. this indicated the high spin cobalt(II) complex with an octahedral environment and a considerable contribution of orbital magnetic moment to the complex. The molar conductivity of the complex was found to be 140 $ohm^{-1}cm^{2}mole^{-1}$ in nitromethane which indicated at 1:2 electrolyte. The infrared spectrum of the complex was found to be helpful in the elucidation of the structure, the broad band about 3500 cm^{-1} showed the presence of an OH group in the complex, also the carbonyl stretching vibration $\nu(C = O)$ in the complex showed some complexity (bands at 1680 cm^{-1} 1698 cm^{-1}, shoulder at 1705 cm^{-1}; di-2-pyridylketone has single $\nu(C = O)$ at 1688 cm^{-1}) this suggests the presence of two types of ligands in the complex, one as free ligand and the other ethanolated. The coupling of the carbonyl vibrations of the two di-(2-pyridyl)ketone ligands may account for this complexity of $\nu(C = O)$ vibration. The comparison of the $\nu(C = O)$ in this cobalt complex with the other complexes which were shown to contain no ethanolated or aquated ligands e.g. $Fe(pyCOpy)_2Cl_2$ showed that the carbonyl stretching vibration in the iron complex was a sharp single band with no complexity. It should also be observed that the position of the carbonyl group in the complex showed no downward shift indicating (N,N) coordination in the complex. Careful examination of the infra-red spectra of the complexes in the region 1570 - 1610 cm^{-1} attributable to $\nu(C = N)$ and $\nu(C = C)$ in the ring revealed that for the ethanolation or aquation of the ligand to occur:



$$>C = O + ROH \longrightarrow >C(OR)(OH)$$

The band at 1585 cm^{-1} will shift upward to 1605 - 1610 cm^{-1}. This upward shift of the ring mode vibration is found to occur in all cases where the ketonic group becomes an acetal or hemiacetal. The i.r.spectra of the complex $Fe(pyCOpy)_2Cl_2$ and other complexes which have no ethanolation or aquation of the ligands do not exhibit this shift, the band due to ν(C = N) and ν(C = C) vibrations of the ring were found to be near or in the same position as in the uncomplexed ligand. The δ(C-H) out of plane deformations modes of the complex $[Co(pyCOpy)_2(pyCOpy{\cdot}EtOH)](ClO_4)_2$ in the region 650 cm^{-1} - 830 cm^{-1} were also found to be more complicated than in the case of complexes with only ketonic ligands e.g. $Fe(pyCOpy)_2Cl_2$ and $Co(pyCOpy)_2Cl_2$, this is also probably due to the presence of mixed ligands in the cobalt(II) perchlorate complex. Another point to mention in the i.r. spectrum of this cobalt(II) perchlorate complex is the ionic nature of perchlorate group which shows a strong band at 1100 cm^{-1}.

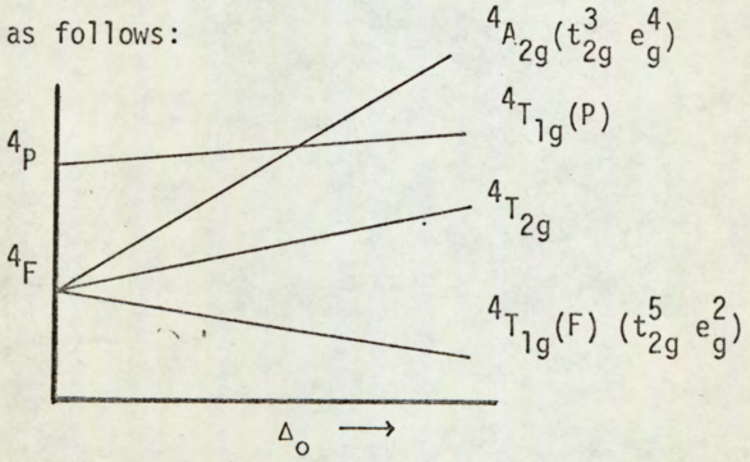
The electronic spectra of octahedral d^7 cobalt(II) complex usually consists of three spin-allowed d-d transitions:

$$^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F) \quad \sim \quad 8 - 9000 \ cm^{-1}$$

$$^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F) \quad \sim \quad 16 - 18000 \ cm^{-1}$$

$$^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F) \quad \sim \quad 20 - 21000 \ cm^{-1}$$

The schematic energy diagram of cobalt(II) complexes could be presented as follows:



The diffuse reflectance spectrum of the complex $Co(pyCOpy)_2(pyCOpy.EtOH)\ (ClO_4)_2$ is consistent with the octahedral stereochemistry with three observed spin-allowed transitions. The tentative assignments will be given as

$$\nu_1 \quad {}^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F) = 9350\ cm^{-1}$$

$$\nu_2 \quad {}^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F) = 19800\ cm^{-1}$$

$$\nu_3 \quad {}^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F) = 21900\ cm^{-1}$$

It is also observed that the $\nu_2({}^4A_{2g} \longleftarrow {}^4T_{1g})$ transition was considerably weaker than the ν_1 and ν_3 (${}^4T_{1g}$ to ${}^4T_{2g}$ and ${}^4T_{1g}$), this can be explained qualitatively since ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ is a two electron jump as the excited state configuration is $t_{2g}^3\ e_g^4$ while the ground state is mainly $t_{2g}^5\ e_g^2$ (125). The ligand field parameters D_q and B were obtained using Lever's graphical methods (126). The Racah parameter B and D_q were found to be 925 cm^{-1} and 1063 cm^{-1} respectively. The reduced Racah parameter value 925 cm^{-1} suggests some covalent bonding character for the complex. The $10D_q$ or Δ value of the ligand (10630 cm^{-1}) could not be taken for the ligand field strength of di-2-pyridylketone since it was calculated from the mixed ligand complex. However the value of Δ_{oct} obtained and magnetic moment data give some idea that the di-2-pyridylketone could be classified as weak field ligand.

A cobalt(III) complex with the formulation $Co(pyCOpy.EtOH)_2(OH)(ClO_4)_2$ was prepared by refluxing $Co(ClO_4)_2 \cdot 6\ H_2O$ with di-2-pyridylketone

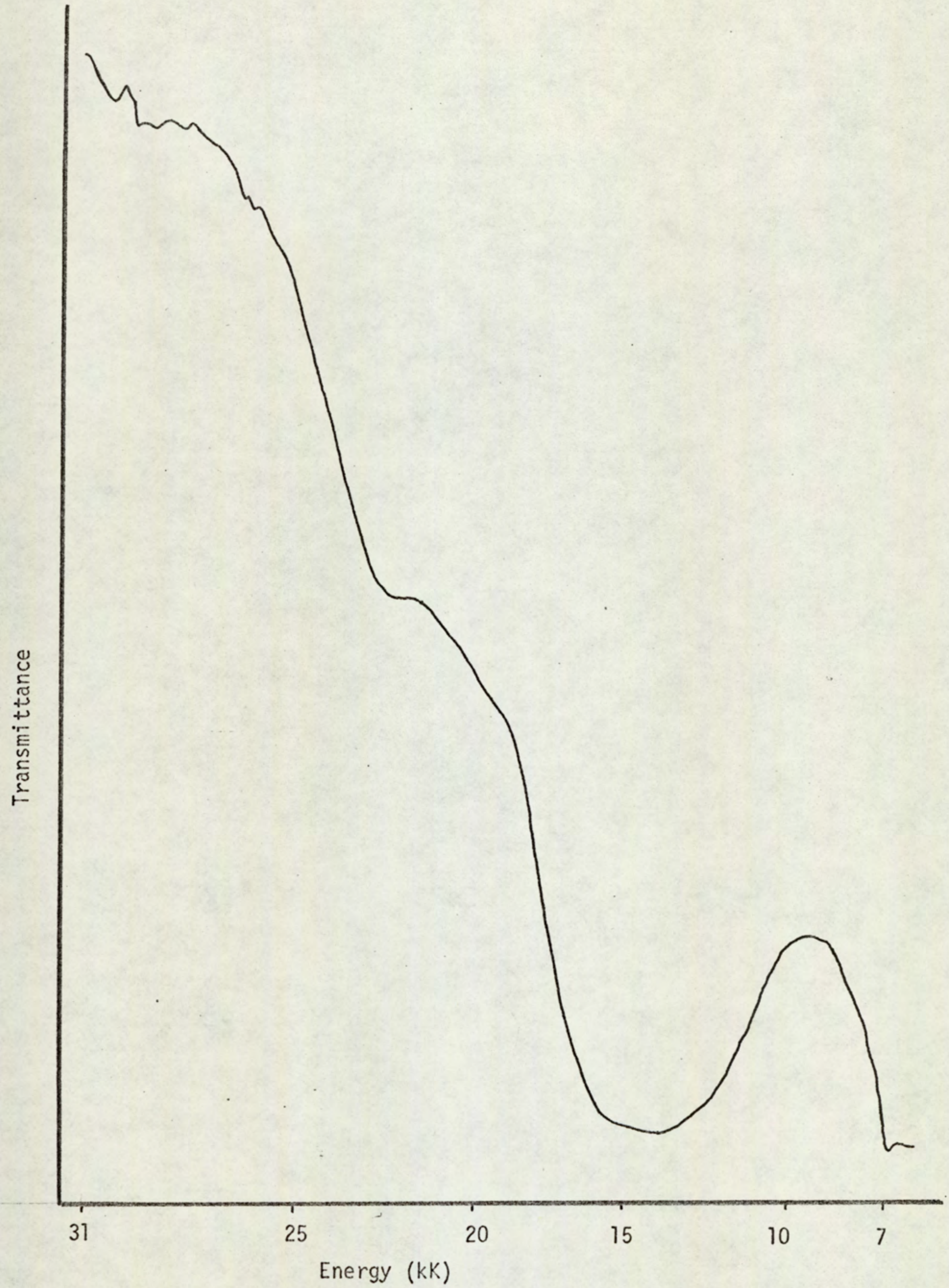


Fig.5.1 Diffuse reflectance spectrum of the complex $Co(pyCOpy)_2(pyCOpy.EtOH)(ClO_4)_2$

with the addition of hydrogen peroxide. Cobalt(III) complexes of di-2-pyridylketone are known to occur in the course of attempting to prepare Co(II) complexes$^{(42)}$, this indicates that the change $Co^{II} \longrightarrow Co^{III}$ of this di-2-pyridylketone complex might occur under some appropriate experimental conditions.

The oxidation state of the cobalt in the complex $Co(pyCOpy.EtOH)_2OH(ClO_4)_2$ is proved to be 3 by the evidence of its magnetic measurement ($\mu = 0$). For the cobalt(III) the $^1A_{1g}$ originating from ^1I term of the free ion drops very rapidly and crosses the $^5T_{2g}$ state at the very low value of Δ, thus all Co(III) octahedral complexes with the exceptions of a few such as $[Co(H_2O)_3F_3]$;$[CoF_6]^{3-}$ have diamagnetic ground states$^{(127)}$. The infra-red spectrum of the complex $Co(pyCOpy.EtOH)_2OH(ClO_4)_2$ showed two sharp strong bands at 3500 cm^{-1} and 3585 cm^{-1}, which confirmed the presence of hydroxide group (OH^-) in the complex. The very broad band around 3200-2800 cm^{-1} indicated some hydrogen bonding in the complex probably from the OH^- group and hemiacetal group of the ligand. The disappearance of the band around 1680 cm^{-1} assignable as ν(C=O) stretching vibration indicated complete ethanolation of the ligands, this was also supported by the upward shift of ν(CN) ring mode to 1610 cm^{-1}, the i.r. spectra of the complex also indicated semi-co-ordinated character of the perchlorate group. The electronic spectra of this cobalt(III) complex showed three bands centred around 18100 cm^{-1}, 21100 cm^{-1} and 25920 cm^{-1} in the visible region, another band around 31000 cm^{-1} was observed in the near U.V. region. The bands observed in these regions were d-d spin-allowed transition, the number and positions of the bands indicate the cobalt(III) complex (^{A}1g)

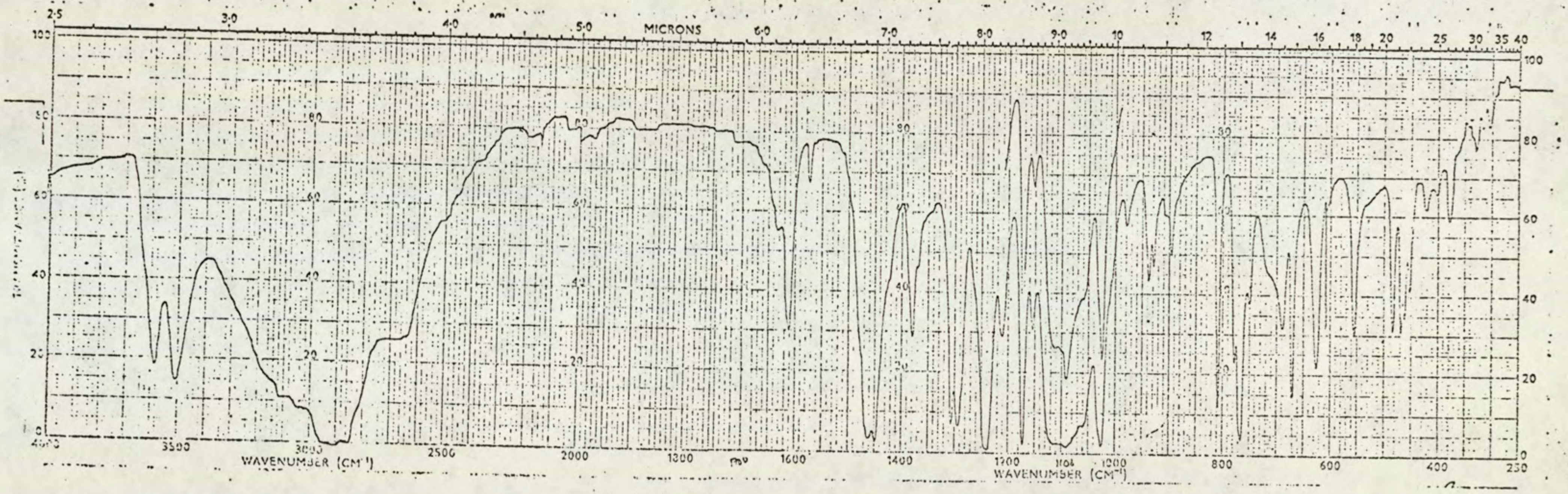
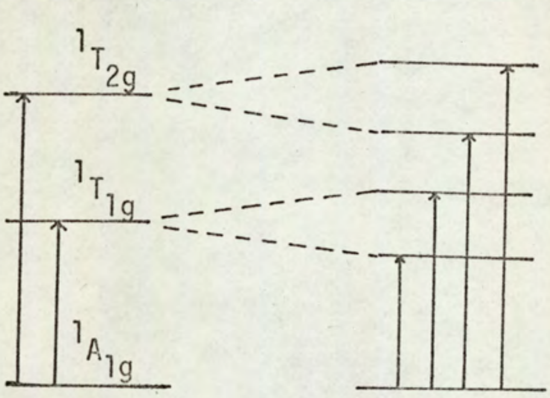


Fig. 5.2 Infra-red spectrum of complex Co(pyCOpy.EtOH)$_2$(OH)(ClO$_4$)$_2$

with some distorted octahedral environment. Only two absorption bands were usually found in the visible spectra of regular octahedral cobalt(III) complex i.e. from ground state $^1A_{1g}$ to upper states $^1T_{1g}$ and $^1T_{2g}$. The low symmetry of the ligand in this cobalt(III) complex $Co(L\text{-}EtOH)_2OH(ClO_4)_2$ might give rise to the splitting of the excited state $^1T_{1g}$ and $^1T_{2g}$, so four bands were observed:



The splitting of $^1T_{1g}$ and $^1T_{2g}$ states in tetragonally distorted complex was also claimed by Dingle (128). The tentative assignments put the bands around 18000 cm^{-1} and 21000 cm^{-1} as the transitions from $^1A_{1g}$ to the split states of $^1T_{1g}$, and the ones at about 26000 cm^{-1} and 31000 cm^{-1} as $^1A_{1g}$ to the split states of $^1T_{2g}$.

Due to the limited solubilities the molecular weight measurement of this cobalt(III) complex could not be carried out to check the nature of association of the complex. The complex could either be monomeric distorted octahedron with one ethanolated ligand acting as a terdentate ligand and the other as a bidentate ligand and OH^- as the sixth co-ordinated ligand (Fig. 5.3a) or the complex could have a hydroxo bridged dimeric structure, Fig.5.3b, or structure C where two ketones are bidentate and one perchlorate group is co-ordinated.

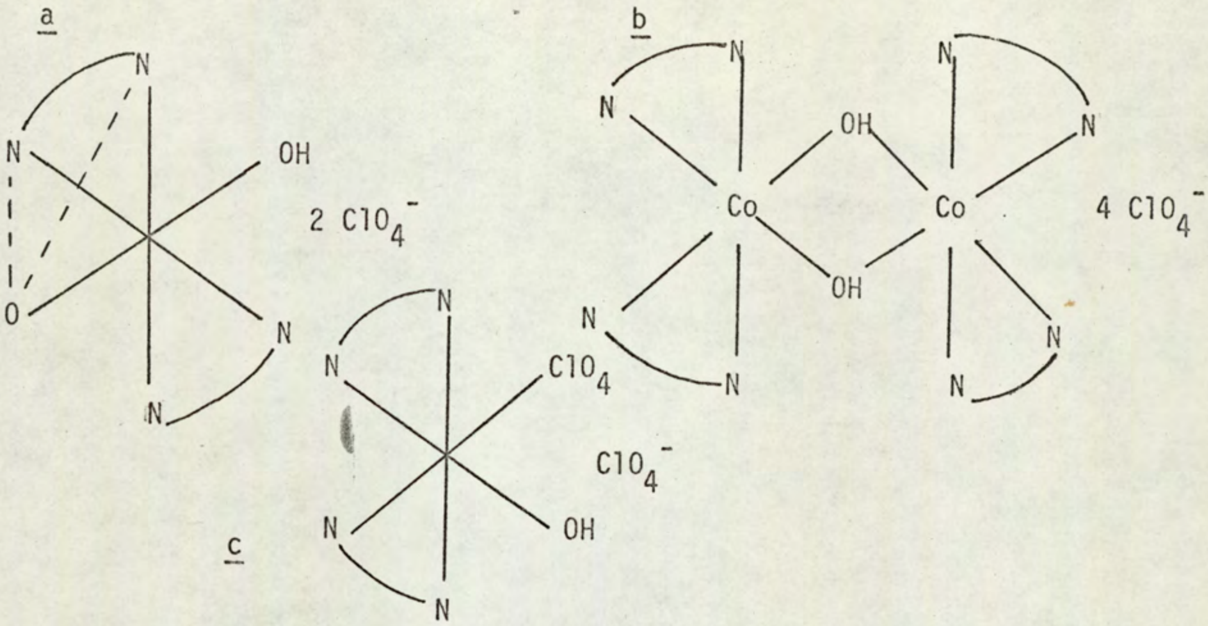


Fig. 5.3 Possible structures of Complex $Co(pyCOpy.EtOH)_2OH(ClO_4)_2$

The molar conductivity in DMF of the complex suggests a 1:1 electrolyte complex conforming to structure C, but the conductivity data alone could not exclude the possibility of the bridged structure, since the bridged structure may possible be ruptured by DMF. The possibility of a structure with a ligand acting as a bidentate was favoured (structure C) since the solution spectrum of the complex in DMF shows similar features to the diffuse reflectance spectrum of the complex which indicated the true nature of the molar conductivity value.

The cobalt(II) nitrate complex of di-2-pyridylketone was synthesised and shown by the elemental analysis to have the formula as $[Co(pyCOpy)_2(OH)(NO_3)]2H_2O$. The magnetic moment of the complex was found to be 4.97 B.M. which is slightly lower than the truly octahedral environment of cobalt(II) (5.1 - 5.2 B.M.).

The weak broad band around 3400 cm^{-1} in the infra-red spectrum indicated the presence of an OH group in the complex. The absence of a sharp band around 3500 cm^{-1} characteristic of the hydroxide vibration made the formulation of the complex, $Co(pyCOpy)_2OH(NO_3)\cdot 2H_2O$ rather tentative. No alternative formulation of the complex fits the elemental analysis obtained. The carbonyl stretching vibration at 1690 cm^{-1} was sharp and confirmed the presence of the free carbonyl ligand in the complex. The characteristic upward shift of the $\nu(CN)$ ring mode (1595 $cm^{-1} \longrightarrow$ 1610 cm^{-1}) in the ethanolated or aquated complexes does not occur but a shoulder at 1605 cm^{-1} was observed. The pattern of the $\delta(CH)$ deformation modes was similar to the free carbonyl ligand complexes and the nitrate group in the complex was shown to be co-ordinated by the presence of the bands at 1460 cm^{-1}, 1290 cm^{-1}, 1020 cm^{-1} the rich pattern of the bands due to coordinated nitrate is expected since on coordination the nitrate lowered its symmetry from D_{3h} to $C_{2\nu}$.

The diffuse reflectance spectrum of this cobalt(II) nitrate complex is consistent with the octahedral stereochemistry and similar to the spectrum of the cobalt(II) perchlorate di-2-pyridylketone complex mentioned above. The calculation of the ligand field parameters by the graphical method gave the values of β Racah parameter equal to 835 cm^{-1} and Δ = 11160 cm^{-1}. The position of ν_2 was calculated to occur around 21.3 kK, thus it is probably hidden under ν_3, so the band at 19.7 kK is probably a spin forbidden band. The bands at 10 kK were assigned as the ${}^4T_{1g} \longrightarrow {}^4T_{2g}$ transition and the band at 22.3 kK as ${}^4T_{1g} \longrightarrow {}^4A_{2g}$ and ${}^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ transitions.

Cobalt halide complexes of di-2-pyridylketone

For the compounds with the ligand: metal ratio 1:1, two complexes formulated as $Co(pyCOpy)Cl_2$.n.MeOH and $Co(pyCOpy)Br_2$ were obtained. The elemental analysis of the violet $Co(pyCOpy)Cl_2$.nMeOH showed the fluctuation of n values between n = 0 - 3, behaviour which was also observed by Osborne(41) in the complex $Co(pyCOpy)Cl_2$n.EtOH. The green bromo complex $Co(pyCOpy)Br_2$ does not show this behaviour and has a good analysis conforming to the proposed formula. The i.r. spectrum of the complex $Co(pyCOpy)Cl_2$.nMeOH showed a strong broad band about 3120 cm^{-1} which is probably due to the hydrogen bonded OH with polymeric association. The disappearance of the $\nu(C = O)$ band indicated the methanolation of the complex, this methanolation is also supported by the upward shift of $\nu(C = N)$ ring mode vibration characteristic of the attacked carbonyl ligand. For the bromo complex $Co(pyCOpy)Br_2$ the $\nu(C = O)$ vibration was observed at 1675 cm^{-1} indicating an (N,N) mode of co-ordination, and the $\nu(C = N)$ ring mode was not shifted (1590 cm^{-1}).

Comparison of the far infra-red spectra of the chloro and bromo complex showed that in the bromo complex two very strong bands at 245 cm^{-1} and 268 cm^{-1} could be assigned as $\nu(Co - Br)$ stretching vibrations. Taking the useful formula $^{\nu(M-Br)}/\nu(M-Cl) = 0.7$, $\nu(Co-Cl)$ stretching vibrations are expected to be around 350 cm^{-1} and 382 cm^{-1} but instead two strong bands which probably are $\nu(Co-Cl)$ stretching vibrations were observed at 235 cm^{-1} and 249 cm^{-1}. This suggests that the co-ordination number of cobalt in the chloro and bromo complexes is different.

The solid state electronic spectra of a green Co(pyCOpy)Br_2 complex indicates a tetrahedral environment, the longest wavelength transition was observed at 7.3 kK which is low for the octahedral stereochemistry (9-10 kK) also the band at about 16 kK consisted of fine structure caused by spin-orbit coupling. The lower values of ligand field in the tetrahedral case make the effects of vibronic interaction, spin-orbit coupling and low symmetry ligand field components rather more pronounced than in the octahedral complexes. The final point woth observing in the electronic spectrum of Co(pyCOpy)Br_2 is the high intensities of the bands compared with the octahedral complexes. This is due to d-p mixing of the tetrahedral complex.(129) The magnetic moment of 4.23 B.M. of Co(pyCOpy)Br_2 also supports the tetrahedral configuration. In the case of the violet Co(pyCOpy)Cl_2.nMeOH, the far infra-red spectrum mentioned above suggests that it has a different stereochemistry from the green tetrahedral Co(pyCOpy)Br_2 complex. The electronic spectrum of this violet complex consists of four bands at 7.9 kK, 14.9 kK, 17.8 kK and 19.3 kK, which probably indicated some type of distorted octahedral environment, the rather low value of 7.9 kK in the longest wavelength (compared with the usual value of 9-11 kK of Co(II) in octahedral environment) is probably due to the low symmetry of the ligand field components. The magnetic moment of the complex at 4.95 B.M. also showed the octahedral stereochemistry of the complex with some perturbation by a low symmetry ligand field. The structure of the complex could possibly then be proposed as a polymeric octahedral structure in which the methanolated ligand is terdentate.

One bis complex of cobalt formulated as $Co(pyCOpy)_2Cl_2$ was synthesised. The i.r. spectrum consists of a sharp free carbonyl $\nu(C = O)$ band at 1690 cm^{-1} which indicated (N,N) co-ordination. The ring mode vibration at 1590 cm^{-1} is characteristic of unattacked carbonyl ligand. The single metal-halogen stretching frequency at 254 cm^{-1} suggests that the two chlorine atoms are trans to each other in the complex. The magnetic moment of the complex at 4.85 B.M. and the diffuse reflectance spectrum are consistent with the distorted octahedron environment.

To conclude the cobalt complexes studied, the following observations can be made:

a) The anomolous magnetic moment of the cobalt perchlorate complex studied by the previous worker(47) and the one synthesised in this work was caused by the contamination withcobalt(III).

b) A cobalt (III) complex can be synthesised.

c) The aquation or ethanolation of the carbonyl group in the ligand is accompanied by the upward shift of $\nu(C = N)$ ring mode frequency from about 1590 cm^{-1} to 1610 cm^{-1}.

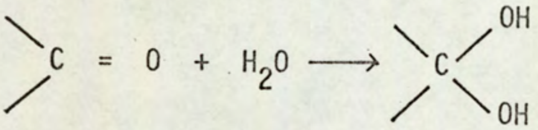
d) The ethanolated or aquated carbonyl ligand may act as terdentate ligand.

(2) Nickel(II) complexes of di-2-pyridylketone

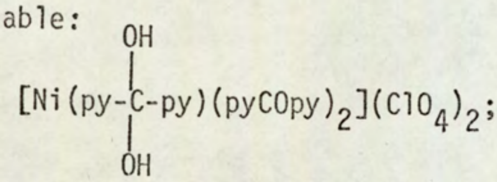
After completion of the work on this chapter we recently came across the literature(130) describing the coordination behaviour of di-2-pyridylketone in some nickel complexes. Although their complexes were not the same with the ones prepared in this study, the observation they made about the aquation of the carbonyl group of di-2-pyridylketone agreed with our observations.

The reaction of nickel(II)perchlorate hexahydrate with di-2-pyridylketone in triethylorthoformate affords a light brown solid which was shown by the analysis to have the formula $Ni(pyCOpy)_3(ClO_4)_2.2H_2O$. The molar conductivity in nitromethane of 170 $ohm^{-1}\ cm^2\ mole^{-1}$ is consistent with the 1:2 electrolyte. The infra-red spectrum of the complex showed the presence of water molecules.

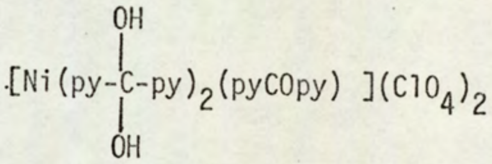
The shape of $\nu(OH)$ band around 3500 cm^{-1} has a slight splitting at 3520 cm^{-1} and 3600 cm^{-1}, this might indicate that ligand molecules are aquated i.e.



The band characteristic for a water molecule in the lattice is usually broad and located about 3200 - 3300 cm^{-1}. The possibility that one or two carbonyl ligandsare aquated with the following formulations are quite probable:



$$[Ni(py\text{-}C(OH)_2\text{-}py)(pyCOpy)_2](ClO_4)_2;$$



$$[Ni(py\text{-}C(OH)_2\text{-}py)_2(pyCOpy)](ClO_4)_2$$

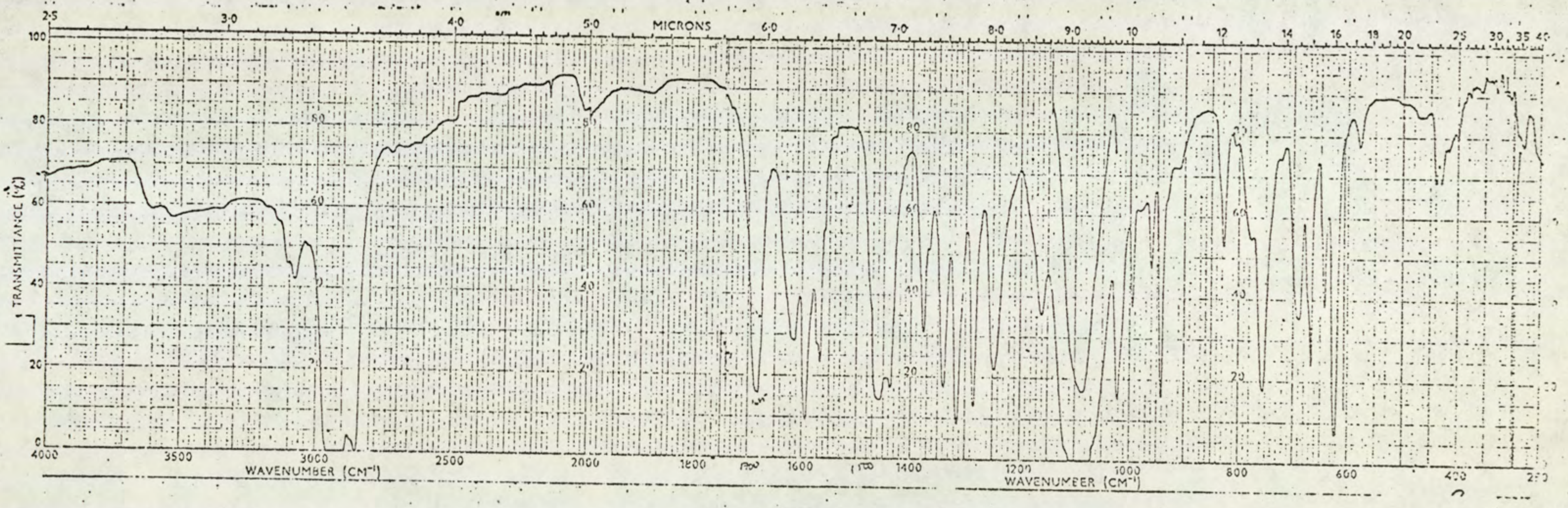
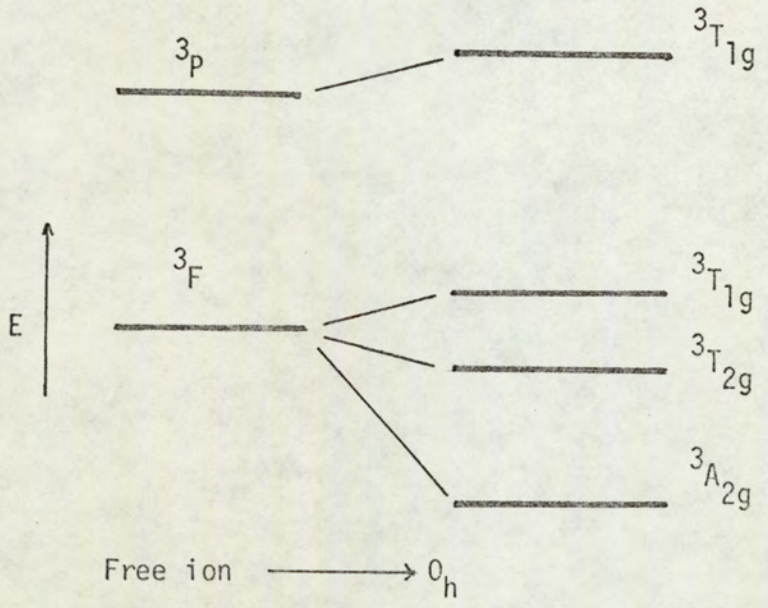


Fig. 5.4 Infrared spectrum of complex $Ni(pyCOpy)_3(ClO_4)_2.2H_2O$

The position of the carbonyl ligand at 1685 cm^{-1} shows that the ligand is N,N co-ordinated and at least one free carbonyl ligand is present. The $\nu(C=N)$ ring mode vibration is observed at 1590 cm^{-1}, but also the medium band at 1610 cm^{-1} is present, this might mean that two types of ligands are present in the complex, one aquated, the other free carbonyl. The perchlorate groups are ionic, the frequency ν_3 is at 1090 cm^{-1}. The differentiation between ionic and co-ordinated perchlorate (and other co-ordinating anions) could be found in the literature(131), the recent one is (132). The magnetic moment of 3.20B.M. is consistent with an octahedral nickel(II) complex. The diffuse reflectance spectrum of the complex contains three bands in the visible region (23.5 kK, 17.5 kK and 11.0 kK), another broad band at 28 kK which was mixed with charge transfer band is also observed, this indicates the O_h symmetry of the complex. The electronic spectrum of the nickel(II) complex usually consists of three spin allowed transition bands which could be labelled in the following order of increasing energy $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)\nu_1$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)\nu_2$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}, \nu_3$



The longest wavelength transition $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ theoretically yields directly the value of ligand field strength Δ. Using Lever's graphical method$^{(126)}$ and assigning ν_1, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ at 11000 cm^{-1}. ν_2, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ at 17500 cm^{-1} the value of ν_3, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}$ was predicted at 28050 cm^{-1} which could be observed as a broad band in the blue region, the shoulder at 23.5 kK is probably a spin forbidden band. The value of Racah's parameter is 835 cm^{-1} and represents a 25% lowering of the free ion value of 1040 cm^{-1}, which suggests a considerable degree of covalency in the bonding of ligand to metal. The ligand field strength Δ was found to be 11090 cm^{-1} in a reasonable agreement with the value 11000 cm^{-1} obtained from the longest wavelength transition ν_1, $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$. The Δ value is not for di-2-pyridylketone if the complex is considered to have mixed ligands in the molecules i.e. some carbonyl ligands are aquated and some are not. It is however reasonable to consider di-2-pyridylketone as a weak field ligand with respect to nickel(II) as also proved by the magnetic measurement.

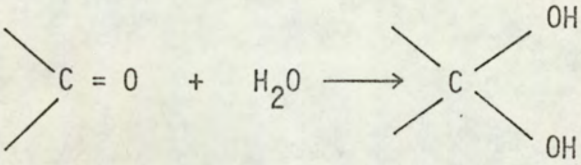
Reaction of $Ni(NO_3)_2.6H_2O$ with di-2-pyridylketone in triethylorthoformate yielded the green complex which could be formulated as $Ni(pyCOpy)(pyCOpy\text{-}EtOH)(NO_3)_2.3H_2O$. The infra-red spectrum showed the presence of water molecules with a large broad band at about 3400 cm^{-1}, the carbonyl stretching vibration at 1690 cm^{-1} is not so strong as in the case of the other free carbonyl ligand complexes e.g. $Co(pyCOpy)_2Cl_2$, $Fe(pyCOpy)_2Cl_2$ which might indicate but not prove that the carbonyl intensity was reduced by the coupling with other ligands which present in the complex. The upward shift of theν(C=N) ring made from 1590 cm^{-1}

to 1605 cm^{-1} also supports that the ethanolation of the ligand occurred. The nitrate group is found to be co-ordinated by the i.r. spectrum probably only one group of nitrate is co-ordinated since the conductivity indicated a 1:1 electrolyte in solution, but the conductivity value could also be interpreted by the other cases i.e. the dissociation of the co-ordinated nitrate group in the solution, or solvolylis of the complex. The electronic spectrum of the complex is consistent with the distorted octahedral stereochemistry with two bands were observed in the visible regions at 9.2 kK and 16.6 kK, the lower value will be assigned as $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition and the higher one as $^3A_{2g} \longrightarrow {}^3T_{1g}$. The other spin allowed transition $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ could not be located since it is mixed with the charge transfer band.

From the above evidences the structure of this nickel nitrate complex could possibly be the distorted octahedron with the ethanolated ligand acts as terdentate and the free carbonyl ligand as the bidentate and the sixth co-ordination site was filled with one nitrate group. The other possibility is that both ligands behave as bidentate and both nitrate groups are co-ordinated.

(3) Copper(II) complexes of di-2-pyridylketone

The complex formulated as $[Cu(pyCOpy)_2(H_2O)_2](ClO_4)_2$ was synthesised similarly to the previous work(41). The observations about the physical properties and the spectra agree with the previous work but additional explanations will be briefly given. The complex $[Cu(pyCOpy)_2(H_2O)_2](ClO_4)_2$ has ionic perchlorate groups and OH groups in the i.r. ($\nu(OH) = 3500\ cm^{-1}$ with slight splitting). The carbonyl stretching vibration $\nu(C=O)$ disappeared and this will be explained as both ketones are aquated.



The upward shift of the $\nu(C=N)$ ring mode vibration is consistent with the aquation of the carbonyl group in the ligand. The d-d spectrum of the complex could provide some information about the stereochemistry. For the complex with O_h symmetry only one band could be observed, but with Jahn-Teller effect another shoulder or unsymmetrical of the band could probably be observed. The band at 19 kK was observed in this copper perchlorate complex, the shape of the band is slightly unsymmetrical but no shoulder was observed as in the previous assignment when two bands at 17.4 kK and 15.4 (sh) were observed in the visible spectrum. The magnetic moment of 1.78 B.M. and the unsymmetrical of the d-d band could possibly infer that this copper perchlorate complex has some distorted octahedral environment with each ligand acts as terdentate. It should be noted that only metal analysis was obtained in this complex due to the breakdown of the C, H, N analyser, further discussion of the complex could lead to more speculations.

Reaction of copper nitrate and di-2-pyridylketone in ethanolic solution yielded the complex which could be formulated by the analysis as $Cu(pyCOpy\text{-}EtOH)_2(NO_3)_2.H_2O$. The infra-red spectrum contains the band at $3400\ cm^{-1}$ characteristic of the OH group, and the ketone is ethanolated as shown by the disappearance of the free carbonyl band and the upward shift of the $\nu(C=N)$ ring mode. The nitrate groups are found to be ionic.

The electronic spectrum of this complex is sufficiently similar in band shape and position (18 kK) of the $E_g \rightarrow T_{2g}$ transition to the perchlorate complex to suggest a similar environment around the copper atom. The likely structure for this complex is distorted octahedral in which each ethanolated ligand behaves as a terdentate base. When the complex is heated to remove water the grey-mauve solid is obtained, the i.r. spectrum of this solid showed no ν(OH) band and indicated the N,N co-ordination of the ligand (νC=O) = 1700 cm^{-1}). The nitrate groups now appear to be co-ordinated which is not surprising since the ketone ligand now acts as bidentate and copper could have two co-ordination sites for the nitrate groups to fill. When copper nitrate and di-2-pyridylketone were reacted in triethylorthoformate, a blue-green complex is obtained. The preparation of the complex is reproducible but the micro analysis cannot be fitted to any likely stoichiometry. The i.r. spectrum of the complex showed complete aquation or ethanolation by the disappearance of ν(C=O) stretching vibrations and the upward shift of ν(C=N) ring mode vibration. The i.r. also showed that the nitrate groups are ionic. The last point that should be mentioned about this solid is the rather low frequency d-d transition (13 kK) compared with the above two copper complexes (18 - 19 kK).

(4) Iron complexes of di-2-pyridylketone

Iron(II) and iron(III) complexes of di-2-pyridylketone were synthesised and studied by various physical techniques including the use of ^{57}Fe Mössbauer spectroscopy which is one of the most powerful tools in the investigation of iron chemistry.

The complex formulated as $Fe(pyCOpy)_2Cl_2$ was synthesised by refluxing ferrous chloride with di-2-pyridylketone in ethanol. The blue complex obtained has an infra-red spectrum which showed no $\nu(OH)$ absorption, the $\nu(C{=}O)$ stretching vibration was observed at 1680 cm^{-1} indicative of (N,N) co-ordination of the ligand. The characteristic $\nu(C{=}N)$ ring mode vibration was found at 1590 cm^{-1} which is consistent with the unattacked carbonyl ligand, also the $\delta(CH)$ out of plane deformation modes of the complex in the region 650 cm^{-1} - 830 cm^{-1} was similar to the uncomplexed ligand,this might indicate the presence of the unperturbed ligands in the complex contrary to the case of mixed ligand complexes i.e. $Co(pyCOpy)_2(pyCOpy.EtOH)(ClO_4)_2$ which showed more complexities in this $\delta(CH)$ out of plane region.

Far infra-red spectra of compounds of the type ML_4X_2 could provide some information about the stereochemistry of the complexes, for the trans complex with D_{4h} symmetry only one band of $\nu(M-X)$ metal-halogen stretching was expected while in the cis case with $C_{2\nu}$ symmetry two bands due to $\nu(M-X)$ stretching vibrations should be observed. In a similar type of complex $Fe(dipyam)_2Cl_2$; (dipyam = di-2-pyridylamine), the band due to the $\nu(Fe-Cl)$ stretching vibration was assigned at 253 cm^{-1}(133). The authors suggested that there might be another $\nu(Fe-X)$ band located lower than 200 cm^{-1}. In the complexes of the type $[Fe(diamine)_2X_2]$ especially for the bis(phenanothroline) compounds the cis stereochemistry were confirmed(134). In the case of di-2-pyridylketone complexes, Morgan(46) considered the cis structure to be more probable for the complexes of the type $M(pyCOpy)_2Cl_2$ due to the absence of steric effect (no non-bonded H-H interaction if the ligands were treated as planar), but as mentioned earlier in the general introduction (Chapter 1), di-2-pyridylketone has more flexibility of the pyridyl rings than in the 2,2'bipyridyl and 1,10 phenanthroline, and the molecules need not be planar which makes the trans configuration of complexes also plausible. The complex $Fe(pyCOpy)_2Cl_2$ prepared in this work has the strong absorption band in the far infra-red at 260 cm^{-1} which will be assigned as ν(Fe-Cl) stretching vibration, the asymmetry of the band at 258 cm^{-1} is probably not proof of cis configuration, this might occur from other effects, i.e. coupling with lattice vibrations. It is seen that in this case it is rather untenable to be conclusive about the stereochemistry of the complex $Fe(pyCOpy)_2Cl_2$ based on the evidence of vibrational spectroscopy.

The magnetic moment of the complex of 5.30 B.M. is consistent with the high spin iron(II) complex of $^5T_{2g}$ ground state with some distorted octahedral environment. In some cases it is difficult to differentiate between the oxidation state of iron in the complexes, the range given by Figgis & Lewis(135) for iron(II) is 5.10 - 5.70 B.M. and for iron(III) from 5.70 - 6.0 B.M. This problem could be solved by the use of Mössbauer spectroscopy from which the parameters obtained will give the nature and oxidation state of iron in the complexes. Apart from above, the Mössbauer parameters can give, in favourable cases, a great deal of information on the electronic configurations of atoms and their local symmetry, some of these important parameters will be briefly given here.

1. The isomer shift δ which is defined as the displacement of the centre of the spectrum from the zero velocity. It arises because the nucleus of an atom is not a point charge but has a finite volume. The electrostatic interaction between the charge distribution of the nucleus and those of orbital electrons that have a finite probability of existing in the region of nucleus will bring about a change in the energy levels of the nucleus. The isomer shift measures the difference between the total s-electron densities at the nuclei of source and absorber according to(136)

$$\delta = \frac{2}{5}\Pi Ze^2[R_{ex}^2 - R_{gr}^2]\{|\psi_s(0)|_a^2 - |\psi_s(0)|_s^2\}$$

R_{ex} and R_{gr} are the effective radii of the nuclear excited and ground states of 14.4 keV γ-transition in ^{57}Fe respectively. The isomer shift δ in the iron(II) compounds with $^5T_{2g}$ ground state are generally larger than $^1A_1$ ground state and this was explained in terms of increased covalency of the metal-ligand bond in the $^1A_1$ state, since a larger d-electron delocalisation is expected to decrease the shielding of s electrons.

2. The quadrupole splitting ΔE_q which is caused by the interaction of the nuclear quadrupole moment Q with an electric field gradient in the region of the nucleus(137)

$$\Delta E_Q = \frac{1}{2} e_q^2 Q(1 + {}^1/3\eta^2)^{\frac{1}{2}}$$

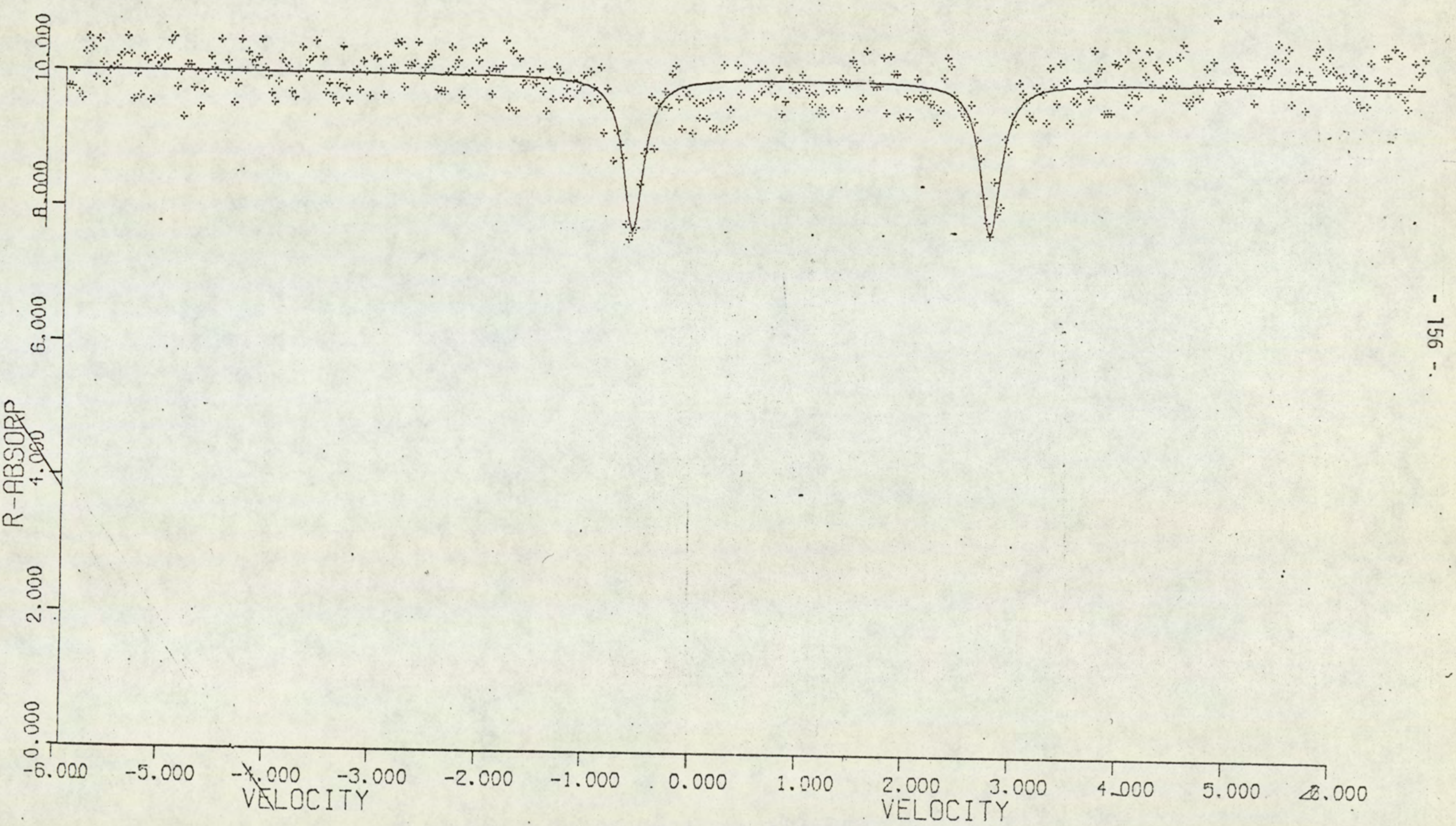
where $e_q = V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, V = electric potential.

Generally the largest contribution to the electric field gradient comes from incompletely-filled d electron shells, and rather small values of ΔE_Q will be expected from the term $^1A_1(t_2{}^6)$ whereas substantial value of ΔE_Q should result from $^5T_2(t_2{}^4e^2)$ term in the absence of octahedral symmetry. In iron(III) high spin complexes ΔE_Q values of 0 - 0.5 mm sec^{-1} are expected whereas values of as much as 2 mm sec^{-1} are found for low-spin systems.

The magnetic hyperfine splittings are not expected in the compounds studied due to the relatively low concentration of iron.

The isomer shift δ and quadrupole splitting of the $Fe(pyCOpy)_2Cl_2$ were found to be 1.12 mm sec^{-1} (w.r.t. stainless steel) and 3.32 mm sec^{-1} respectively. This is consistent with the values generally obtained for the high spin iron(II) complexes $^5T_{2g}$ ground term with some degree of distorted octahedral environment(138) for example the complex $Fe(phen)_2Cl_2$ was found to have δ = 1.15 ± .10 mm sec^{-1} (w.r.t.stainless steel) and ΔE_Q of 3.28 ± 10 mm sec^{-1} respectively(134). For the similar complex $Fe(dipyam)_2Cl_2$ studied by McWhinnie et al.(139) and Goodgame and Burbridge(133) the isomer shift was found to be 2.23 mm sec^{-1}. The higher value of quadrupole splitting found in this $Fe(pyCOpy)_2Cl_2$ indicates that the local symmetry is lower than in the complex $Fe(dipyam)_2Cl_2$,also the magnetic moment of 5.3 B.M. found in this ketonic complex is lower than the complexes $Fe(dipyam)_2Cl_2$ and $Fe(dipyam)_2Cl_2.2H_2O$ which were found to be around 5.4 - 5.5 B.M. showing larger distortion from octahedral symmetry in the ketonic complex case. It is worth observing that the Mössbauer parameters obtained for this ketonic complex

Fig. 5.5 Mössbauer spectrum of complex $Fe(pyCOpy)_2Cl_2$



are very similar to the complex Fe(phen)$_2$Cl$_2$ which is considered to be cis.

The ground state ^5D of a d^6 configuration of iron(II) is split by octahedral and tetrahedral fields into $^5T_2$ and ^5E states. For high-spin octahedral complexes, e.g. $Fe(H_2O)_6^{2+}$, the $^5T_{2g} \longrightarrow {}^5E_g$ multiplicity allowed transition occurs in the visible or near i.r. region and is usually broad or even resolvably split due to a Jahn-Teller effect in the excited state, which derives from a $t_{2g}^3\ e_g^3$ configuration. For the ligand which has high ligand field strength, a low spin $^1A_1(t_2^6)$ ground state as in $[Fe(CN)_6]^{4-}$ occurs. The diffuse reflectance spectrum of the blue Fe(pyCOpy)$_2$Cl$_2$ complex shows broad intense bands in the ultraviolet and tailing into the visible region. The band at 16 kK is too intense and high in energy for the normal d-d transition in the high spin iron(II) complexes, for example in the complex Fe(dipyam)$_2$Cl$_2$, the bands assigned as d-d transition $^5T_{2g} \longrightarrow {}^5E_g$ were found at 10800 cm^{-1} and 88000 cm^{-1}(133). This rather odd electronic spectrum of the Fe(pyCOpy)$_2$Cl$_2$ was probably due to the presence of a small amount of Fe(III) impurities in the complex, which is too slight to affect the analytical results and Mössbauer spectrum but is enough to be observed in the electronic spectrum (mixed with charge transfer band). The band expected for the iron(II) complex around 10 - 12 kK is probably obscured by this strong charge transfer and iron(III) band. The other observation that should be mentioned is the colour of the complex which is blue suggestive of strong charge-transfer bands in the complex.

The complex formulated as $Fe(pyCOpy)(pyCOpy\text{-}EtOH)(ClO_4)_2$ by the analytical results will now be considered. The i.r. spectrum of the complex consists of a broad ν(OH) band around 3500 cm^{-1}, the medium carbonyl stretching vibration ν(C=O) was observed as a split band at 1690 cm^{-1} which suggested the presence of at least one free carbonyl ligand in the complex, also the ethanolation of the ligand is substantiated by the upward shift of ν(C=N) ring mode vibration in the complex to 1605 cm^{-1}. The ionic nature of the perchlorate group is confirmed by the broad band ν_3 at 1100 cm^{-1}, also the molar conductivity of 150 ohm^{-1} cm^2 $mole^{-1}$ in nitromethane could be treated as 1:2 electrolyte. The interesting feature about the i.r. spectrum of this complex is the presence of the band at 1530 cm^{-1} which is suspected as probably an (N,O) mode of co-ordination of the carbonyl ligand. Inspections of the complexes with ligands which can co-ordinate only through (N,O) such as 2-benzoylpyridine complexes for example $Cu(PhCOpy)_2(ClO_4)_2$(41), $Ni(PhCOpy)_2(ClO_4)_2$(44c) and $Rh(PhCOpy)_2Cl_2^-.ClO_4$(44a), the ν(C=O) absorption bands were observed at (1570, 1563, 1550 sh), 1616 cm^{-1} and (1520 - 1530 cm^{-1}) respectively. This supports the possibility of assigning the band at 1530 cm^{-1} as ν(C=O) of an (N,O) mode co-ordinated ligand.

The magnetic moment of 5.25 B.M. and the diffuse reflectance spectrum of the complex are consistent with the high spin iron(II) complex with some distorted octahedral environment, the band at 13.2 kK in the electronic system will be assigned as the d-d spin allowed $^5T_{2g} \longrightarrow {}^5E_g$, the doublet structure of the bands (observed another band at 8300cm^{-1}) is probably due to a Jahn-Teller effect.

The parameters obtained from the Mössbauer spectrum of the complex Fe(pyCOpy)(pyCOpy-EtOH)$(ClO_4)_2$ indicated the main oxidation state of iron in the complex is three. The contamination of iron(III) in the complex is also suspected from the preparation, although the reaction was carried out under dinitrogen, the starting material ferrous perchlorate is suspected of being contaminated with perchloric acid (the salt showed highly positive acid test, litmus test) and this could oxidise iron(II) to iron(III) easily. The analysis although plausible with the above formulation showed some fluctuation of iron analysis for the complexes prepared at different times, the i.r. spectra and the colour of the complexes prepared at different times were found to be slightly different which might be attributable to the presence of a mixture of iron(III) and iron(II) in the complex. Attempts have been made to prepare a genuine iron(II) complex of di-2-pyridylketone by treating the starting material, ferrous perchlorate with iron powder to reduce contamination of iron(III) in the complex.

$$2Fe^{3+} + Fe \longrightarrow 3Fe^{2+}$$

The complex obtained showed the Mössbauer spectrum(Fig.5.7) which contained two iron sites, one is consistent with iron(II) and the other iron(III) and this is a reasonable proof that the contamination of iron(III) in this perchlorate complex is quite extensive.

From this observation it is noteworthy to mention that without the use of Mössbauer technique the green perchlorate formulated as Fe(pyCOpy)(pyCOpy-EtOH)$(ClO_4)_2$ could be believed to be plausible as shown by the other phsical evidence and this proves the usefulness of the Mössbauer technique.

Fig.5.6 Mössbauer spectrum of the solid obtained from the reaction of $Fe(ClO_4)_2.6H_2O$ with di-2-pyridylketone

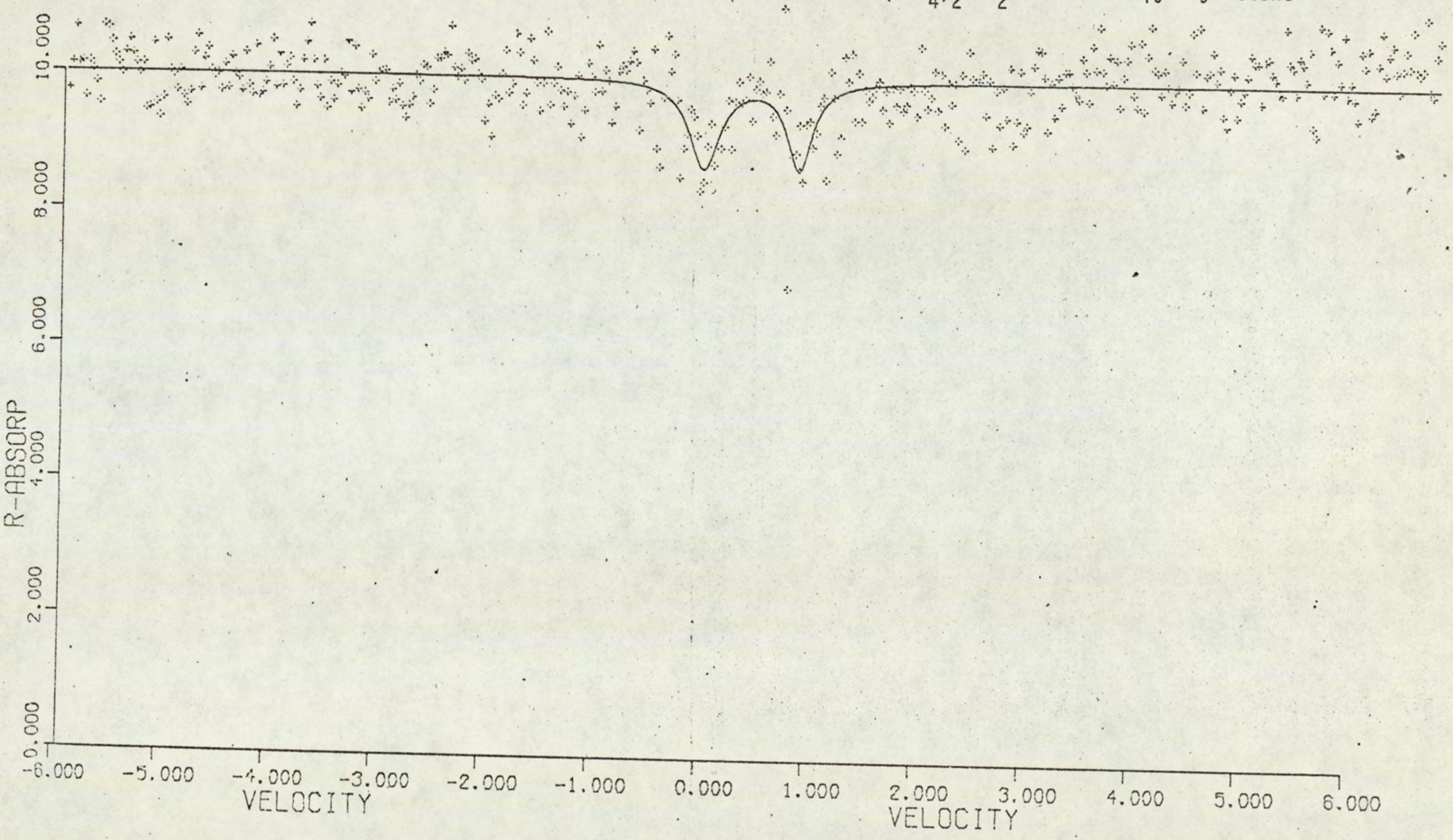
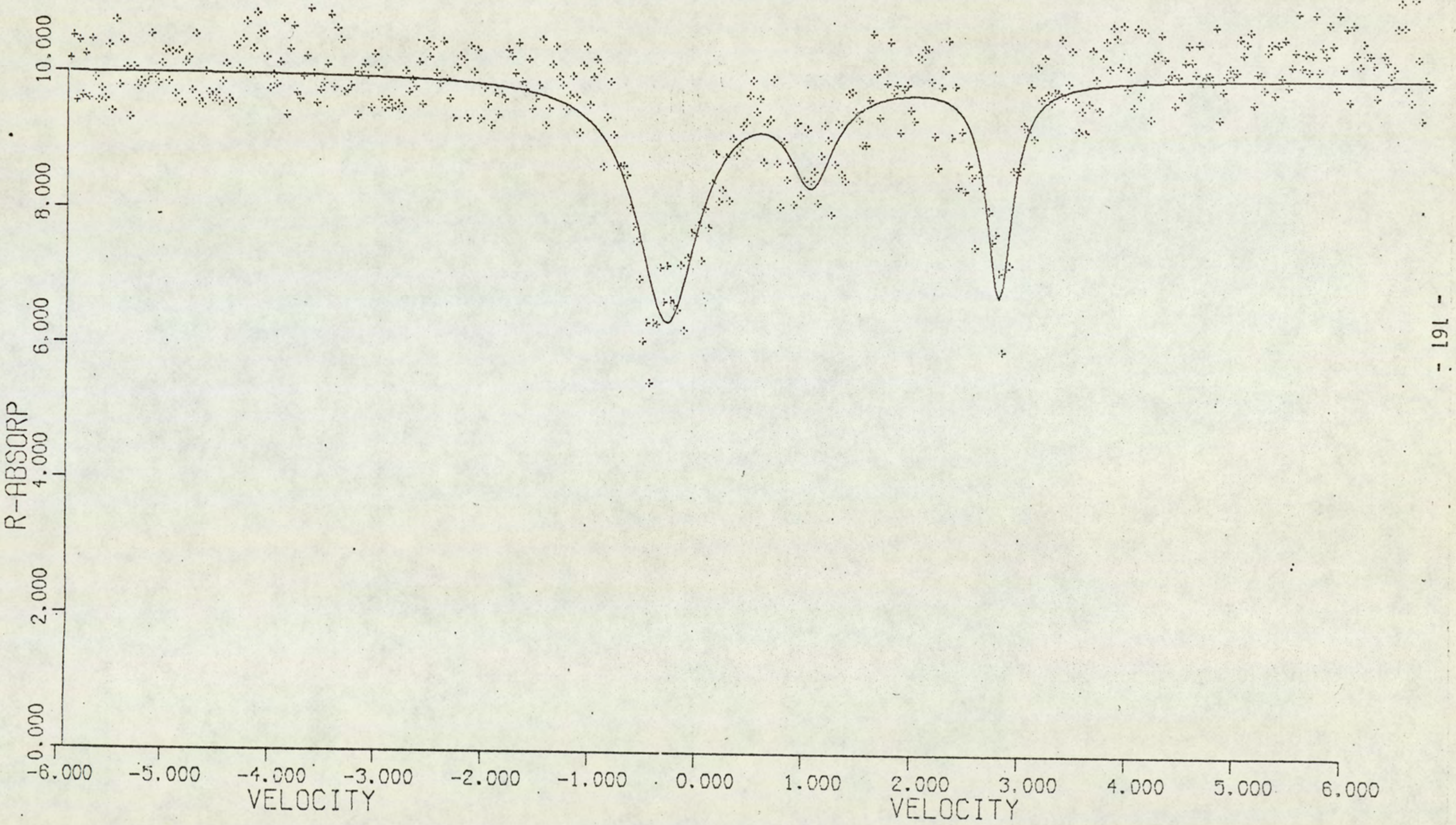


Fig.5.7 Mössbauer spectrum of the solid obtained from reaction of Fe$(ClO_4)_2$ (after treated with iron powder) with di-2-pyridylketone.



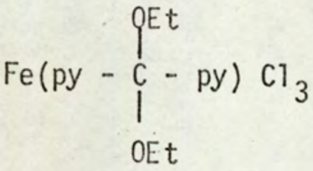
An iron(III) perchlorate complex of di-2-pyridylketone was prepared by refluxing ferric perchlorate hexahydrate with di-2-pyridylketone in ethanol, the pale white complex formulated as $Fe(pyCOpy)(pyCOpy\text{-}EtOH)_2(ClO_4)_3.H_2O$ was obtained. The infra-red spectrum of the complex showed the presence of ν(OH) at 3500 cm^{-1} and the extensive hydrogen bonding. The band at 1695 cm^{-1} appeared only as a very weak band which is very unlikely to account for ν(C=O) vibration of (N,N) mode ketonic ligand. The upward shift of the ν(C=N) ring mode to 1605 cm^{-1} supported the ethanolation of the ligand,it was also observed that the medium to strong band at 1530 cm^{-1} appeared in the spectrum and this was very likely to result from the (N,O) mode of co-ordination of the ketonic ligand, this (N,O) mode of co-ordination was also observed in the mixture of iron(II) and iron(III) perchlorate discussed earlier and the position of the ν(C=O) in (N,O) mode co-ordination corresponds reasonably well with 2-benzoylpyridine complexes which have only (N,O) mode of co-ordination of the ligands. The broad strong band at 1090 cm^{-1} showed the ionic character of the perchlorate group and this was supported by the molar conductivity in nitromethane of 220 ohm^{-1} cm^2 $mole^{-1}$ which suggested a 1:3 electrolyte.

The magnetic moment of this iron(III) perchlorate complex was found to be 5.70 B.M. corresponding to the lower-end-value of the experimental moments 5.7 - 6.0 B.M. shown in the book by Lewis and Wilkins(135) for the high spin octahedral complex. Iron(III) with $^6A_1$ ground term S = 5/2) usually has moments close to the spin-only value of 5.92 B.M., as there are no other states with the same multiplicity; large deviations from the spin-only value cannot be due to the mixing in of excited states into ground states, although sometimes high-order perturbations are probably responsible for the slight deviations, any significant deviations may arise from either impure material i.e. Fe_2O_3 is present or possible dimer formation which through anti-ferromagnetic interaction can lead to low μ_{eff} values.

The electronic spectra of high spin iron(III) complexes are not well studied, in a cubic field the ^6S free ion term transforms into $^6A_1$, no other spin-sixtuplet exists so all d-d transitions are spin forbidden, therefore only the very weak spin forbidden bands are observed. These bands probably occur from the mixing of spin quartet states with the ground state via spin-orbit coupling, another main reason for the difficulty in assigning the electronic spectrum of an iron(III) complex is the great tendency of the trivalent iron to have charge transfer bands in the near ultraviolet which have strong low energy wings in the visible to obscure almost completely, or completely in some cases, the very weak spin forbidden d-d bands. In the complex $Fe(pyCOpy.EtOH)_2(pyCOpy)(ClO_4)_3.H_2O$ three weak bands were observed at 9.0 kK, 18.4 kK and 21.2 kK which probably arise from the mixture of charge transfer band and spin forbidden d-d bands.

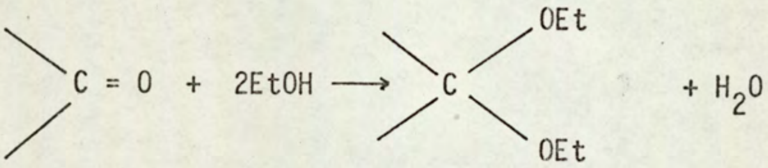
It is unfortunate that a good quality Mössbauer spectrum could not be obtained from this iron(III) perchlorate complex, the most information that could be deduced from the poor spectrum is that the isomer shift δ of 0.45mm sec^{-1} can be classified as the value of high-spin iron(III) complexes (0-0.6mm sec^{-1})(138b), the asymmetric shape of the band suggests the doublet structure but the quadrupole splitting is not measured due to the poor quality of the spectrum.

The other yellow iron(III) complex of di-2-pyridylketone was prepared by refluxing anhydrous ferric chloride with di-2-pyridylketone, the complex obtained was shown by the analysis to be formulated as



$$\mathrm{Fe}(\mathrm{py}-\overset{\mathrm{OEt}}{\underset{\mathrm{OEt}}{\mathrm{C}}}-\mathrm{py})\,\mathrm{Cl}_3$$

In this case the ligand instead of forming a hemiacetal as found in the other cobalt, nickel, and copper complexes has formed an acetal.



The i.r. spectrum of the complex contains no bands than can be attributable to ν(OH) and this can eliminate the hemiacetal structure of the ligand since in hemiacetal ν(OH) vibration should be observed.

The (N,N) mode of co-ordination of the characteristic ν(C=O) stretching vibration is not present and this includes the absence of the band at 1530 cm^{-1} assigned as ν(C=O) vibration in (N,O) mode co-ordinated ligand as found in the iron(III)perchlorate complex. The upward shift of the ν(C=N) ring mode vibration also suggests the ethanolation of the ligand. From the evidence of the i.r. spectrum it is clearly indicated that the carbonyl group of the ligand is attacked to form the acetal as shown in the equation above. From the evidence of the analysis and near i.r. spectrum the structure of the complex could possibly be either monomeric five co-ordinated iron(III) complex which the acetal ligand functions as a bidentate or monomeric

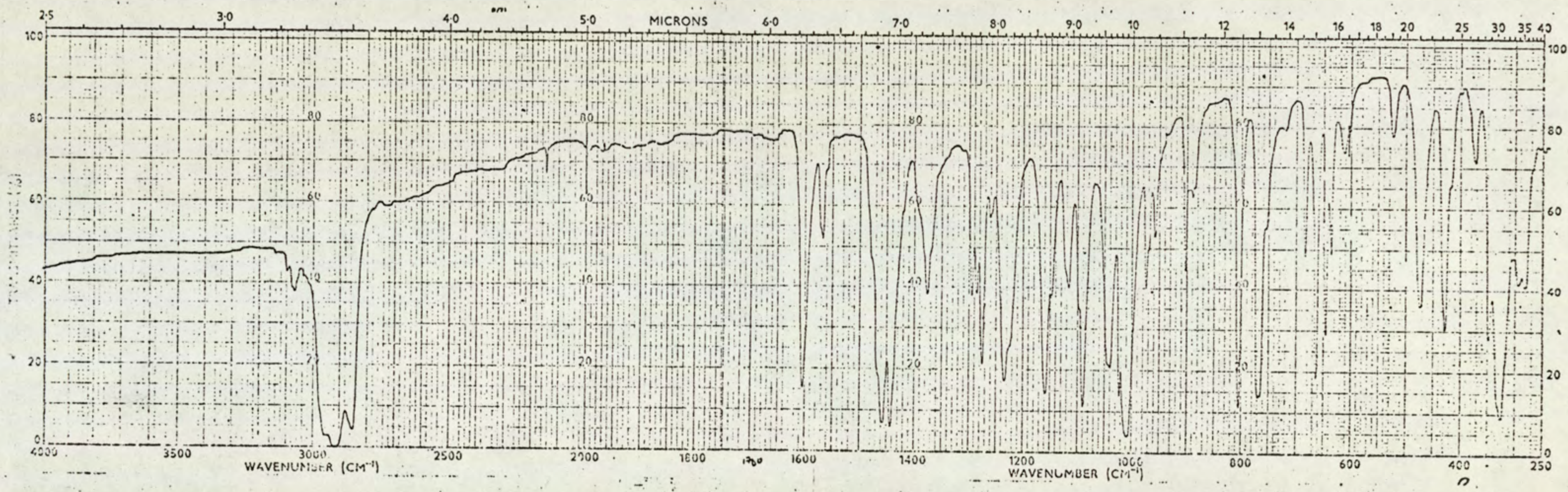
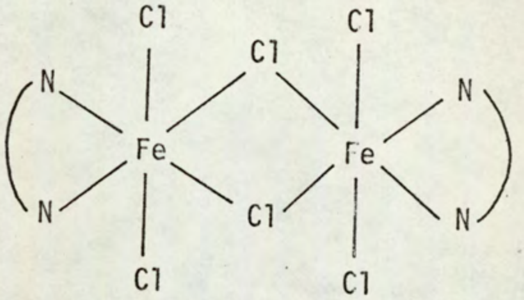
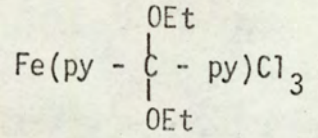


Fig. 5.8 Infrared spectrum of complex $\mathrm{Fe(py - \underset{OEt}{\overset{OEt}{C}} - py)Cl_3}$

six co-ordinated iron(III) complex in which the acetal acts as terdentate ligand by using 2 N of pyridyl ring and one O of-OC_2H_5 group. Another possibility is the six-co-ordinated dimeric structure with chlorine bridging:



Far infra-red spectrum of the complex could possibly be used to differentiate between these monomeric and dimeric structures. In the monomer case three bands due to iron-chlorine stretching vibrations would be expected but four bands would be expected for the dimer case, two will be due to the terminal ν(Fe-Cl) vibrations and the other two of the bridging ν(Fe-Cl). Preparation of iron(III) bromide complex (in the hope that similar type of complex might occur and be useful for the comparison and aid in assigning iron-halogen stretching vibrations) was not successful, the solid obtained does not give a satisfactory elemental analysis. After comparison with spectrum of the free ligand and other complexes in trying to eliminate the bands that might arise from ligand mode vibrations or other vibrarions, four bands were left and will be tentatively assigned as ν(Fe-Cl)stretching vibrations, the higher wave number ones at 326 cm^{-1} and 347 cm^{-1}. were probably due to the terminal iron-chlorine stretching vibrations and the lower ones at 283 cm^{-1} and 293 cm^{-1} might be the bridging ν(Fe-Cl) stretching vibrations.

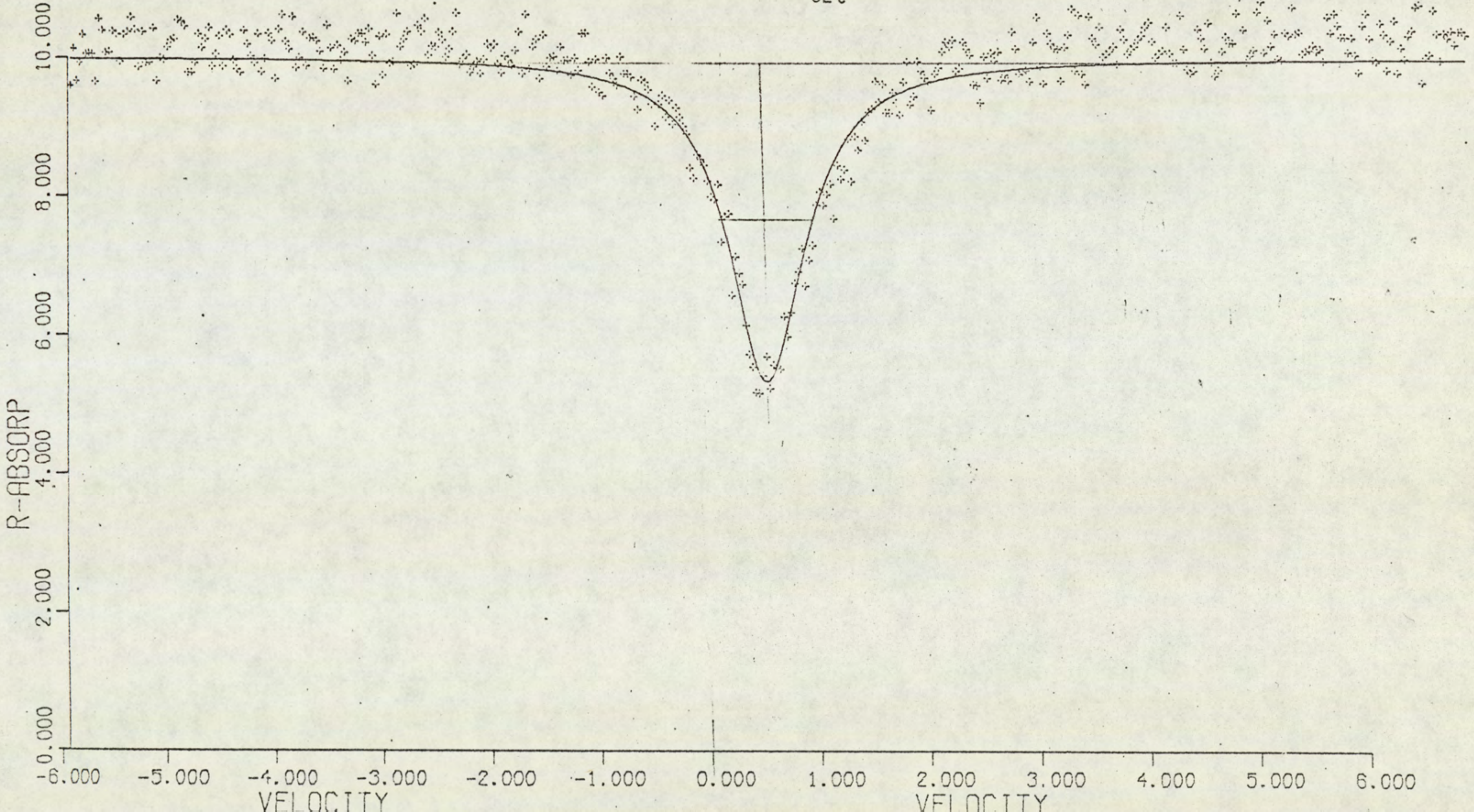
From the evidence of this far-i.r. spectrum, the dimeric structure of the complex  $Fe(py - \overset{OEt}{\underset{OEt}{C}} - py)Cl_3$ might be correct. The conductivity measurement showed that the complex is a non-electrolyte.

The magnetic moment of 6.2 B.M. is slightly higher than the range usually found for high spin octahedral iron(III) complex (5.7-6.0 B.M.) this could possibly be due to the slight contamination of some impurities in the complex, the spin-orbit coupling is not considered since $^6A_1$ ground term have no other terms with the same multiplicity. The electronic spectrum of the complex consists of the charge-transfer bands and some weak d-d spin forbidden bands, four weak bands were observed at 10 kK, 11.5 kK, 17.2 kK and 19.5 kK consistent with high spin iron(III) octahedral complex.

The Mössbauer spectrum of this ferric chloride complex is consistent with the spectra generally obtained for high spin iron(III) complexes(138b), the isomer shift is found to be 0.56 mm sec^{-1} (w.r.t. stainless steel), the spectrum, Fig. 5.9, shows evidence of a small quadrupole doublet which is just resolved and the value of $\Gamma_{\frac{1}{2}}$ of 0.8 mm sec^{-1} also establishes that the peak is not single. The quadrupole splitting ΔE_Q was measured as 0.15mm sec^{-1} which is implied that the environmental symmetry of the complex is slightly distorted from octahedral structure.

It is generally observed that when di-2-pyridylketone complexes are formed, the carbonyl group of the ligand is generally attacked leading to the formation of hemiacetal or in the case of ferric chloride complex, acetal.

Fig. 5.9 Mössbauer spectrum of complex $Fe(py - \overset{OEt}{\underset{OEt}{C}} - py)Cl_3$



The formation of hemiacetal was believed by Feller & Robson(42) to relieve the steric strain in the ligand, but as pointed out earlier in the general introduction (Chapter 1) the flexibility of the ketonic ligand is quite sufficient and the molecule need not be planar which can avoid the non-bonded H-H interaction. An experiment was carried out to check the effect of acidity on this ketal formation by treating di-2-pyridylketone with acid, the i.r.spectrum of the product does not contain the band at 1690 cm^{-1} of $\nu(C=O)$ vibration which might imply that ketal formation has occurred. It was known that under the influence of dry hydrogen chloride a typical aldehyde adds a molecule of ethyl alcohol to form a moderately stable hemiacetal, which combines with a second molecule of alcohol and yield a stable acetal (see Page 21).

Acetal formation is reversible and acetals are hydrolyzed easily with water and a mineral acid catalyst. Acetals are considerably more stable to alkalis than acids, and they are much more stable than free aldehyde to basic reagents and oxidising agents. Ketones are less reactive and are not convertible satisfactorily by acid-catalysed reaction with methanol or ethanol but may be prepared from the ketone and an orthoformate ester(38):

$$R_2CO + HC(OC_2H_5)_3 \overset{H+}{\rightleftharpoons} R_2C(OC_2H_5)_2 + HCO.OC_2H_5$$

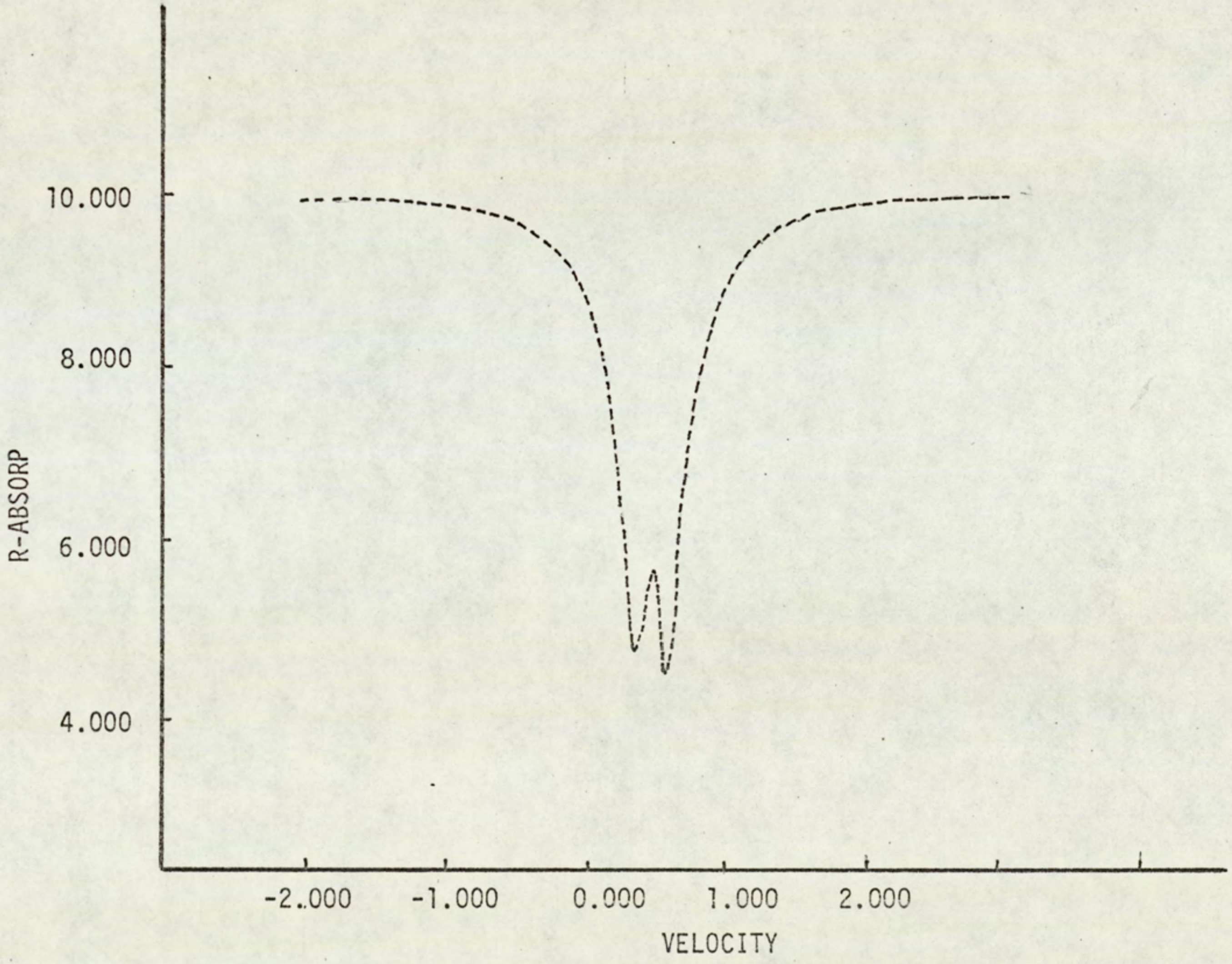
In preparing some complexes of di-2-pyridylketone, triethylorthoformate has been used as a solvent so it is possible that this accounts for the hemiacetal or ketal formation. Reactions using other catalysts rather than acids in the formation of acetals are also known, $ZnCl_2$ has been used as a catalyst in the conversion of 1:2 glycols into cyclic acetals(140). Ammonium chloride or ferric chloride could act as catalyst in ketal formation(141). In the ferric chloride complex the high acidity of the starting material ferric chloride might be responsible for the acetal formation of the ligand rather than the steric strain of the ligand invoked by others(42).

The last iron complex prepared in this work is the thiocyanate complex which was shown by the analysis to be formulated as $Fe(pyCOpy)_2(NCS)_2$. The basic feature of the i.r. spectrum of the complex is similar to the other unattacked carbonyl ligand complexes i.e. $Co(pyCOpy)_2Cl_2$, $Fe(pyCOpy)_2Cl_2$, no ν(OH) band was observed and the ν(C=O) band was found at 1680 cm^{-1} consistent with an (N,N) mode of co-ordination of the ligand. The ν(C=N) ring mode vibration at 1590 cm^{-1} is not shifted which suggests the unattacked carbonyl group of the ligand. The bonds due to NCS group were also present in the complex. The thiocyanate group exhibits three fundamental frequencies i.e. ν_1(C-N) stretch, ν_2(N-C-S) bend and ν_3(C-S) stretch. Since thiocyanate as a di-functional ligand the positions of ν_1, ν_2 and ν_3 depend on whether these groups are attached to the metal ions through N or through S. For N-bonded thiocyanate the following absorption ranges are proposed,
ν_1 = 2040 - 2080 cm^{-1}, ν_2 = 465 - 480 cm^{-1}, ν_3 = 780 - 800 cm^{-1}
for the S-bonded, ν_1 = 2080 - 2120 cm^{-1}, ν_2 = 410 - 470 cm^{-1},
ν_3 = 690 - 720 cm^{-1} (142). The thiocyanate absorption bands in this $Fe(pyCOpy)_2(NCS)_2$ complex are found at 2090 cm^{-1} (ν_1), 805 cm^{-1} (ν_3) and 480 cm^{-1}(ν_2) which indicated the N-bonded thiocyanate ligand.

The diamagnetism of $Fe(pyCOpy)_2(NCS)_2$ indicates a $^1A_1$ ground state for iron(II) this seemed to be rather surprising since in the complexes $Fe(phen)_2(NCS)_2$ and $Fe(dipyam)_2(NCS)_2$ at room temperature they are high spin complexes with $^5T_2$ ground term(143). The ligand field strength of di-2-pyridylketone in cobalt and nickel complexes was found to give rise only to high spin complexes and is lower than phenanthroline. The diffuse reflectance spectrum in the visible region showed two strong bands at 24.9 kK and 16.3 kK and from the very high intensity of the bands these will be assigned as the charge transfer bands, the higher one probably is the internal ligand transition. The spin-forbidden band $^1A_{1g} \longrightarrow {}^3T_{1g}$ generally observed in the complexes such as $Fe(bipy_3)Br_2.6H_2O$ (11500 cm^{-1}), $[Fe(phen_3)]^{2+}$ (12,260 cm^{-1}), $[Fe(phen)_2(CN)_2]$ (12500 cm^{-1})(143) could not be observed in this case due to its weakness and being obscured by the charge transfer band. It is seen that the diffuse reflectance spectrum agreed with the $^1A_{1g}$ ground state iron(II), low spin iron(II) complexes generally have two charge transfer bands and one weak d-d spin forbidden in the visible region(145). The complex is too insoluble to obtain useful data such as molecular weight and conductivity.

The Mössbauer spectrum of the complex (Fig. 5.10) showed a doublet structure, the isomer shift of 0.50 mm sec^{-1} (w.r.t.stainless steel) is consistent with that reported for spin paired iron(II) complexes (0.3 - 0.5 mm sec^{-1} w.r.t. stainless steel) the quadrupole splitting ΔE_q of 0.22 mm sec^{-1} indicated that the distortion from octahedral symmetry is not too large. The possibility that the complex might have the ionic structure of $[Fe(pyCOpy)_3]^{2+}[Fe(pyCOpy)(NCS)_4]^{2-}$ is

Fig. 5.10 Mössbauer spectrum of $Fe(pyCOpy)_2(NCS)_2$



rather unlikely, since in this structure two iron atoms were situated in different environments and would be expected to give different quadrupole splittings which should be observable (except in the case when the two quadrupole splittings and chemical isomer shift are coincident). The presence of the clear single doublet suggested favourably that iron was present in the only one distorted octahedral environment(that is $Fe(pyCOpy)_2(NCS)_2$). Fitzsimmons et al.(144,145) found that in complexes of the type MA_4B_2; (A and B are mono functional ligands) and MA_2B_2; (A is difunctional ligand and B is monofunctional ligand) the differentiation between cis and trans isomers could be made by comparing the values of quadrupole splitting. It was found that the quadrupole splitting of the trans-isomer should be twice as large as that of the cis isomer(for example ΔE_Q value of 0.59 mm sec^{-1} was found for the complex trans-$Fe(CN)_2(CNEt)_4$ while the value of ΔE_Q 0.29 mm sec^{-1} was obtained for the complex cis-$Fe(CN)_2(CNEt)_4$(145).) The ΔE_Q value of 0.2 mm sec^{-1} obtained for the complex $Fe(pyCOpy)_2(NCS)_2$ is in line with values obtained for cis-compounds above but this will not be conclusive to prove the stereochemistry, although the i.r. spectrum of the complex showed a slight splitting of the ν(NCS) vibration at 2690 cm^{-1} to suggest a cis structure, but again this i.r. evidence is very inconclusive since the splitting might occur from other causes.

It is appropriate to summarise the work in this chapter that most of the purposes have been fulfilled and some clarification of the works reported by previous workers were made together with some new observations. The anomolous magnetic moment of the cobalt complex(47) was shown to be due to the contamination by cobalt(III); the ethanolation or aquation of the ligands are accompanied by the upward shift of the ν(C=N) mode of pyridyl rings which might be due to the fact that the electron-withdrawing character of carbonyl group is destroyed, hence the bondings in pyridyl ring is strengthened and leads to an increase in the ring stretching vibration(42). The ethanolation or aquation was shown to depend on the pH of the system and probably not due to the steric effect suggested by Feller and Robson(42). In copper complexes the bands at 1478 cm^{-1} assigned as ν(C=O) of an (N,O) mode of co-ordination of the ligand(41) is not correct but the (N,O) mode of co-ordination was found to occur in the iron(III) perchlorate complex which has ν(C=O) band at 1530 cm^{-1}. The steric strain invoked for preferential formation of cis complex of complexes of the type $M(pyCOpy)_2Cl_2$ is probably not correct because the ligand is shown to have high flexibility of the ring and need not be planar. The use of far infra-red spectra to differentiate between cis and trans isomers is not conclusive and must be treated with reservation. The di-2-pyridylketone ligand is considered as a weak field ligand in most of the complexes studied except, surprisingly, in the complex $Fe(pyCOpy)_2(NCS)_2$ when the compound is shown to be low spin complex.

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