PHOSPHINE AND AMINE
COMPLEXES
OF
TRANSITION METALS

by

JAMES McAVOY B.Sc. A.R.I.C.

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Abstract.

Amine complexes for some first row Transition Metal perchlorates and tetrafluoroborates have been prepared, where the amines are pyridine, γ-picoline and quinoline. The preparative procedure is comparatively simple. The desired salt was obtained by the reaction of the carbonate with either aqueous perchloric or tetrafluoroboric acids. Various methods have been employed for the preparation of the complexes. Thus, the ligand was added to an ethanolic solution of the salt hydrate, when, in some instances, the complex precipitated. Several new complexes have been prepared in this study. These are described by the general formula:- $L_nM X_2$

where L = pyridine or γ-picoline for n = 4.

L = quinoline for n = 2.

M = Mn, Co, Ni, Cu or Zn.

X = perchlorate or fluoroborate.

The stoichiometries of the complexes are discussed, and their structure deduced in terms of the spectra in the near and far infra-red, and the reflectance spectra in the ultraviolet and visible regions. Where possible magnetic moments have been obtained, and are related to the proposed structures of the complexes.

Perchlorate and tetrafluoroborate ions have Td symmetry. Evidence is presented for some co-ordinate bond character between the anion and the metal. The effect of this on the symmetry of the anion is discussed. The stretching frequencies of the metal-nitrogen bond in the far infrared are interpreted in terms of the Irving-Williams order, and it is shown, where relevent, that ring skeletal vibrations also follow this sequence. The effect of ligand mass and basicity on the stereochemistry of the complexes is also discussed.

The number of compounds known having phosphorus or nitrogen bonded to a metal, which in turn, is also bonded to fluorine, are relatively few. A method, involving the use of liquid anhydrous hydrogen fluoride, has been found for the preparation of such compounds. The metals studied were confined to the second and third row Transition Elements, although attempts are described to extend the study to include some first row Transition Metals. Derivatives of the unknown platinum difluoride have been prepared in which the compound is stabilised by phosphine ligands. Some reactions of these complexes have been investigated, and phosphine metal carbonyls obtained. Few carbonyl fluorides are known, and in general, they are difficult to prepare. In this study, several new carbonyl fluorides have been obtained in which the complexes are stabilised by the presence of phosphorus or nitrogen donor ligands. Examples of such compounds are:-

$(P(OPh)_3)_2Pt(CO)_2F_2$, $(PPh_3)_2Os(CO)F_3$, $Py_2Mo(CO)_2F_2$.

where Ph = phenyl and Py = pyridine.

In these systems, hydrogen fluoride acts as an oxidising agent. Thus, for example, tetrakis(triphenylphosphine)platinum(0) is oxidised to bis(triphenylphosphine)platinum(11)fluoride, and tripyridinemolybdenum(0)tricarbonyl is oxidised to bispyridinedicarbonylmolybdenum(11)fluoride. The spectra of the complexes in the near infra-red are recorded, and the influence of the fluoride ion on the carbonyl stretching frequency is discussed.

The reaction of liquid anhydrous hydrogen fluoride on tripyridinemolybdenumtricarbonyl gives, as a by-product, a complex analysing to a ten co-ordinate molybdenum(VI) species. Attempts have been made to investigate the extent of this co-ordination number in Group VIa Metals, and some evidence is presented in support of the formulation.

Introduction.

The relative affinities of ligand atoms or molecules of Group Vb Elements for acceptor molecules or ions, discussed by Arhland et al[1a], largely depends on the acceptor concerned. Two regular features are apparent, however, in spite of this seeming lack of uniformity. There is a very great difference, in general, between the coordinating affinities of nitrogen donors from donors of the other elements of this Group. The other feature concerns the acceptor species. Generally speaking, there are two classes of acceptors; those which form their most stable complexes with the first atom of the Group, designated class (a), and those which form their most stable complexes with the second or subsequent atom, designated class (b). Most metals in their common valency states are class (a) acceptors, and consequently the affinities of ligands for these acceptors follow their basicities, except where steric and other factors become important. Class (b) acceptors are less numerous, and, with one or two exceptions, appear to be confined to the Transition Metals. This suggests that the character type depends on the availability of electrons from the lower d orbitals of the metal for pi bonding. A modified form of Arhland's classification has been drawn up by Booth[1], and this is reproduced in Fig. 1.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

Table 1.

To the right of the line are the elements which, in their normal oxidation states are of the class (b) type, ie. the coordinating affinities of the donor atom are in the sequence $N < P > As > Sb > Bi$. All these metals form stable phosphine complexes, less stable arsines and much less stable stibine complexes. To the left of the line, the metals tend to class (a) character, and the sequence of stability changes to $N > P > As > Sb > Bi$. However, the border line between the two types is quite diffuse, and this may be attributed to the variable valency exhibited by the elements in the border regions, ie. it is possible to classify the elements not only with respect to position in the Periodic Table, but also with respect to the oxidation states of the metals. In this context metals to the left of the Nickel Group tend to class (a) character for the higher oxidation states, and to class (b) character for the lower oxidation states; since there are more d electrons available for dative pi bonding the lower the oxidation state. Thus, iron(III), in its spin free complexes, belongs to class (a), but iron(o) is undoubtedly class (b)[1a].

The formation of pi bonds depends, not only on suitable filled metal orbitals, but also on the availability of vacant ligand orbitals of the appropriate symmetry and energy. This requirement is fulfilled in phosphines, which act as sigma bond donors and pi bond acceptors, the empty 3d orbitals of the phosphorus atom being capable of interaction with filled nonbonding d orbitals of a Transition Metal. Such orbitals on nitrogen are incapable of this kind of interaction because of energy considerations. Thus, in general, nitrogen ligands coordinate to a metal by the formation of sigma bonds. This behaviour needs qualification, however, since, if the nitrogen atom is part of an aromatic ring system, eg. pyridine, substituted pyridines, then pi bonding may become possible by interaction of the pi orbital system of the aromatic ring with the suitable d orbitals of the metal. This effect has been discussed by Kraihanzel and Cotton[1b] for pyridine substituted Group VI Metal carbonyls. These authors predict that, as the number of carbonyl substituents decrease, the CO groups remaining have less complete command of the metal d pi electrons, thus increasing metal-pyridine pi bonding to a detectable extent. It should be pointed out, however, that pyridine, and substituted pyridine, Group $\overline{\underline{VI}}$ Metal carbonyls are rather unstable, and decompose with loss of amine on exposure to the atmosphere, whereas phosphine substituted metal carbonyls are quite stable.

It has recently been shown[75], however, that $M \rightarrow Py$ pi bonding, where Py is pyridine, may be controlled by the nature of the halogen in complexes of the type $CoPy_2X_2$, where X is chlorine, bromine or iodine. These authors consider that steric effects are less important than electronic effects except when pyridine is replaced by its 2-methyl analogue. The influence of steric factors in complexes of this type have also been noted by Allan et al[76], who report the order of ligand field strength for tetrahedral CoL_2X_2 complexes as $Py \approx \beta\text{-Pic} \approx \gamma\text{-Pic} > \alpha\text{-Pic} >$ Quinoline, where L is the amine and X is a halogen. This order of ligand field strength does not follow the order of basicity of the ligands, which, measured by pK_{α} value[77], is $\gamma\text{-Pic} > \alpha\text{-pic} > \beta\text{-Pic} > Py >$ Quinoline (Pic is picoline). The order of ligand field strength observed, must be associated with increasing steric hindrance of the particular amine. The order of basicity, however, is unaffected by steric factors.

The ligands of Group $\overline{\underline{Vb}}$ studied in the present work were confined to pyridine, γ-picoline, quinoline and triphenylphosphine. The latter was chosen because it had already been showen that it stabilised carbonyl fluorides of some Platinum Group Metals. The others were chosen in an attempt to characterise infrared active metal-nitrogen vibrations, and to study the effect of increased steric hindrance on these vibrations.

Chapter 1.

Phosphine Metal Fluoride Complexes.

Introduction.

A recent review article by G. Booth[1] discusses the present knowledge of phosphine complexes. Tertiary phosphines show a marked tendency to form nonionic complexes, readily soluble in organic solvents. This is in contrast to the salt-like complexes formed by ammonia and amines. Phosphines are particularly useful and versatile ligands, in that they form compounds containing both the highest and lowest valency states of the Transition Metals. The characteristics of phosphines as ligands are not very different from those of carbon monoxide (c.f. Chapter 2). Phosphines have empty 3d orbitals capable of accepting pi-electrons, and, in addition, they have a lone pair of electrons capable of forming a sigma-bond. Thus, phosphines are strong bases, and combine strong sigma-bond donor functions, such as are found in amines with strong pi-bond acceptor properties, such as is the case with carbon monoxide.

These effects are also evident in phosphites. Triphenylphosphite might be expected to exhibit stronger bonding properties than triphenylphosphine, by virtue of the fact that conjugation between the lone pair of electrons on the phosphorus atom and the aromatic ring, could be expected to be hindered by the interposition of the oxygen atom, thus rendering the phosphorus lone pair more available for sigma-bond formation. This argument appears to be substantiated by the fact that triphenylphosphine is displaced by triphenylphosphite in metathetical reactions[2,3].

Attempts to prepare complexes with trialkylphosphites have, in the past, had only limited success. Trialkylphosphites form complexes with heavy Transition Metals, eg. platinum(11), and a few post Transition Metals, eg. mercury(11). Reactions with first row Transition Metals, eg. cobalt(11), nickel(11), yield intractable oils, although some reaction is indicated by the observation of colour changes[4]. Some of the difficulty experienced in attempts to prepare complexes of trialkylphosphites must be ascribed to steric hindrance. However, a new alkylphosphite, first prepared by Verkade and Reynolds[5], has shown remarkable complexing properties[4,6]. Its ability to form stable, crystalline complexes is derived from the fact that the lone pair of electrons on the phosphorus atom are readily available for co-ordination, and that steric hindrance is reduced to a minimum. The alkyl moiety of the molecule is a ring system, which is essentially strainless. Studies by nuclear magnetic resonance spectroscopy[4] show the molecule to have the structure depicted in Fig. 1.1

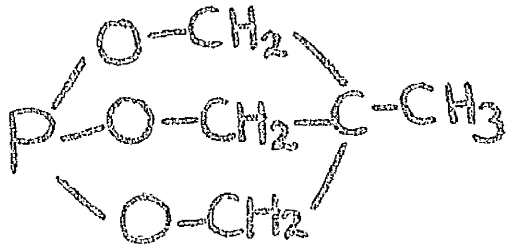


Fig. 1.1

This ligand, systematically named 4-methyl-2,6,7-trioxa -1-phosphabicyclo(2,2,2)octane (hereafter referred to as M.T.P.), also displaces triphenylphosphine in metathetical reactions.

In many cases, however, the acceptor character of the phosphine may be at least as important as the donor character. Thus trifluorophosphine yields stable complexes, and in this ligand the donor character of the phosphorus lone pair is non-existant due to the electronegativity of the fluorine atoms. Since no complex is obtained when trifluorophosphine is reacted with boron trifluoride; and, since a very stable complex results by reaction of platinum(II)chloride with trifluorophosphine, Chatt[7] reasons that suitable d orbitals are a requirement for the formation of stable trifluorophosphine complexes. The lack of donor character in this ligand, however, is more than offset by the much enhanced electron affinity of the empty 3d-orbitals of the phosphorus atom. Because of the increased pi-bonding character, trifluorophosphine shows even greater similarity to carbon monoxide than do the tertiary phosphines. In a complex of the type $X_2M(PR_3)_2$, where M is a Transition Metal, as the electronegativity of the R atoms or molecules increases, the drift of electrons forming the pi-bond will partially neutralise the inductive effect of the R groups. Hence the availability of the lone pair forming the sigma-bond will not be impaired to the same extent as would occur in the absence of the pi-bond.

Phosphine metal halides are well known where the halogen is chlorine, bromine or iodine. There are, however, relatively few characterised complexes containing phosphorus and fluorine bonded to the same metal. Until recently the only such complexes were the derivatives of trifluorophosphine discussed by Peacock[8], viz, PF_3OsF_2, PF_3IrF_2, PF_3PdF_2 and PF_3CoF. No details as to the structure of these compounds have been given, although the latter two are reported to be diamagnetic. Peacock also suggests that Moissan's[9], platinum compound should be formulated PF_3PtF_2. As such, the compound is a presumably have a phosphorus-platinum bond analogous to would

presumably have a phosphorus-platinum bond analogous to

the phosphorus-nickel bond in Wilkinson's[10] $Ni(PF_3)_4$.

If these adducts owe their stability to pi-bonding then the adducts of sulphur tetrafluoride, selenium tetrafluoride and bromide trifluoride, with Transition Metal fluorides, could also be considered to possess bonding from suitable d-orbitals of the Transition Metal to an unoccupied d-orbital of the non-metal. Some adducts reported involving these ligands are recorded in Table 1.1

Adduct.		Reference.
$MF_5.BrF_3$	M = Os, Ru, Ir	11, 12
$MF_4.2BrF_3$	M = Pt	13
$MF_3.BrF_3$	M = Pd, Au	14
$MF_5.XF_4$	M = Os, Ir, X = S, Se	12
$MF_4.2SeF_4$	M = Pt	8
$MF_3.SeF_4$	M = Pd, Au	14

Table 1.1

The adduct formed by the action of bromine trifluoride on platinum(IV)fluoride[13], could be a complex in which there is interaction between lone pairs of electrons on the bromine atom and the platinum, although it is usually considered as being ionic.

The first phosphine metal fluoride prepared, involving triphenylphosphine, was that reported by Muetterties[15].

Reaction of tungsten hexafluoride with triphenylphosphine gives a 1:1 adduct, which, on the basis of n.m.r. studies, has been assigned the structure shown in Fig. 1.2. This structure is supported by the fact that the complex behaves as an electrolyte in liquid sulphur dioxide.

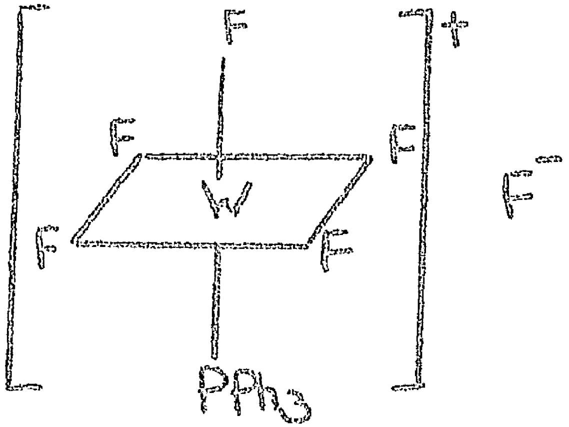


Fig. 1.2

The range was extended by Moss[16], who reports the preparation of bis(triphenylphosphine)platinum (11)fluoride, the palladium analogue and tris(triphenylphosphine)hydridoiridium(111)-difluoride. This work was repeated in the present study, but only the existance of the platinum compound could, unequivocally be confirmed. The yield of product from the iridium reaction precluded elemental analysis determination. However, the spectrum of the complex was similar to that reported by Moss. The palladium compound could not be prepared because of the instability of the intermediate.

Moss attempted to extend the series to the first row Transition Metals, particularly to Nickel. Attempted fluorinations of bis(tri-n-propyl)nickel(11)chloride or bis(triphenylphosphine)nickel-dicarbonyl, in a variety of organic solvents, with silver fluoride or hydrogen fluoride resulted in the formation of nickel fluoride, identified by X-ray powder photography. Moss' studies, however, showed that hydrogen fluoride was a useful fluorinating agent for the preparation of phosphine fluorides of the second and third row Transition Metals.

During the last few years many molecular hydrides have been prepared, showing that metal-hydrogen linkages are much more common than was previously thought[17], and complexes of this type have been established for the metals of the Transition Groups V to IX. The study of such species has been facilitated by the advent of nuclear magnetic resonance spectroscopy. The proton in the metal-hydride has a characteristic high field shift[18]. This technique has been used to show that protonation of the metal atom in metallocenes[19], carbonyls[20], and phosphine metal carbonyls can be achieved by reaction with strong acids such as concentrated sulphuric acid, trifluoroacetic acid and boron trifluoride monohydrate. Another very useful method is the reduction, with borohydride, of compounds such as phosphine metal halides or cyclopentadienyl metal halides[21,22].

A very interesting method of producing hydrides, and one which has also been shown to result in reductive carbonylation, is that involving the reaction of a Transition Metal halide, a substituted phosphine or arsine and an alcohol, usually in the presence of an alkali. Vaska and Sloane[23] reacted ruthenium and osmium halides with triphenylphosphine and arsine in methyl cellosolve and obtained stable products formulated as $[MX(LPh_3)_3]$, where M is Ru or Os, X is a halogen other than fluorine and L is phosphorus or arsenic. Chatt and Shaw[24], however, showed that the alcohol was involved in the reaction of ruthenium, iridium and osmium halides with diethylphenylphosphine in boiling ethanolic solution. From these reactions they were able to isolate the complexes $IrH_2Cl(PEt_2Ph)_3$, $RuCl_2(CO)_2(PEt_2Ph)_2$ and $OsHCl(CO)(PEt_2Ph)_3$, (Et is ethyl and Ph is phenyl). These findings have since been confirmed by Vaska and Diluzio[25] who have shown that their compounds are in fact carbonyl hydrides. The use of hypophosphorus acid[26] has also resulted in the formation of hydrides such as $[RhCl_2H(AsPh_2Me)_3]$. These complexes were initially incorrectly formulated. Carbonylation of rhodium halides has also been achieved by reaction with tertiary phosphines in hot alcoholic alkali[24,27].

Recent developments with ditertiary phosphines and arsines have led to the preparation of vanadium[28,29], chromium[28,29], molybdenum[30], tungsten[28,29], iron[29], cobalt[29,31], nickel[32], palladium[32,33], and platinum[34], complexes in which the metal is formally in the zero oxidation state. There are relatively few zero valent Transition Metal complexes reported where the ligand is a monotertiary phosphine, and there are no reports of such complexes where the ligand is triphenylphosphine, with the exception of the metals platinum and palladium.

Malatesta and Cariello[35] reported the preparation of the complexes tetrakis(triphenylphosphine)platinum(0) and its palladium analogue. These can be prepared by reaction of the potassium chlorometallite(11) salts in hot alcoholic alkali with triphenylphosphine. Chopoorian[36] et alia suggested that the platinum complex should be formulated as a dihydride. Their evidence for this was based on the identification of chloroform from the reaction of the tetrakis complex with carbon tetrachloride, and from the spectrophotometric titration of the complex with bromine in methylene chloride solution. Alkali titration of a water extract of the resulting solution showed that two equivalents of hydrogen bromide had been produced. Moss[16] agreed with the formulation of these authors and suggested that, by anology, the palladium complex should be similarly formulated.

Since the platinum complex is an intermediate in the formation of the phosphine metal fluoride it was thought relevent to make some attempt to substantiate one or other of the formulations. It had been shown that decomposition of the complex occurred in benzene solution[35]. Consequently, various concentrations of the complex were shaken in a closed flask with benzene at room temperature. A yellow solution was obtained, from which, on standing overnight, a white precipitate was isolated. The infra-red spectrum of this white material, obtained as a nujol mull, showed absorption at 1675cms^{-1} and 815cms^{-1}, which were attributed to metal-hydrogen vibrations[36], and which were not observed in the parent material. The isolation of chloroform from a carbon tetrachloride solution of a hydride species is characteristic of hydrogen bonded to a metal[37]. In consequence, varying concentrations of the complex were dissolved in carbon tetrachloride and allowed to stand at room temperature for intervals of time ranging from two to twenty-four hours. In each case a white precipitate was obtained, the infra-red spectrum of which was identical with that of an authentic sample of bis(triphenylphosphine)platinum(11)chloride. V.P.C. analysis of the filtrates in all cases showed no trace of chloroform, nor could any other such chloro solvent be identified. The tetrakis complex was boiled in distilled water for thirty minutes. The yellow colour of the starting material was discharged and a white solid obtained. The infra-red spectrum of this material also showed absorption at 1675cms^{-1}, although the absorption at 815cms^{-1} was not identified. N.M.R. studies on the yellow tetrakis phosphine complex did not exhibit resonance which could be attributed to hydrogen bonded to a metal.

Unfortunately, at this time, Malatesta[38] published a paper following similar lines to the above experiments, the conclusions of which are identical with the above observations. Malatesta suggests that hydride formation may result from traces of water in the solvent, according to the equation

$$Pt(PPh_3)_4 + H_2O \longrightarrow PtH_2(PPh_3)_4 + OPPh_3$$

On the basis of the evidence presented it was concluded that the parent complex is a zero valent platinum compound.

Bis(triphenylphosphine)platinum(11)fluoride, a derivative of the unknown platinum(11)fluoride can be prepared by passing a stream of anhydrous hydrogen fluoride through a benzene solution of tetrakis(triphenylphosphine) platinum(0). So treated, the solution undergoes a series of colour changes with final precipitation of a white solid.

Alternatively, the zero valent tetrakis complex dissolves in liquid anhydrous hydrogen fluoride, and the same product can be isolated from this solution after removal of the excess acid. The product is soluble in polar solvents such as methylene chloride, chloroform and nitrobenzene. It is stable to concentrated nitric acid and is unaffected by alkali. Because it is insoluble in nonpolar solvents its dipole moment has not been obtained. Some evidence to substantiate the formulation has been obtained from ^{19}F and ^{31}P n.m.r. studies in methylene chloride. It was obvious from these, however, that halogen exchange occurred at the high concentrations necessary for measurement. Such a complex of platinum(II) should have a square planer coordination about the metal. When warmed gently in a suitable solvent, a pink form is obtained, which, on successive recrystallisation, reverts to the original white derivative. By analogy with the corresponding dichloride[39], it is suggested that the white form is the cis isomer. In all other complexes of this type the trans isomer is the more highly coloured[39]. The cis arrangement is also predicted by the Trans Effect[40].

The platinum atom in this, and analogous compounds prepared in this study, appears to be electronically unsaturated. Carbonyls of general formula $L_2Pt(CO)_2F_2$, where L is a phosphorus ligand, can be prepared by pressurising a solution of the complex in anhydrous hydrogen fluoride in a steel bomb. For complexes in which L is either triphenylphosphine or triphenylphosphite, three peaks are observed in the metal-carbonyl region of the infra-red, one strong the other two weak or as shoulders on the main absorption. The pattern of peaks is different from that observed for the complexes $L_2Fe(CO)_2X_2$, where L is triethylphosphine, phenyldiethylphosphine or ethyldiphenylphosphine and X is chloride, bromide, iodide or thiocyanate[41].

Experimental.

For the reactions involving anhydrous hydrogen fluoride, polythene apparatus was used, except in pressure reactions, in which case experiments were carried out in a stainless steel bomb of 25ml capacity. The polythene apparatus consisted of a flat bottom reaction vessel equipped with a screw cap into which was welded polythene inlet and outlet tubes. It proved possible, with suitable precautions, to evacuate this apparatus by attaching the exit tube to a water pump.

Bis(triphenylphosphine)platinum(11)fluoride.

This was prepared according to the method of Moss[16], from tetrakis(triphenylphosphine)platinum(0), which was obtained by the method of Malatesta and Cariello[33].

Tetrakis(triphenylphosphine)platinum(0), (1gm.) was reacted with liquid anhydrous hydrogen fluoride (5-10ml.), in a polythene vessel immersed in an acetone-drikold bath, the anhydrous fluoride being condensed into the vessel from a cylinder. The bath was removed, and the reactants allowed to come to room temperature, when the excess acid was removed in a stream of dry nitrogen. The greyish residue remaining was dissolved in methylene chloride, and this solution stirred into anhydrous diethyl ether, yielding a white precipitate. This was washed with distilled water, followed by diethyl ether and dried in vacuum.

Analysis. C = 57.3%, H = 3.37%, Pt = 25.9% (found)

$(PPh_3)_2PtF_2$ requires C = 57.1%, H = 3.96%, Pt = 25.7% (theory)

Bis(triphenylphosphite)platinum(11)fluoride.

Tetrakis(triphenylphosphite)platinum(0), was prepared from tetrakis(triphenylphosphine)platinum(0) by the method of Malatesta and Cariello[25].

Tetrakis(triphenylphosphite)platinum(0), (2gm.) were treated with anhydrous hydrogen fluoride exactly as described for the phosphine complex. On removing the excess acid, a greyish, viscous liquid was obtained, which was dissolved in methylene chloride (5ml). Attempts to precipitate the complex from anhydrous diethyl ether were unsuccessful. The only solvent found to effect precipitation was n-heptane. Treated successively in this way, the complex was eventually obtained as a white solid.

Alternatively, triphenylphosphite, (0.25g) in methylene chloride (5ml), was added to bis(triphenylphosphine) platinum(11)fluoride (0.2g) in methylene chloride (5ml). The resulting solution, when added to diethyl ether, filtered, washed with ether and dried in vacuum gave 0.15g of a white solid. The complex prepared by either method analysed to the formula $(PO_3C_{18}H_{15})_2PtF_2$

Analysis.

% C	% H	% P	% F	% Pt	
52.75	3.79	7.66	5.0	22.68	(found)
53.05	4.14	8.01	5.08	22.91	(found)
50.65	3.54	7.26	4.45	22.87	(theory)

The analysis for carbon was always high for this complex but the analysis for other elements is satisfactory. The displacement of phosphine by phosphite in this reaction is analogous to the displacement reaction which occurs when tetrakis(triphenylphosphine)platinum(0) is treated with triphenylphosphite[35] or M.T.P. the structure of the latter is shown in Fig. 1.1. The physical properties of the phosphite fluoride are similar to those of the phosphine fluoride. It is stable in both acid and alkali, insoluble in nonpolar solvents, and extremely soluble in polar solvents, particularly halogenated solvents. On warming a solution in methylene chloride a pink form of the complex is obtained, from which the white form can be regenerated by treating with diethyl ether.

Tetrakis(M.T.P.)platinum(0).

(M.T.P. = 4-methyl-2,6,7-trioxa-1-phosphabicyclo(2,2,2) octane).

M.T.P. was prepared by the method of Verkade and Reynolds[5].

Tetrakis(triphenylphosphine)platinum(O), (2.7g) were dispersed in hot ethanol (10ml). The yellow colour of the aryl complex was discharged on adding, with stirring, a hot ethanolic solution of M.T.P. (1.4g). A clear solution was obtained (15 minutes), from which, on cooling, a white precipitate gradually developed. The solid was filtered, washed with hot ethanol and dried in vacuum. The complex analysed to the formula $Pt(PO_3C_5H_9)_4$.

Analysis.

% C	% H	% P	% Pt	
30.56	4.60	15.81	24.6	(found)
30.5	4.61	15.73	24.78	(theory)

The infra-red spectrum of this complex, in the region 4000-7000cms^{-1}, was not particularly different from that of the ligand. No evidence, from infra-red, was obtained which would indicate hydride formation or carbonylation.

Bis(M.T.P.)platinum(11)fluoride.

Tetrakis(M.T.P.)platinum(O), (0.6g) was reacted with liquid anhydrous hydrogen fluoride as described previously. After removal of the excess acid, the crude product, dissolved in methylene chloride, was added with stirring to diethyl ether yielding a slightly pink coloured solid. This was washed with ether and dried in vacuum. The analysis indicates the formation of the bisligand metal fluoride.

Analysis.

% C	% H	% Pt	
23.14	3.36	35.06	(found)
22.69	3.43	36.86	(theory)

Alternatively, M.T.P. (0.15g) in methylene chloride was added to bis(triphenylphosphine)platinum(11)fluoride, (0.35g) in methylene chloride at room temperature and stirred for 15 minutes. The resulting solution was added to diethyl ether with precipitation of a white solid. This was filtered, washed with diethyl ether and dried in vacuum. Analysis of this complex gave C = 39.31%, H = 4.19%, Pt = 30.0%. These analyses appear to fit with a formulation in which only one triphenylphosphine is replaced by M.T.P. Such a formulation requires C = 42.92%, H = 3.73%, Pt = 30.33%. This is very peculiar in view of the fact that M.T.P. replaces all the triphenylphosphine in the zerovalent tetrakis complex. The real explanation may be that the compound isolated is in fact a mixture. The spectrum, while similar to that of the compound isolated in the first method, is certainly more complex. However, all attempts to effect purification failed.

Reaction of tetrakis(triphenylphosphine)platinum(0) with:-

(a) Benzene.

Tetrakis(triphenylphosphine)platinum(0), (0.5g) was added to 10ml benzene in a clean dry conical flask. The flask was stoppered, shaken to effect dissolution, and left overnight at room temperature. The yellow colour gradually faded with precipitation of a white solid. The spectrum of this material showed absorption at 1675cms^{-1} and 815cms^{-1}.

(b) Carbon Tetrachloride.

Tetrakis(triphenylphosphine)platinum(0), (0.5g) was added to 5ml Analar carbon tetrachloride in a clean dry conical flask. The flask was stoppered and shaken for two hours in a mechanical shaker at room temperature. The yellow colour of the solvent was gradually discharged and a white precipitate obtained, the infra-red spectrum of which, in the region 4000-700cms^{-1}, was identical with that of an authentic sample of bis(triphenylphosphine)platinum(11) chloride. V.P.C. analysis of the filtrate showed no trace of chloroform. This reaction was repeated for intervals of time up to twenty-four hours. The same observations were noted.

(c) Water.

Tetrakis(triphenylphosphine)platinum(0), (0.05g) was boiled for thirty minutes with distilled water. The yellow colour of the complex gradually faded and a white solid was obtained. This was filtered, washed with ethanol and diethyl ether and dried in air. The spectrum of this material showed an infra-red peak at 1675cms^{-1}.

Reactions of L_2PtF_2.

L = triphenylphosphine or triphenylphosphite).

Reaction with Carbon Moxoxide.

Bis(triphenylphsophine)platinum(11)fluoride, (0.5g) was added to a stainless steel bomb, which was then evacuated. Anhydrous hydrogen fluoride was condensed into the bombanda pressure of carbon monoxide applied. After rocking overnight, the volatile products were released, and the residue taken up in methylene chloride. On adding this solution to diethyl ether, a pale yellow solid was obtained, which, after filtration, washing with ether and drying in vacuum, analysed to the formula $(PC_{18}H_{15})_2Pt(CO)_2F_2$.

Analysis.

% C	% H	% Pt	
56.3	4.69	23.6	(found)
57.0	4.00	24.1	(found)
56.0	3.79	24.0	(theory)

Carbon monoxide was evolved on treatment with an excess of pyridine; the residue after this reaction showed no carbonyl bands in the infra-red spectrum. 1 mol. of complex gave 1.63 moles of carbon monoxide. This figure is not corrected for the solubility of carbon monoxide in the solvents used and is taken to confirm the complex as a dicarbonyl.

Bis(triphenylphosphite)platinum(11)fluoride was similarly treated. The residue was pale yellow and was recrystallised from methylene chloride -n- heptane, and analysed to $(PO_3C_{18}H_{15})_2Pt(CO)_2F_2$.

Analysis.

% C	% H	% P	% F	
51.01	3.98	7.81	4.70	(found)
50.17	3.33	7.10	4.18	(theory)

Reaction with Boron Trifluoride.

Bis(triphenylphosphine)platinum(11)fluoride, (0.5g) was added to a stainless steel bomb, which was then evacuated. Anhydrous hydrogen fluoride was condensed into the bomb. Boron trifluoride, from a cylinder, was bubbled through a concentrated sulphuric acid-boric oxide mixture, and the issuing gas collected in a trap, containing boric oxide, cooled to -180°C. Atmospheric moisture was excluded by means of a calcium chloride - phosphorus pentoxide drying tube. The trap was then transferred to a vacuum line, cooled to -180°C, and evacuated. The boron trifluoride was distilled into the bomb, cooled with liquid nitrogen, by heating the trap in an acetone - drikold slurry. Finally a pressure of carbon monoxide was applied to the bomb which was then left to shake overnight.

Volatile gases were allowed to escape into a fume chamber. A brown gummy residue remained after the excess solvent had been removed by distilling, in vacuum, into a silica trap. The residue was taken up in methylene chloride (5ml) and added to diethyl ether which precipitated a pale yellow solid. This was filtered, washed with ether and dried in vacuum. The solid analysed to the formula $(PC_{18}H_{15})_2Pt(CO)_2(BF_4)_2$

Analysis.

% C	% H	% P	% F	% B	
54.55	4.1	6.61	15.93	2.26	(found)
48.05	3.16	6.53	16.02	2.32	(theory)

It is difficult to account for the high carbon analysis in view of the good correlation between theory and found for the other elements. However, each time analysis was carried out a high value for carbon was obtained.

Reaction with Hydrogen.

Bis(triphenylphosphine)platinum(11)fluoride, (0.5g) dissolved in methylene chloride (15ml) was added to a stainless steel bomb which was then pressurised with hydrogen from a cylinder, and shaken at room temperature for twenty-four hours. The excess gas was released and the solution stirred into diethyl ether. A white precipitate was obtained, the infra-red spectrum of which was almost identical with that of the starting material. Differences were confined to the presence of weak infra-red peaks at 2358 and 2326cms^{-1}. However, attempts to repeat this spectrum were unsuccessful. It would seem, therefore, that an unstable hydride is formed during the reaction. This reaction is analogous with that reported by Vaska and DiLuzio[42]. These authors reacted $IrCl(CO)(PPh_3)_2$ in benzene solution with molecular hydrogen at room temperature and obtained an air stable, though light sensitive, hydride species, $IrH_2Cl(CO)(PPh_3)_2$. Formally, at least, this is an oxidation of iridium(1) to iridium(111) by molecular hydrogen. This complex reacts with hydrogen chloride, liberating hydrogen, forming a monohydride species $IrHCl_2(CO)(PPh_3)_2$. This latter complex can also be obtained by reacting the original monochlorocarbonyl with hydrogen chloride. Further, the monochlorocarbonyl reacts with elemental chlorine giving a trichloro derivative $IrCl_3(CO)(PPh_3)_2$. In these reactions both hydrogen chloride and chlorine are acting as oxidising agents. The authors state that these molecules, hydrogen, hydrogen chloride and chlorine '' must be considered as Lewis acids (or oxidants) in these reactions, that is to say, accepting electrons form univalent iridium for covalent bond formation.''

In the platinum reaction described, hydrogen may be acting as an oxidant; on the other hand it may be that the hydrogen is chemisorbed on the metal atom. Pliskin and Eischens[43] have studied the chemisorption of hydrogen on alumina supported platinum. Their results show that such a species has a detectable infra-red spectrum for hydrogen chemisorbed on platinum.

Reaction of bis(triphenylphosphine)platinum(11)chloride.

Bis(triphenylphosphine)platinum(11)chloride, (1g) was added to a polythene reaction vessel into which was condensed anhydrous hydrogen fluoride as previously described. Removal of the excess acid left a faintly pink coloured solid, which was dissolved in methylene chloride and the solution stirred into diethyl ether. A white solid precipitated. This was washed with diethyl ether and dried in air. Unfortunately, only a partial analysis could be obtained for this complex. This data suggests a P:F:Cl ratio of 4:5:2 and is taken as indicating a mixture of substances.

%P = 7.58, %F = 5.54, %Cl = 3.85.

Phosphine Palladium Fluorides.

Moss[19] reports the preparation of bis(triphenylphosphine)palladium(11)fluoride from tetrakis(triphenylphosphine)palladium(0). He was unable to prepare the zero valent tetrakis complex by the method of Malatesta and Angoletta[44]. Reduction of bis(triphenylphosphine)palladium (11)chloride in alcohol in the presence of an excess of triphenylphosphine by sodium borohydride, however, gave the desired product. In the present study, attempts to prepare the tetrakis complex by methods of Malatesta were also unsuccessful. Consequently, bis(triphenylphosphine) Palladium(11)chloride, (1g), and triphenylphosphine, (0.75g) were added to ethanol (35ccs) in a three-neck reaction flask fitted with a nitrogen inlet, mecury seal stirrer, reflux condenser and dropping funnel. The reaction mixture was heated on a steam bath and 0.05g sodium borohydride in 10ccs ethanol was added dropwise over a period of five minutes to the stirred reaction mixture. Heating and stirring were continued for one hour, and a nitrogen atmosphere maintained throughout. A yellow solid was obtained which immediately turned orange in air, (as was reported by Malatesta and Angoletta) and eventually turned black. Attempts to isolate sufficient of the material by filtering in a nitrogen bag were unsuccessful.

Since hydrogen chloride is virtually insoluble in liquid anhydrous hydrogen fluoride, attempts were made to prepare the phosphine fluoride by reacting the phosphine chloride with liquid anhydrous hydrogen fluoride. Bis(triphenylphosphine)palladium(II)chloride (0.5g) was added to a polythene reaction vessel and anhydrous hydrogen fluoride condensed into the vessel at -78°C. The solution was allowed to come to room temperature and appeared to have a reddish tinge. On removing the excess hydrogen fluoride, with a stream of nitrogen, a deep red coloured product was obtained. A solution of this in methylene chloride was stirred into diethyl ether giving an orange-red precipitate which was filtered, washed with ether, and air dried. The reaction was repeated several times, but insufficient material was obtained for elemental analysis. However, the infra-red spectrum of the orange solid, in the region 4000-700cms^{-1} was different from that of the starting material, although Beilstein's test showed the presence of chlorine. The main difference in the spectra was the presence of a strong absorption at 833cms^{-1} with medium to weak shoulders at 848, 358 and 878cms^{-1}. These may be due to P-F vibrations. In PF_5, absorptions at 938, 948 and 957cms^{-1} are attributed to the P-F vibrations[5,7] and in $(PF_6)^-$ the infra-red active peak[59] is observed at 345cms^{-1}.

Other Platinum Group Metals.

Relatively few characterised carbonyl fluorides are known. The first such complex was prepared by Sharp[45] by reaction of platinum(IV)fluoride with carbon monoxide. Sublimation of the reaction product gave a yellow complex which, on the basis of infra-red and analytical data, was formulated $Pt(CO)_2F_2$. An analogous reaction with rhodium-(IV)fluoride gave an orange-red product, volatile at room temperature in vacuum, and more stable than the platinum compound. On the basis of infra-red, analysis and molecular weight determinations the complex is formulated as $(Rh(CO)_2F_3)_2$. The absence of peaks in the bridging carbonyl region of the infra-red suggest that dimerisation is via fluorine bridges.

Russell[66] has found evidence for the existance of other carbonyl fluorides of the Platinum Group. Reaction of platinum(IV)fluoride with carbon monoxide at room temperature gives a non-volatile product formulated as $Pt(CO)_2F_4$. This compound disproportionates violently if heated above 80°C giving $Pt(CO)_2F_2$. For ruthenium, the product differs depending on the method of preparation of the metal fluoride. Ruthenium(III)bromide, fluorinated with bromine trifluoride, gives a product which, when pressurised with carbon monoxide at room temperature, gives a dark solid from which a white compound can be sublimed at 100°C in vacuum. An infra-red solution spectrum of this material in carbon tetrachloride shows two weak and one strong band in the carbonyl region. The fluoride, prepared from the elements, shows little or no reaction with carbon monoxide under pressure unless the temperature of reaction is raised to about 100°C. In this instance, no sublimate was obtained, but a carbon tetrachloride extract of the product showed an infra-red spectrum similar to that of the white sublimate. The yield of product from these reactions precluded elemental analysis. Similar attempts, by Russell, to prepare carbonyl fluorides for osmium, iridium and palladium proved unsuccessful. Methods involving the reaction of fluorine or metal fluorides with metal carbonyls have also been unrewarding[47].

Since carbonyl fluorides of platinum are quite stable when phosphorus donor molecules are also present in the complex, attempts were made to produce similar species for some other Platinum Group Metals. The reactions involving the phosphine fluoride pressurised with carbon monoxide give very low yields of the desired species. Since fluorination with anhydrous hydrogen fluoride appeared to be quite well established, attempts were made to fluorinate phosphine carbonyls with this reagent.

Ruthenium.

Ruthenium(III)chloride, (1g) and triphenylphosphine (5g), were refluxed together in 2-methoxyethanol (200ml) for two hours. The excess solvent was removed by distillation until the volume in the reaction vessel was 25-50ml. This was filtered hot to remove insoluble material giving a dark brown crystalline solid and a deep red solution.

Excess methanol was added to the filtrate and an orange precipitate was obtained.

Brown Crystals.

Beilstein's test showed the presence of chlorine. An infra-red spectrum of this material as a nujol mull, showed absorption attributable to metal-carbonyl at 1875cms^{-1}. Peaks attributable to metal-hydrogen were absent.

This complex melted, with decomposition at 240-245°C.

Analysis.

C = 57.87%, H = 4.06%, P = 7.98%, Cl = 13.87% (found)

$(PPh_3)_2Ru(CO)Cl_3$ requires C = 58.46%, H = 3.98%, P = 8.16%

Cl = 14.0%

Orange Precipitate.

Beilstein's test showed the absence of chlorine. An infra-red spectrum (nujol mull), showed peaks in the metal-hydrogen region at 2005cms^{-1} and 1958cms^{-1}, and an intense sharp peak at 1923cms^{-1} with a weak shoulder at 1902cms^{-1} attributable to metal-carbonyl. This orange compound melted at 140°C, and elemental analysis gave, C = 66.78%, H = 4.71%, P = 9.66% (found).

$(PPh_3)_2Ru(CO)H_2$ requires, C = 67.67%, H = 5.06%, P = 9.43%.

Both of these products were reacted with liquid anhydrous hydrogen fluoride in the manner previously described.

The reaction of the trichloro carbonyl gave some decomposition, but the only isolable compound recovered proved to be the starting material. The trishydrido carbonyl, however, gave a pale green solid from the reaction with hydrogen fluoride, which was isolated by precipitating a methylene chloride solution of the crude reaction product with diethyl ether. The infra-red spectrum of this material in the region 4000-700cms^{-1} was very similar to that of the parent material. The only differences occurred in the metal-carbonyl and metal-hydrogen regions. Vibrations attributable to the latter were absent in the product, and the frequency of vibration of the former was observed as a single intense peak at 1965cms^{-1}, ie. a shift of some 40cms^{-1} from that observed in the parent complex.

Analysis.

C = 62.78%, H = 4.17%, P = 9.01%, F = 7.93% (found).
$(PPh_3)_2Ru(CO)F_2$ requires C = 62.53%, H = 4.26%, P = 8.72%, F = 8.02%.

Osmium.

Ammonium hexabromoosmate(IV) was prepared by the method of Dwyer and Gibson[48]. 1g of the osmate and 4.5g triphenylphosphine were mixed in a beaker with 2-methoxyethanol after the method of Vaska[49]. The spectrum of the white carbonyl hydride, obtained by precipitation with methanol from the hot solution, was identical with that reported by the author.

1.2g of this complex, of formula $(PPh_3)_3Os(CO)HBr$, was reacted in polythene apparatus with liquid anhydrous hydrogen fluoride in the manner already described. On removing the excess acid, a rather dirty brown sludge was obtained. This dissolved completely in methylene chloride (2ml). On adding the solution to diethyl ether, a pale yellow solid precipitated. Filtration and washing with ether gave a pale ivory-yellow solid, the spectrum of which, as a nujol mull, showed a single sharp absorption at 1945cms^{-1} as compared with three peaks for the parent material. These absorptions are assigned to the C-O stretch in the metal-carbonyl. The absorption at 2100cms^{-1}, assigned to metal-hydrogen vibration in the parent, is not observed in the product. Analysis of the fluorinated species gives

C = 55.97%, H = 3.78%, P = 7.57%, F = 6.89% (found)

$(PPh_3)_2Os(CO)F_3$ requires C = 55.58%, H = 3.78%, P = 7.75%, F = 7.13%

General Discussion.

Anhydrous hydrogen fluoride is extremely reactive. Sulphuric and nitric acids are both protonated in liquid anhydrous hydrogen fluoride. It resembles water and ammonia in its physical properties. All three have anomolous boiling points, with respect to other compounds in their groups, attributable to strong hydrogen bonding between the molecules. The dielectric constant of hydrogen fluoride is comparable with that of water and ammonia. Table 1.2. shows the comparison of these physical properties.

Compound	HF	HCl	HBr	HI
Dielectric Constant	83.6(0 °C)	4.6(27.7 °C)	3.82(24.7 °C)	2.9(21.7 °C)
Boiling Point °C	19.5	-85.8	-67.1	-36.0
Compound	H_2O	H_2S	H_2Se	H_2Te
Dielectric Constant	81 (25 °C)	5.75(10 °C)	-	-
Boiling Point °C	100	-61.8	-42	-1.8
Compound	H_3N	H_3P	H_3As	H_3Sb
Dielectric Constant	22(-34 °C)	2.71(-25 °C)	2.05(15 °C)	2.58(-50 °C)
Boiling Point °C	-38.5	-86.4	-54.8	-18

Table 1.2

It is doubtful if the specific conductivity of the pure anhydrous compound has been obtained, although several workers have made vigorous efforts to do so. Runner et alia[50] report the specific conductivity of liquid anhydrous hydrogen fluoride as 2.6×10^{-6} ohms^{-1}. cms^{-1}. at 0°C. These authors also report that the conductivity of their extremely carefully prepared samples increases with time, and particularly so if the liquid is in contact with a metal, presumably the electrode. Considering these facts, ionisation may be appreciable in any reaction involving the use of the anhydrous liquid. The ionisation may be considered as,

$$2HF \rightleftharpoons H_2F^+ + F^-$$

in spite of the fact that the solvated proton has not been identified. On solvent theory, any substance which increases the concentration of the anion character of a self ionising solvent is basic with respect to that solvent. Any substance which increases the concentration of the cation character is an acid. Clifford et alia[51] have studied the hydrogen fluoride system and find that there are relatively few substances capable of acting as acids in this system. Of the many substances investigated, only four were found which were capable of dissolving electropositive metals. These are antimony and arsenic pentafluorides, boron trifluoride and stannic fluoride. In order to ensure that their criterion of acidity was valid, viz, the dissolution of electropositive metals, they used several different metals whose salts might be expected to vary in solubility, in an attempt to obviate passivity. A second reason for failure in their chosen criterion might be attributed to a slow rate of evolution of hydrogen. However, Clifford[51] has shown that the hydrogen overvoltage on a dropping mercury electrode is only 0.4V in HF compared with about 2V in water. They conclude that this latter factor should be unimportant in liquid hydrogen fluoride solutions.

In view of these facts it is difficult to imagine any of the complexes in the present study acting as acids in liquid anhydrous hydrogen fluoride. Consequently they are probably either neutral or basic in the solvent. There is an abundance of evidence for protonated species of Transition metal complexes in the literature, (references 19,20,21 and 22). For example, Iron pentacarbonyl is protonated in trifluoroacetic acid-boron trifluoride hydrate mixtures and bis(triphenylphosphine)irontricarbonyl is protonated in concentrated sulphuric acid. It is suggested, therefore, that the complexes prepared in the present study act as bases in liquid anhydrous hydrogen fluoride, the protonated species loosing hydrogen with formation of the fluoride. The reaction for the preparation of, for example, the phosphine platinum fluoride, is therefore,

$$Pt[PPh_3]_4 + 2HF \longrightarrow [PPh_3]_2PtF_2 + H_2 + 2PPh_3$$

the liberated triphenylphosphine being present as the phosphonium fluoride. No attempt was made to detect the presence of hydrogen. The presence of the phosphonium fluoride is inferred from the reaction of triphenylphosphine with hydrogen fluoride. A water soluble product was obtained which, on treating with alkali gave triphenylphosphine.

In all of the reactions described, oxidation of the central metal is achieved. This is, perhaps surprising considering the nature of the reaction medium. It is, however, no more surprising than Vaska's[42] oxidation of an iridium(l) complex to one of iridium(lll) by molecular hydrogen at room temperature, or the similar oxidation with hydrogen chloride. Indeed, if the suggestion that the molecules, hydrogen, hydrogen chloride, chlorine, and, for this study, hydrogen fluoride, act as Lewis acids in these reactions is valid, then this also supports the idea of protonation of the central metal.

Platinum Complexes.

The bonding in L_2PtF_2, where L is triphenylphosphine or triphenylphosphite is visualised as donation of the lone pair of electrons from the donor to the metal, with formation of a sigma bond, the dative pi-bond being formed by overlap of a filled d or dp hybrid of the metal with a vacant p,d or dp hybrid of the donor. This will confer strong bonding in the plane of the molecule and the central metal should then be electron deficient above and below the molecular plane. It is to be expected, therefore, that this complex should further react with donor molecules, provided ligand-ligand repulsion is not too great.

That other ligands can be accomodated is shown by the reaction with carbon monoxide, with the formation of $L_2(CO)_2PtF_2$. Since the pattern of peaks in the metal carbonyl region of the infra-red for these complexes is different from that observed by Chatt et alia[41], it is presumed that the stereochemistry of the present complexes must be different from that described by these authors, who assign to their complexes the structure (Fig. 1.4) on the basis of infra-red spectra. The peaks observed in the carbonyl region for the

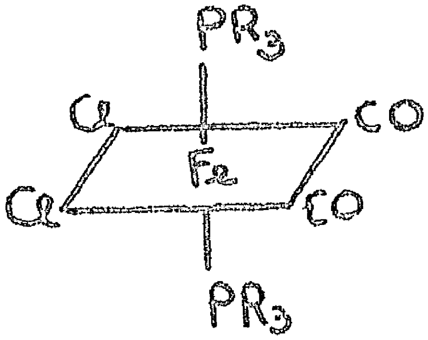


Fig. 1.4

phosphine metal carbonyls, related carbonyl fluorides and Chatt's carbonyl complexes are recorded in Table 1.3

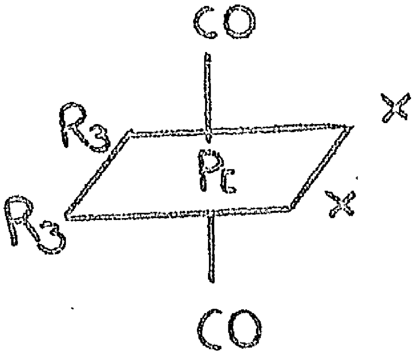
Compound.	Frequency (cms^{-1}.)	Reference.
CO	2143	52
$Pt(CO)_2F_2$	2161, 2120	45
$Pt(CO)_2F_4$	2217, 2175, 1842	46
$(PPh_3)_2Pt(CO)_2F_2$	2152, 2105, 2083	16
$[P(OPh)_3]_2Pt(CO)_2F_2$	2179, 2127, 2092	present work*
$(PPh_3)_2Pt(CO)_2(BF_4)_2$	2127, 2123, 2105	present work*
$[Rh(CO)_2F_2]_2$	2103, 2086, 2035	45
$Ru(CO)_xF_y$	2180, 2126	46
$(PPh_3)_2Ru(CO)F_2$	1965	present work†
$(PPh_3)_2Os(CO)F_2$	1945	present work†
$(PEt_3)_2Fe(CO)_2Cl_2$	2014, 1963	41
$(PEt_3)_2Fe(CO)_2Br_2$	2009, 1958	41
$(PEt_3)_2Fe(CO)_2I_2$	2003, 1953	41

(* Recorded as nujol mulls on a Grubb-Parsons DB-1 S4 Spectrophotometer

† Recorded as nujol mulls on a Perkin-Elmer 125 Spectrophotometer.)

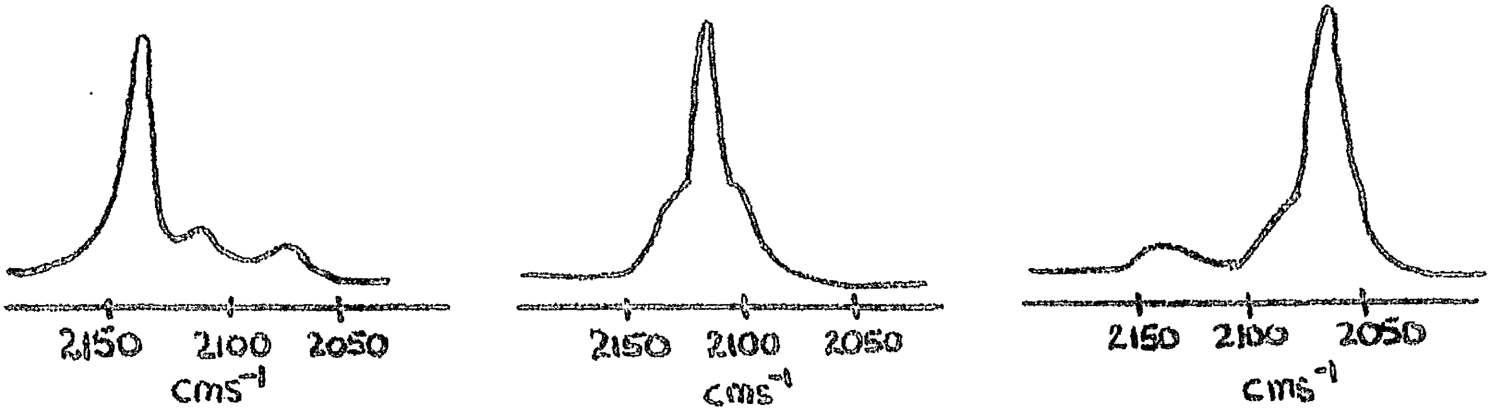
Table 1.3

It is reasonable to expect donation of lone pairs of electrons into regions of low electron density. If the postulate that L_2PtF_2 is electron deficient above and below the molecular plain is valid, then it is suggested that the stereochemistry of the present complexes is described by Fig. 1.5. Such a stereochemistry should result in only one infra-red active C-O stretching vibration[53]. In the spectra, Fig. 1.6, there is only one strong peak in the carbonyl region, although shoulders or weak peaks are apparent. These may arise from small proportions of other isometric species or they may be overtones of the fundamental vibration.



(R = triphenylphosphine or triphenylphosphite, X = fluorine or tetrafluoroborate)

Fig. 1.5



$(PPh_3)_2Pt(CO)_2F_2$ $(PPh_3)_2Pt(CO)_2(BF_4)_2$ $[P(OPh)_3]_2Pt(CO)_2F_2$

Fig. 1.6

The infra-red spectrum of the tetrafluoroborate complex in the region 1250-830cms^{-1} is not much different from that of the parent fluoride. Triphenylphosphine has bands at 1086, 1064 and 1030cms^{-1}, the phosphine fluoride has bands at 1092, 1053 and 995cms^{-1}. The tetrafluoroborate complex shows absorption at 1092 and 995cms^{-1}, and, in addition, has two intense bands, with ill-defined maxima, in the regions 1064-1047cms^{-1} and 1030-1021cms^{-1}. This is in the region in which the tetrafluoroborate ion is expected to absorb. However, in ionic tetrafluoroborates, the absorption at 1100cms^{-1} is usually very broad and intense. The fact that in this complex the absorption is resolved into two peaks is taken to indicate some partial covalency in the bonding between the anion and the metal[84]. (Coordinated tetrafluoroborates are discussed in Chapter 4). Since the pattern of peaks in the carbonyl region for the tetrafluoroborate complex is not much different from that for the phosphine metal carbonyl fluoride, it is suggested that this is evidence for the coordinate nature of the bond between the anion and the central metal in the tetrafluoroborate complex.

The instability of the phosphine hydrido-metal fluoride could also be accounted for by this structure (Fig. 1.5), considering hydrogen in the sites occupied by carbon monoxide. If, as Vaska[63] suggests, hydrogen in this type of reaction acts as a Lewis acid, then the platinum-hydrogen bond will be very weak because of the electron deficiency above and below the molecular plane in bis(triphenylphosphine)platinum(11)fluoride.

Bonding in $L_2Pt(CO)_2F_2$.

To account for six coordination in these complexes, one must invoke the use of a 6d orbital. The formation of six equivalent bonds using a $5d6s6p^36d$ combination has been shown by Craig et alia[55] to be energetically unlikely. As an explanation of the bonding in these complexes it is suggested that the planar part of the molecule can be regarded as a hybridisation of the $5d6s6p^2$ orbitals, the other two bonds in the completed octahedron being a hybrid of the remaining 6p with a 6d orbital. This explanation has been used by Harris and Nyholm[56] to explain the bonding in $[Au(Arsine)_2I_2]^+$.

The $d_{x^2-y^2}$ orbital combines with the 6s and two 6p orbitals to give four planar hybrid bonds. The filled d_{z^2} orbital is perpendicular to the plane, pointing towards the remaining two positions of the octahedron. Ligands along this axis are, therefore, expected to suffer a repulsion, with consequent elongation of bond length. X-ray results on the gold diarsine complex[56] show that two of the bonds are longer than usual, supporting this prediction. Harris and Stephenson[57] have also used this explanation to account for the configuration and diamagnetism of $[Pt(NH_3)_4(CH_3CN)_2]Cl_2$. X-ray and magnetic moment studies on bis(triphenylphosphine)dicarbonylplatinum(II)fluoride would be well worthwhile.

Far Infrared Spectra.

The far infra-red spectra of these platinum complexes has been particularly unrewarding. The spectra observed in the region 650-200cms^{-1}, for the complexes studied are recorded in Table 1.4 (for the phosphine complexes) and Table 1.5 (for the phosphite complexes.)

PPh_3	$(PPh_3)_4Pt$	$(PPh_3)_2PtF_2$	$(PPh_3)_2Pt(CO)_2F_2$	$(PPh_3)_2Pt(CO)_2(BF_4)_2$
617^{m}	-	617^{w}	613^{w}	613.5^{w}
599^{sh}	-	-	-	-
-	-	552.5^{w}	552.5^{w}	555.5^{w}
540.5^{m}	546.4^{m}	540.5^{sh}	-	-
510^{s} sh	509^{s}	510^{s}	511^{s}	518^{s}
495^{s}	-	500^{s}	507.6^{s}	507.6^{s}
-	-	480.7^{s} sh	480^{s} sh	460.8^{m}
427^{m}	449^{m}	449.5^{m}	449^{m}	436.7^{w}
420^{m}	418.5^{w}	420.2^{m}	420^{m}	420.2^{w}
398^{w}	400^{w}	400^{w}	400^{w}	-

(Triphenylphosphine also has a weak peak at 270cms^{-1} and a weak doublet at 251 and 245cms^{-1}. Absorption in this region was not observed for the complexes. All frequencies are reported in cms^{-1}.)

Table 1.4

$P(OPh)_3$	$[P(OPh)_3]_4Pt$	$[P(OPh)_3]_2PtF_2$	$[P(OPh)_3]_2Pt(CO)_2F_2$
606^{s}	617.3^{s}	617.3^{w}	–
597^{s}	591.7^{s}	595.3^{w}	–
555.7^{s}	571.5^{sh}	555.7^{w}	555.7^{w}
540.5^{sh}	543.6^{m}	–	–
–	526.2^{s}	$518.5^{v.s}$	$515.4^{v.s}$
–	–	$502.4^{s\ sh}$	$502.4^{s\ sh}$
$492.6^{v.s}$	487.7^{s}	–	–
465.1^{s}	467.3^{s}	–	–
444.4^{sh}	436.7^{sh}	446.5^{w}	–

(Spectra recorded as nujol mulls on polythene plates, on a Grubb-Parsons DM2 Far Infra-red Spectrophotometer.

s = strong, m = medium, w = weak. sh = shoulder.

Frequency in cms^{-1}.)

Table 1.5

The platinum-carbon stretch in $K_2[Pt(CN)_4]3H_2O$ is assigned to the vibration observed at 505cms^{-1} in this compound[58]. In mononuclear carbonyls, the metal-carbon stretching vibration varies considerably depending on the symmetry of the species, and also varies for the metals in a Transition Group. In the Group VI hexacarbonyls, where the symmetry is Oh, the M-C stretch is assigned to the vibrations at 436, 368 and 432cms^{-1} for chromium, molybdenum and tungsten respectively[58]. In the phosphine complexes the vibrations circa 555cms^{-1} may be due to the M-C stretch, although such a value would be much higher than that expected.

The triply degenerate vibration at 520cms^{-1} of the tetrafluoroborate ion should be split if the ion is co-ordinated to the metal. By analogy with the spectra of other tetrafluoroborate complexes in this region (cf. Chapter 4) it is suggested that the observed weak band at 460.8cms^{-1} be assigned to a vibration arising from the, now non-degenerate, fundamental.

The absorptions recorded in rows 7 and 6 of Tables 1.4 and 1.5 respectively may be due to platinum-fluorine vibrations. Woodward and Ware[59] have studied the vibrational spectra of the hexafluoroplatinate(IV)ion and report the asymmetric platinum-fluorine stretch at 571cms^{-1}. A direct comparison for the platinum-fluorine vibrations between the spectra reported by these authors and those recorded in this study is not valid because of the complexity of the species in the latter. Further, the absorptions of the phosphorus ligands effectively screen the regions of particular interest in these complexes making it very difficult to be precise about any of the observed vibrations.

Osmium and Ruthenium Complexes.

The reaction between ruthenium(III)chloride and triphenylphosphine must be very dependent upon conditions such as reaction time, reaction temperature and perhaps the molar ratio of phosphine to metal. Vaska[23] obtained a product, which, on reconsideration, he formulated as $RuHCl(CO)(PPh_3)_3$, for convenience labelled A in this study. This is a yellow solid which melts at 139°C. Absorption in the infra-red at 2020cms^{-1} is assigned to the metal-hydrogen stretching vibration, and those at 1916 and 1900cms^{-1} to the C-O stretching vibration of the metal carbonyl. In the present study, two products were obtained, with a very small amount of a third. The major products of the reaction are formulated $(PPh_3)_2(CO)RuCl_2$ and $(PPh_3)_2(CO)RuH_2$, labelled compounds B and C for convenience. The spectrum of the third product, compound D, a yellow solid, was very similar to compound A reported by Vaska[23]. Insufficient of D was obtained for analysis, but on the basis of infra-red spectra and melting point, 138.5°C, it is presumed that D is identical with A.

The variety of complexes obtained from the ruthenium reaction contrasts markedly with the uniformity of product obtained from the osmium reaction for the same conditions of time, temperature and molar ratio of phosphine to metal. It may be that the products B and C isolated from the ruthenium reaction in this study would react with more triphenylphosphine with evolution of hydrogen chloride according to the equation,

$$(PPh_3)_2(CO)RuCl_3 + (PPh_3)_2(CO)RuH_3 + 2PPh_3 \longrightarrow 2(PPh_3)_3(CO)RuHCl + HCl$$

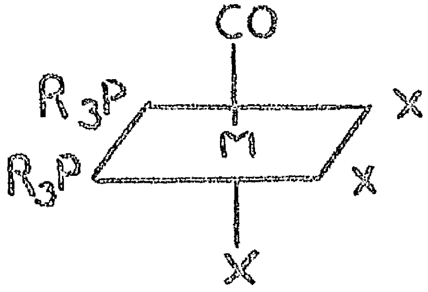
However, this was not tested.

It is strange that the ruthenium chloro complex, compound B, does not react to any great extent with liquid anhydrous hydrogen fluoride, whereas the osmium bromo complex, $(PPh_3)_3(CO)OsHBr$, and the ruthenium hydrido complex, compound C, both give reaction. It may be a purely kinetic effect and that a much longer reaction time is required for compound B. It is, therefore, particularly unfortunate that the quantity of compound D, obtained precluded reaction with hydrogen fluoride. In all the reactions attempted in this study involving a chloro complex and liquid anhydrous hydrogen fluoride, chlorine was always retained in the product species in spite of the fact that hydrogen chloride is virtually insoluble in anhydrous hydrogen fluoride. It would, therefore, be interesting to compare the reactions of a series of complexes, such as $(PPh_3)_3(CO)MHX$, where M is ruthenium or osmium and X is chlorine, bromine or iodine, with liquid anhydrous hydrogen fluoride.

Structure and Bonding.

The central metal in the complexes prepared in this study, viz $(PPh_3)_2(CO)RuX_3$ where X is fluorine, chlorine or hydrogen, and in $(PPh_3)_2(CO)OsF_3$, has a d^5 configuration. Magnetic moment measurements should be rewarding for these complexes, since if these are low spin octahedral complexes, the magnetic moment should be equivalent to one unpaired electron. However, insufficient product was obtained in these reactions to permit such a measurement. To obtain reasonable accuracy in the measurement of the magnetic susceptibility of powders by the Gouy method, a Gouy tube of dimensions, internal diameter not less than 3mm and length of from 3 to 10 cms, is required. Such a tube required about 1g of sample. The maximum yield of product obtained from these reactions was of the order of 0.5g, and in most cases was less than this.

The orbitals available for hybridisation are the normal dsp combination. Six equivalent bonds would then be expected for an octahedral structure, in contrast to the postulated unequivalent bonds for the platinum complexes. The structure postulated for the complexes of ruthenium and osmium prepared in the present study is described by Fig. 1.7. In this, the strongest trans directing ligands are opposite the weakest.



(R = phenyl, X = fluorine, chlorine or hydrogen)

Fig. 1.7

Spectra.

In Table 1.6 are recorded the vibrations observed in the metal-hydrogen and metal-carbonyl regions for the ruthenium and osmium complexes.

Compound	Frequency (cms^{-1})		Reference
	ν(M-H)	ν(C ≡ O)	
$RuHCl(CO)(PPh_3)_3$	2020	1916, 1900	23
$RuCl_3(CO)(PPh_3)_2$	-	1875	present work
$RuH_3(CO)(PPh_3)_2$	2005, 1958	1923, 1902	present work
$RuF_3(CO)(PPh_3)_2$	-	1965	present work
$OsHCl(CO)(PPh_3)_3$	2097	1927, 1912, 1894	49
$OsHBr(CO)(PPh_3)_3$	2100	1930, 1913, 1896	49
$OsF_3(CO)(PPh_3)_2$	-	1945	present work

(Spectra, as nujol mulls on KBr plates, were recorded on a Perkin - Elmer 125 Spectrophotometer).

Table 1.6

The spectra in the region 650-400cms^{-1} are screened by absorptions due to triphenylphosphine and no assignments are made for these vibrations since the data available is limited. In Table 1.7 are listed the peaks observed in this region. In addition to the absorptions recorded in the table, bis(triphenylphosphine)monocarbonylruthenium(111) chloride has a strong peak at 331cms^{-1} with a shoulder at 326cms^{-1}, and three other peaks, a weak doublet at 290 and

286cms^{-1}, and a weak singlet at 257cms^{-1}. Since these peaks are absent in the hydrido analogue, it is suggested that these are due to metal-chlorine vibrations.

L	$RuCl_2YL_2$	RuH_2YL_2	RuF_2YL_2	$OsHBrYL_2$	OsF_2YL_2
617^{w}	617^{w}	617^{w}	617^{w}	617^{w}	617^{w}
599^{sh}	592^{m}	593^{m}	599^{m}	595^{m}	595^{m}
-	-	563^{w}	-	-	-
541^{w}	532^{sh}	541^{s}	544^{w}	549^{w}	549^{w}
510^{s} sh	521^{s}	518^{s}	515^{s}	521^{s}	513^{s}
495^{s}	508^{s} sh	505^{s}	505^{s}	502^{s}	502^{s}
-	-	498^{m}	-	-	490^{m}
-	457^{m}	-	457^{m}	461^{m}	456^{m}
427^{w}	439^{w}	-	429^{m}	441^{m}	429^{m}
420^{w}	422^{w}	417^{w}	-	420^{w}	412^{w}

(Spectra, as nujol mulls on polythene plates, were recorded on a Grubb-Parsons DM2 Far Infra-red Spectrophotometer.
w = weak, m = medium, s = strong, sh = shoulder. L is PPh_3 and Y is CO.

Table. 1.7.

Chapter 2.

Group VI Metal Carbonyl Fluorides.

Introduction.

In the last decade, one of the most active fields of research has involved the preparation and characterisation of a large number of Transition Metal complexes. One aspect of this activity has been concerned with the complexes formed between pi-bonding ligands, d - Group Transition Metals and halogens. A great variety of ligands has been employed, but probably the most extensive studies have been carried out where the ligand is carbon monoxide.

Carbon monoxide has three occupied sigma orbitals which correspond to the unshared electron pairs on the carbon and oxygen atoms, and to the sigma bond between the atoms. The remaining four electrons occupy a doubly degenerate bonding pi-orbital, and this contributes greatly to the bond strength. The remaining orbitals of the molecule are a very strongly antibonding sigma orbital and a strongly antibonding pi-orbital. It is conceivable that any of the three occupied orbitals could act as the donor orbital in complex formation. However, the electronegativity difference between carbon and oxygen suggests the use of the carbon lone pair in preference to that of oxygen. This leads to two extreme possibilities; either donation of the carbon lone pair, in which case a linear arrangement is to be expected, M-CO, or donation of pi electrons giving an arrangement of the type $M \leftarrow \overset{C}{\underset{O}{\vert\vert\vert}}$. Experiment has shown that only the linear arrangement is observed, so far.

Carbon monoxide is not basic, as the absence of simple complexes with the normal vacant orbital acceptors illustrates. The only exception to this is the borine H_3BCO, and this is rather unstable[81].

The nature of the bond formed by a pi bonding ligand may be visualised as, first the formation of a dative bond by overlap of a sigma orbital of the ligand with an empty sigma orbital of the metal, Fig. 2.1a, and secondly, overlap of a filled d pi or hybrid d p pi metal orbital with an empty antibonding p pi or d pi orbital of the ligand, Fig. 2.1b.

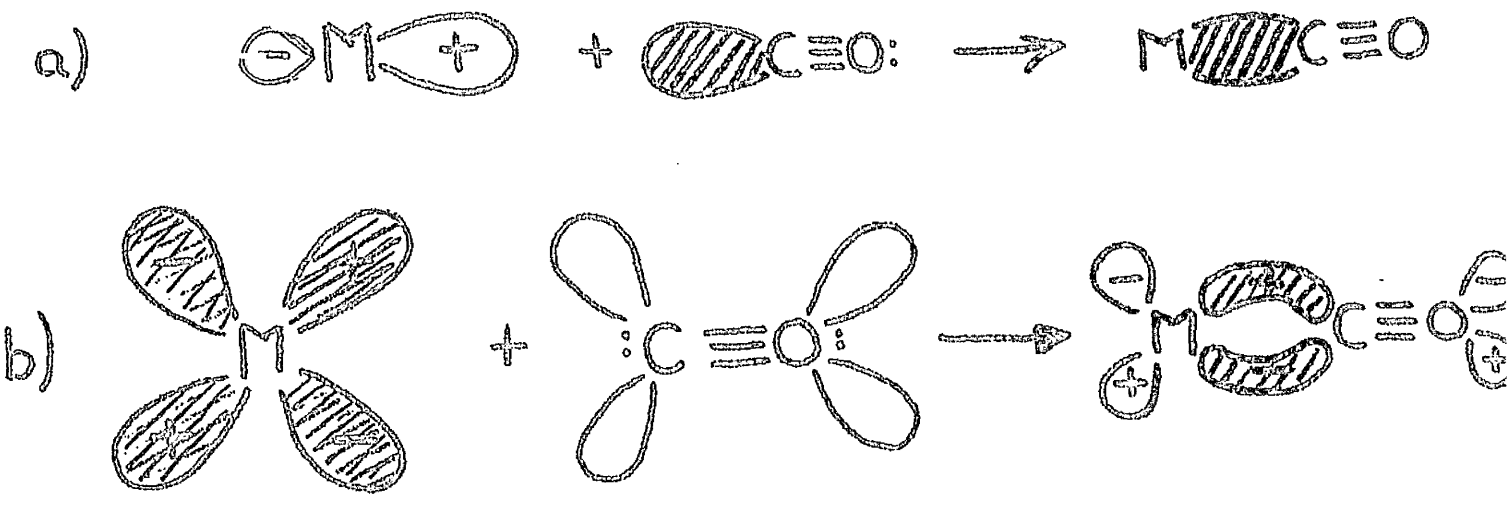


Fig. 2.1.

The current theory of bonding in metal carbonyl complexes, which is the subject of a recent review article by Abel^{63}, is embodied in the above description. This theory permits the excess negative charge, which would accumulate on the central metal by the sigma bond donation from the ligand, to be dispersed via the pi bond. This gives rise to what Orgel^{64} has described as a synergic interaction between the two types of bonding, and is probably the major reason for the strength of the metal-carbon bond.

A lowering of bond order is associated with a reduced force constant, and the force constant of the carbon-oxygen bond stretching vibration is quite sensitive to changes in bond order. The presence of electrons in the pi antibonding orbital of carbon monoxide, from filled metal d or hybrid d p pi orbital, causes a reduction in the order of the C-O bond. Thus, it is generally accepted that M-C pi-bonding is accompanied by a lowering of the frequency in the C-O stretching vibration in complexes containing carbon monoxide.

The extent of effective pi bonding will be governed by the electron density around the central metal. A metal in an enviroment of low electron density will not experience the same necessity for relieving the donated negative charge, compared with a metal in a field of higher electron density. Consequently the extent of pi bonding will be increased in the latter, and this will be reflected, in the C-O stretching vibration. This effect is clearly seen in the ions of general formula[65] $[\pi\text{-}C_5H_5M(CO)_3]^{n-}$, where M is V(-1), Cr(0), Mn(+1) andFe(+2), the numbers in brackets referring to the formal oxidation state of the metal. The two C-O stretching frequencies for each compound are, V, 1748, 1645; Cr, 1376, 1695; Mn, 2035, 1953 and Fe, 2120, 2070cms^{-1}.

In substituted metal carbonyls, the electron density around the metal will vary with the substituent. Many carbonyl halides are known, and it might be expected that in such complexes the density of the metal electron cloud would follow the order of electronegativity found for the halogens. This need not necessarily be so, since the possibility of backbonding between the metal and the halogen must also be considered. Thus, if the filled p orbitals of the halogen have energies comparable with empty d orbitals of the metal, then a metal-halogen pi bond could occur. This would tend to reduce the inductive effect of the halogen, and would act in the opposite sense on the C-O stretching frequency. In many cases, however, the inductive effect seems to be the more important, especially so in the platinum complexes discussed in the previous chapter, (cf. Table 1.3), where it is observed that some of the compounds have C-O stretching frequencies higher than that in carbon monoxide itself. This may be interpreted by suggesting that the demand for electrons by the fluorine atoms has become so great that it has been transmitted to the carbon atom of the carbonyl group, with a consequent reduction in the electronegativity difference between the carbon and oxygen atoms. This in turn will tend to increase the force constant of the C-O sigma bond. It must be pointed out, however, that too much relience cannot be placed on comparisons made between vibrational spectra measured in the gas phase, for carbon monoxide, and those obtained from solutions or mulls.

For pi bonding to occur, suitable filled and empty orbitals must be available. In an octahedral environment, the suitable metal orbitals for the formation of pi bonds are the d_{xy}, d_{xz} and d_{yz}[64]. In the platinum(II) complexes, the central metal has a d^8 configuration, consequently these orbitals must be filled. If backbonding from fluorine to platinum does occur, it can only be a relatively weak effect, because of the presence of electrons already in the suitable orbitals of the platinum atom. It could be, however, that there is a harmonic back donation from fluorine to metal which coincides with the back-donation from the metal to the carbon atom. This leads to the suggestion of synergic bonding throughout the molecule. On balance, however, it would seem that the inductive effect of the fluorine atom is the dominating factor.

In the substituted carbonyl fluorides of ruthenium and osmium, (Chapter 1), and the carbonyl fluorides of molybdenum and tungsten, prepared in the present work, the situation is slightly different. In the former complexes ruthenium and osmium are formally in the +3 oxidation state, and consequently have a d^5 configuration, while in the latter complexes molybdenum and tungsten are in the +2 oxidation state and consequently have a d^4 configuration. In these complexes, the metal orbitals suitable for pi bonding are only partially filled, and this factor could enhance the extent of $M \leftarrow F$ back bonding.

Experimental.

Tris(pyridine)molybdenum(0)tricarbonyl.

Molybdenum hexacarbonyl, (5g) was refluxed with Analar pyridine (30ml). Gas evolution was immediate and the colour of the resulting solution became yellow and rapidly turned deep red as the gas was evolved. The theoretical volume of gas was given off very quickly (approx. 10 mins). Gas evolution was measured by collection over water in a 2-litre measuring cylinder. The solution was allowed to reflux for one hour to ensure complete reaction. The hot solution was filtered and the filtrate allowed to cool slowly when well-formed canary-yellow crystals of the tricarbonyl were obtained. Some of the crystals were sealed into a glass tube in a nitrogen atmosphere for elemental analysis.

Analysis.

% C	% H	% N	
51.63	3.62	10.27	(found)
51.7	3.60	10.08	(theory)

Reaction with hydrogen fluoride.

Tris(pyridine)molybdenumtricarbonyl, (5g) was added to a polythene vessel and liquid anhydrous hydrogen fluoride (25ml), from a cylinder, condensed into the vessel cooled in an acetone-drikold bath at -78°C. The bath was removed and allowed to come to room temperature. Excess acid was removed in a stream of dry nitrogen. This treatment, however, did not remove all of the liquid. Consequently the reaction vessel was attached to a water pump via a tube containing sodium fluoride, calcium chloride and phosphorus pentoxide, and the pressure slowly reduced as the vessel was heated with a hair drier. In this way most, of the liquid was removed. The crude damp blackish solid, was transferred to a sublimation apparatus in a dry box and then attached to a high vacuum line via a silica trap, containing sodium fluoride, cooled to -78°C. The liquid was distilled out of the sublimer, leaving a deep crimson to brown coloured solid.

The sublimer was heated in an oil bath, the temperature being raised slowly. At a bath temperature of about 80°C, a white solid sublimed onto the cold finger. The temperature of the bath was slowly raised to about 100°C until no more sublimate was obtained. The residue remaining, by far the bulk of the material, was a rather blackish - brown solid with a greenish tinge.

Sublimate.

The white sublimate was twice resublimed, the final treatment giving a pure white solid, subliming at 65°C in vacuum. This solid dissolves immediately in water giving a colourless solution. If, however, the solid is left exposed to the atmosphere for several days it slowly turns blue. Complete elemental analysis for the white sublimate gave the following data.

Analysis.

% C	% H	% N	% F	% Mo	
39.79	4.15	9.02	30.05	16.09	(found)
39.61	3.83	9.13	30.03	16.25	(found)

This data fits the stoichoimetry $C_{30}H_{36}N_6MoF_{10}$, which requires %C = 39.59, %H = 3.99, %N = 9.24, %F = 31.33 and %Mo = 15.85.

On the basis of its solubility in water and its infra-red spectrum in the region 4000 - 700cms^{-1} it is suggested that this complex is a ten coordinate molybdenum VI species, and formulated $(P_yH)_6MoF_{10}$.

Residue.

The residue was pulverised in a dry box, and extracted with methylene chloride, giving a deep green solution and a brown insoluble solid. Extraction with the solvent dissolved about half the total residue. The combined extracts were then added to sodium dry diethyl ether giving a brilliant green solid. The brown residue proved to be extremely soluble in water, and, apart from obtaining a nujol mull spectrum in the infra-red region 4000 - 700cms^{-1}, was not further investigated. The green solid was insoluble in water, and exposure of the solid to the atmosphere over a period of a few days resulted in decomposition. The product of decomposition was brown in colour, and water soluble. The green product analysed to the empirical formula $(C_5H_5N)_2Mo(CO)_2F_2$. A nujol mull spectrum of the solid absorbed in the metal-carbonyl region.

Analysis.

% C	% H	% N	% F	% Mo	
41.44	3.22	7.89	10.75	27.91	(found)
41.34	3.02	7.96	10.69	27.86	(found)
41.38	2.89	8.05	10.91	27.55	(theory)

Tris(γ-picoline)molybdenumtricarbonyl.

Molybdenum hexacarbonyl, (5g) was refluxed with redistilled γ-picoline (30ml). The reaction is completely analogous to that described for the pyridine derivative. A 75% yield of a bright yellow crystalline product was obtained from the cooled solution.

Analysis.

% C	% H	% N	
55.1	4.55	9.22	(found)
55.0	4.58	9.20	(found)
54.9	4.61	9.15	(theory)

This complex tends to decompose more readily than its pyridine analogue. Whereas the colour of the pyridine derivative is unaffected over a period of one to two days, the picoline derivative darkens in colour in a matter of hours if exposed to the atmosphere. Samples for analysis were sealed in glass tubes in a dry nitrogen atmosphere.

Reaction with Hydrogen Fluoride.

Tris(γ-picoline)molybdenumtricarbonyl, (5g) was reacted with liquid anhydrous hydrogen fluoride according to the procedure already described. Final removal of liquid in a high vacuum line gave a blackish - brown solid, which was also treated as described for the pyridine analogue. Again etching of the glass sublimer was observed. The residue gave a white sublimate at about 100 °C in high vacuum, the unsublimed material remaining was blackish green in colour.

Sublimate.

This, the major product of interest obtained from this reaction, was resublimed twice, the final treatment giving a pure white product subliming in vacuum at 98 °C. The observed physical properties of this product are analgous to those of the pyridine derivative, and elemental analysis gave data consistant with the stoichiometry $C_{26}H_{32}N_4Mo_2F_8$.

Analysis.

% C	% H	% N	% F	% Mo	
43.63	4.85	8.45	13.83	29.06	(found)
43.45	4.86	8.45	14.32	28.92	(theory)

This may be a species similar to that suggested for the pyridine product. The infra-red spectrum indicates the presence of the picolinium ion. It is, however, quite difficult to formulate a structure from the stoichiometry obtained. It is particularly unfortunate that a molecular weight determination could not be obtained. Any formula suggested must take into account the ion $(C_6H_7NH)^+$, and since there are possibly four of these, only Mo_2F_5 remains. Magnetic moment measurement by the Gouy method showed the material to be diamagnetic.

Residue.

The residue was extracted with methylene chloride giving a very dark green solution, and leaving a water soluble brown solid. Precipitation of the solid with diethyl ether yielded a green solid, which decomposed immediately in air giving a black gum. Some of the solid was obtained by filtering in a nitrogen atmosphere. The yield, from several attempts at this reaction was of the order of a few milligrams, and only an incomplete analysis of the product could be obtained. This gave %N = 6.69, %F = 8.97, which gives a ratio of nitrogen to fluorine of 1:1. A nujol mull spectrum of the solid did not have any absorption in the metal-carbonyl region. In the absence of metal analysis, it is difficult to make any predictions as to the formulation of this product. It was particularly difficult to obtain reasonable mulls for spectral studies. The best, of numerous attempts, showed a medium to broad band, with maximum absorption at 1045cms^{-1}, a weak intensity band at 1210cms^{-1}, and three other peaks at 840 (weak shoulder), 800 (medium intensity) and 720cms^{-1}, the latter of intensity comparable with that of the 1045cms^{-1} band.

Tris(pyridine)tungstentricarbonyl.

Tungsten hexacarbonyl (5g), was refluxed with Analar pyridine, (30ml), for six hours. The rate of evolution of gas was very much slower than for the molybdenum reactions. The hot solution was filtered and allowed to cool slowly giving the tricarbonyl as well formed yellow - orange crystals. The colour darkens markedly on exposure to the atmosphere over a period of time.

Analysis.

% C	% H	% N	
42.71	2.86	8.31	(found)
42.63	2.98	8.29	(theory)

Reaction with Hydrogen Fluoride.

Tris(pyridine)tungstentricarbonyl, (5g) was treated with hydrogen fluoride as described for the molybdenum reaction. The final traces of hydrogen fluoride were removed in a high vacuum line, the residue remaining was a brown coloured solid. Again etching of the glass apparatus was apparent. A pale yellow solid sublimed out of the brown residue, at a bath temperature of about 100 °C. The remainder of the residue, blackish in colour, was insoluble in methylene chloride but dissolved immediately in water giving a blue solution. This product was not investigated further.

Yellow Sublimate.

This was resublimed twice, and each time a pale yellow solid was obtained over the temperature range 90-100 °C at 10^{-4}mm. The sublimate was extracted with 2-3ml Analar chloroform giving a deep yellow solution and a white insoluble solid. The white solid was resublimed giving a pure white sublimate at 90 °C in vacuum. Analysis of the white sublimate gave the data.

% C	% H	% N	% F	% W	
27.63	3.59	8.04	26.43	27.0	(found)
27.59	3.61	3.07	26.38	26.81	(found)

This data fits the stoichiometry $C_{20}H_{24}N_4WF_{10}$ which requires %C = 27.48, %H = 3.46, %N = 8.07, %F = 27.38, %W = 26.51.

This substance on exposure to the atmosphere over a period of days gradually turned blue. On the basis of its solubility in water, and its infra-red spectrum in the region 4000 - 700cms^{-1} it is suggested that this complex is a ten coordinate tungsten VI species, and formulated $(P_yH)_4WF_{10}$.

Chloroform Solution.

The solution spectrum in the infra-red region 4000 - 625cms^{-1} was obtained. This gave bands in the metal - carbonyl region similar to that observed for the green molybdenum complex. Evaporation of the solvent at room temperature in a rotary evacuator gave a few milligrams of a green solid which rapidly decomposed to a black gum. The reaction was repeated but not enough of this product could be isolated for elemental analysis.

Reaction of Tris(pyridine)chromiumtricarbonyl with Hydrogen Fluoride.

Tris(pyridine)chromiumtricarbonyl, (5g), prepared by Mr. J.H. Valentine of this Department, was reacted with liquid anhydrous hydrogen fluoride as previously described. The excess acid was removed by the procedure already outlined. However, after evacuating the reaction vessel under water pump pressure it was observed that no fumes were given off from the product, although a small amount of liquid, remained in the vessel. This liquid was green in colour, and there was also present some, apparently white, solid. The solid was removed by filtration. On further investigating the green liquid it was found that, when absolute ethanol was added, a white precipitate formed. this was filtered off and an attempt made to sublime the combined solids without success. An infra-red spectrum of the white solid showed a broad absorption band at 740cms^{-1}, attributable to the hexafluorosilicate ion.

Green Solution.

The solvent was removed with a rotary evacuator yielding a green gum. This was redissolved in the minimum of hot ethanol and the solution allowed to cool slowly giving pale green crystals which were filtered and dried in vacuo over P_2O_5. Only a partial analysis could be obtained for this material, which gave Cr = 16.84%, N = 7.56% and F = 33.23%, which corresponds to the ratio Cr: N: F of 1: 1.6: 5.3. Unfortunately this reaction could not be repeated.

Discussion.

Group VI Metal Carbonyl Fluorides.

The previous chapter describes some reactions of triphenylphosphine complexes with anhydrous hydrogen fluoride. In all of these, it was noted that some of the phosphine substituents were displaced from the parent compound during the reaction. It was thought that the same effect would be achieved with amine substituted Group VI metal carbonyls.

Group VI trisamine metal carbonyls decompose very readily. Even the pure compounds smell strongly of the particular amine substituent. Tris(pyridine)chromiumtricarbonyl decomposes, with loss of amine, within minutes when exposed to the atmosphere, and a similar phenomenon was observed for the trisamine complexes of molybdenum and tungsten carbonyls prepared in the present study.

The variety of colour changes observed in the reactions of $L_3M(CO)_3$, where L is pyridine or γ-picoline, and M is chromium, molybdenum or tungsten, with hydrogen fluoride, indicates the complexity of this new field of study. As already indicated in the experimental section only one substituted carbonyl fluoride has been characterised in the present study, namely, bis(pyridine)dicarbonylmolybdenum-

(11)fluoride. On the basis of infrared spectra it is suggested that a similar tungsten species can be prepared. There were no absorptions observed in the infrared spectra of the products isolated from the reaction of tris(pyridine)-chromiumtricarbonyl with hydrogen fluoride which could be attributed to carbon monoxide bonded to the metal. Other workers[66] have found that there is an increasing tendency for carbon monoxide to be lost on oxidation of Group V1 metal carbonyls in the order chromium > molybdenum > tungsten. The molybdenum carbonyl fluoride, like the platinum carbonyl fluorides, is insoluble in nonpolar solvents, consequently its dipole moment has not been obtained. It is extremely soluble in polar solvents, eg. methylene chloride, chloroform, but such a solution results in gradual decomposition of the complex. Because of this, it has not proved possible, as yet, to obtain the n.m.r. spectrum of the molybdenum carbonyl fluoride.

In general, the yields of isolable products from the present reactions are very small, only two compounds being obtained in quantity sufficient for magnetic moment determinations. In the main, information concerning the properties of the complexes prepared in this study has been derived from their infrared spectra.

It is expected that the magnetic moment of a low spin molybdenum(11) complex should be about 3.3BM at 300°K, and that it should be temperature dependent[67]. The diamagnetism of molybdenum complexes, in which the central metal is formally in the +2 oxidation state, eg. MoX_2, $[(Mo_6Br_8)X_6]^{2-}$, where X is Cl^-, Br^- or I^- and Y is Cl^-, I^- or OH^-, is attributed to polymeric structures and to metal - metal bonding. The magnetic moment of the complex $[Mo(diars)_2X_2]$, diars is $o\text{-}C_6H_4(AsMe_2)_2$, has been measured over the range 77 to 303 °K for X = Cl^-. At the upper limit, the magnetic moment is 2.85 B.M. falling to 2.60 B.M. at the lower temperature. The bromide and iodide have magnetic moments 2.91 at 298 °K and 2.80 B.M. at 297 °K respectively. The molar susceptibility of $Mo(CO)_2Py_2F_2$, as determined by the Gouy method, was found to be 4388×10^{-6} c.g.s units at 293 °K, which corresponds to a magnetic moment of 2.87 B.M. This is consistant with a second row Transition Metal d^4 ion with two unpaired electrons in an octahedral configuration. It contrasts with the magnetic moment for $[Mo(CO)_2\ diars\ I_2]$ of 1.98 B.M. This latter octahedral complex is obtained when $[Mo(CO)_4\ diars]$ is refluxed with iodine in carbon tetrachloride solution[68]. If, however, chloroform is used as the refluxing solvent, the molybdenum(111)species $[Mo(CO)_2\ diars\ I_2]I$ is obtained, and the magnetic moment of this complex is 1.40 B.M.. Nigam et al[69] have reacted the Group VI Metal hexacarbonyls with the diarsine ligand, o-$C_6H_4(AsMe_2)_2$, and obtained complexes of the type [$M(CO)_4$diars] and [$M(CO)_2$diars$_2$]. Oxidation of these complexes with bromine or iodine in suitable solvents give seven co-ordinate species[66,68] of the type [$Mo(CO)_3$diarsX_2], where X is the halogen. A pentagonal bipyramidal structure has been suggested for these seven coordinate complexes, Fig. 2.2, in which the halogen atoms are presumed to occupy the apical sites since the two axial bonds are longer than the other five[68], and since they are expected to be the positions where the most electronegative ligands would be attached. It would be reasonable to suggest that the planar part of the molecule for the octahedral molybdenum(11) complex, [$Mo(CO)_2$diarsI_2], should differ only in the number of attached carbonyl groups.

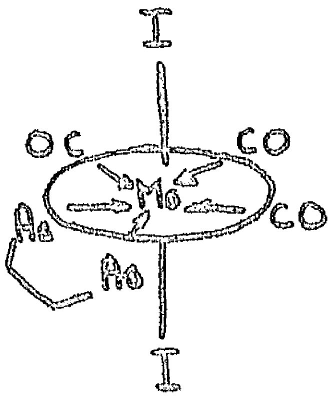


Fig. 2.2

The similarity in stoichiometry between [$Mo(CO)_2Py_2F_2$], [$Mo(CO)_2$diarsI_2] and [$Pt(CO)_2(PPh_3)_2F_2$] is in contrast to the infrared spectra of these compounds in the metal carbonyl region. Details of the spectra in this region for the complexes of the present work, other related carbonyls and carbonyl fluorides are given in Table 2.1.

Compound	Frequency (cms^{-1})	Medium	Reference
$Mo(CO)_6$	2000	gas	70
$Mo(CO)_3Py_3$	1900^{s}, 1762^{s}	mull	✣
$Mo(CO)_3\gamma\text{-}Pic_3$	1915^{s}, 1787^{s}, 1758^{s}	mull	✣
$Mo(CO)_2Py_2F_2$	2072^{w}, 2010^{w}, 1975^{m} 1930^{s}, 1880^{s}, $1320^{m\ sh}$	solution	✣
$Mo(CO)_2diarsI_2$	1942, 1887	mull	68
$W(CO)_6$	1980		71
$W(CO)_3Py_3$	1900^{s}, 1762^{s}	mull	✣
$W(CO)_aPy_bF_c$	2060^{w}, 1935^{w}, $1973^{m\ sh}$ 1925^{s}, 1915^{s}, $1900^{m\ sh}$	solution	✣
$Ru(CO)(PPh_3)_2F_3$	1965^{s}	mull	✣
$Os(CO)(PPh_3)_2F_3$	1945^{s}	mull	✣
$Pt(CO)_2(PPh_3)_2F_2$	2152, 2105, 2083	mull	16
$Pt(CO)_2[P(OPh)_3]_2F_2$	2179^{w}, 2127^{sh}, 2092^{s}	mull	✣

(s = strong, m = medium, w = weak, sh = shoulder, Mull refers to nujol and solution to $CHCl_3$. ✣ represents present work).

The mull spectra in the present work were recorded on a Perkin-Elmer 237 Spectrophotometer. The solution spectra were recorded on a Perkin-Elmer 125 Spectrophotometer.

Table 2.1

Two strong infrared active absorptions in the metal-carbonyl region are in accord with cis-dicarbonyl substituents in hexa-coordinated complexes[69]. On the basis of infrared spectra, analytical data and by analogy with [$Mo(CO)_2diarsI_2$], it is suggested that the structure of the present complex is described by Fig. 2.3.

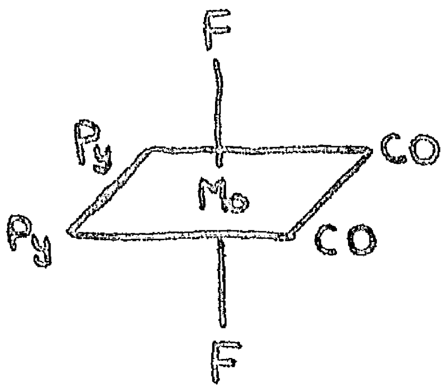


Fig. 2.3.

Group VI Metal Complex Fluorides.

The infrared spectra of the pyridinium and picolinium complexes, in the region 4000 - 700cms^{-1}, differ quite markedly from those of the free amines, and from those in which the amine is coordinated to a metal. Details of the infrared spectra of these ''salt-like'' complexes prepared in the present work, together with the reported spectra for similar complexes[72,73] are given in Tables 2.2 and 2.3.

$(PyHBF_4)$✧	$(PyH)_4MoF_{10}$	$(PyH)_4WF_{10}$	$(\gamma\text{-PicH})_4Mo_2F_8$
1625	1630	1640	1640
1597	1605	1613	1622
1525	1530	1537	1530
1477	1480	1485	1505
1367	1370	1375	1373
1327	1329	1337	1325
1250	1245	1250	1262
–	1190	1199	1208
–	1165	1165	–
BF_4^-	1065	1067	1040
absorbs	1045	1036	1010
here	943	945	960
744	740	744	800
677	670	680	730

✧ reference 72

Table 2.2

XHF_2✧	XBF_4✧	$XBPh_4$✧	X_4MoF_{10}	X_4WF_{10}	$(\gamma\text{-PicH})_4Mo_2F_8$
3203	3250	3230	3200	3230	3250
3180	3160	3173	3110	3120	3155
–	3120	3130	–	–	3110
3080	3080	3050	3040	3045	3065
–	2900	3010	–	–	–
–	–	2930	2950	2960	–
2300	2327	2360	2350	2355	2350

(+ reference 73 X = (PyH). The spectra were obtained as nujol and hexachlorobutadiene mulls on sodium chloride plates and were recorded on a Perkin-Elmer 237 Grating Spectrophotometer. Frequency in cms^{-1}).

Table 2.3.

Nuttall et alia[73] observed three peaks above $3100cms^{-1}$ for the compounds they studied, irrespective of the presence or absence of hydrogen bonding. In compounds of simple anions, eg. the halogens, in which hydrogen bonding is expected, these three peaks were of low intensity, whereas in the spectra of the complex anions studied, eg. BF_4^-, BPh_4^-, in which hydrogen bonding is not expected, three strong absorptions were observed in this region. The band observed at about $2800cms^{-1}$ was strong in the hydrogen bonded complexes, and is of only weak intensity in the non-hydrogen bonded complexes. They concluded that the presence of a strong broad absorption in this region was diagnostic of hydrogen bonding. Comparing the spectra obtained in the present study with those reported by these authors, it is concluded that the base is present as a cation and that the compounds are hydrogen bonded.

It is difficult to account for the difference in stoichiometry between the pyridinium and picolinium complexes of the present work. It can only be said that insufficient data are at present available to make any comment on this aspect, apart from suggesting that the most likely explanation may be that the picolinium complex is a mixture of (γ-PicH)F and MoF_6. This appears to be a reasonable conclusion. This substance is diamagnetic which could be explained by either metal - metal bonding or bonding via fluorine bridges, if it is not a mixture. Such an arrangement would be expected to be coloured whereas the product is colourless. If, however, the product is a mixture containing molybdenum($\overline{\underline{VI}}$) ions then both the lack of colour and the diamagnetism are reasonable physical properties. The far infrared spectrum of the picolinium complex is not particularly illuminating. The region 650 - 400cms^{-1} is obscured by vibrations which may be attributed to the picolinium ion by visual comparison with the spectrum of γ-picolinium chloride. There are, however, two intense absorptions at 239cms^{-1} and 230cms^{-1} which are not observed in γ-picolinium chloride. These may be due to metal-fluorine symmetric and asymmetric stretching vibrations, but such assignments are very doubtful and are much lower than what might reasonably be expected. Peacock et al[60] have assigned the Mo-F asymmetric stretching vibration, in $(MoF_6)^-$, MoF_6 and $(MoF_7)^-$ to the absorptions which occur at 623, 741 and 645cms^{-1} respectively.

The infrared spectrum of the pyridinium molybdenum fluoride in the region 650 - 200cms^{-1} is very similar to that of pyridinium chloride. The vibrations observed can be attributed to the pyridinium ion, with the exception of a strong broad band occurring at 274cms^{-1}. This may be due to metal - fluorine vibrations, but again this value is very low when compared with the values, quoted by Peacock and Sharp[60], for fluoro complexes of molybdenum.

It is extremely difficult to make any predictions with respect to structure on the evidence obtained from this brief exploratory study. The formulation suggested for this complex, $(PyH)_4MoF_{10}$, is perhaps only one of several which would fit the stoichiometry. The product may be a mixture of MoF_6 and $(PyH)F$, but all attempts at purification failed to effect a separation of the components. Examples of ten coordinate species are not particularly common, although there are some examples in the literature[63]. Jakob et alia[74] report the preparation of salts of ten coordinate complexes of molybdenum and tungsten in which the central metal is surrounded by eight cyanide ions and two ammonia molecules, and tungsten hexafluoride is reported[62] to react with ammonia giving a species formulated $WF_6 \cdot 4NH_3$. No structural data are given for any of these complexes.

Chapter 3.

Amine Complexes of Transition Metal Perchlorates.

Introduction.

Until recently, vibrations which are essentially metal - nitrogen stretches have only been located for ammonia complexes of trivalent metal ions, eg. Co-N in $[Co(NH_3)_6]^{3+}$[78], where they are assumed to occur at about 500cms^{-1}. The metal - nitrogen stretching frequency is of particular interest since it provides direct information about the coordinate bond. Because of the low bond order associated with the coordinate bond, and the relatively heavy mass of a Transition Metal, this vibration is expected to occur in the low frequency region of the infrared[68]. Bicelli, from an empirical relationship involving C-N bonds in the pyridine ring, has predicted that M-N frequencies, in pyridine metal complexes, would occur in the range 150 - 250cms^{-1}.

Gill et al[72], studied the infrared spectra of a large number of complexes of the type MX_2Py_2, where Py is pyridine, M is Mn, Co, Ni, Cu, Zn, Cd, or Hg, and X is a halogen or pseudo halogen, in the range 2000 - 400cms^{-1}. These authors did not observe any bands above 400cms^{-1} which could not be assigned to pyridine vibrations. It was unfortunate that they could not extend their studies to include the region of the spectrum down to 200cms^{-1}. Their studies showed, however, that there are few systematic changes in the bands observed for the free base when compared with those observed when the base is coordinated to a metal. Since changes in the electron density over an aromatic ring system invariably result in wide difference in the observed spectra[79], Gill suggests that the observed similarity in spectra between free and coordinated pyridine is consistant with a virtually unaltered electron density over the ring system. While this could result from back bonding from the metal atom, the authors themselves state that they have no positive evidence for such back bonding. However, this would be in agreement with the greater stability of α,α'-dipyridyl and o-phenanthroline metal complexes, which is believed to be due to similar back bonding. Over a series of first row Transition Metal complexes, it would be expected that nickel and copper would exhibit the greatest degree of back bonding in these complexes, since in these metals there are more d electrons available for dative pi bonding. This is also in agreement with the general classification of acceptor ions. It is doubtful, however, if such evidence will be readily accessible, since the effect, if it exists in pyridine complexes, will be relatively weak.

The first paper in the literature assigning metal - nitrogen vibrations, in complexes containing pyridine as the donor molecule, is attributed to Clark and Williams[80], who studied the infrared spectra of, and, on this basis assigned structures to, complexes of the type MX_2Py_2, where M is Mn, Co, Cu, Zn, or Hg and X is chlorine or bromine. These authors report, as did Gill et al, that two of the lowest ring vibrations, the in-plane ring deformation at 604cms^{-1} and the out-of-plane ring deformation at 405cms^{-1} in the spectrum of liquid pyridine, suffer significant shifts towards higher frequencies when pyridine is coordinated to a metal. Both authors agree that these shifts seem to be functions, whether directly or indirectly, of the metallic radius. In some cases, splitting of these bands was observed[72,80,81]. Since these vibrations are nondegenerate[82], it would appear that some interaction between different pyridine molecules exists, either within a single molecule or between different molecules of the unit cell. Clark and Williams[82], in a more detailed publication, observe that the magnitude of shift for these ring deformation modes, of the order of 30cms^{-1}, is dependent on the stereochemistry of the complex and on the metal atom, but is independent of the halogen, as are the absorptions assigned to the metal - nitrogen stretching modes[81,82]. On this assumption, the bands observed at about 250 and 230cms^{-1} have been assigned to the metal - nitrogen vibrations in tetrahedral and octahedral environments respectively. In general, there is little variation in the stretching frequency of metal - nitrogen vibrations for a series of substituted pyridine complexes of similar stereochemistry, but differing in the amine substituent. Such changes as are observed can be attributed to steric factors. It is also apparent from the values quoted that the M-N stretching frequencies are a function of stereochemistry. These features are illustrated in Table 3.1.

Compound	Structure	ν (M-N)cms^{-1}	Reference
Py_2CoCl_2	T	243	81
γ-Pic_2CoCl_2	T	244	81
β-Pic_2CoCl_2	T	240	81
α-Pic_2CoCl_2	T	260, 233	81
Py_4NiCl_2	O	236	82
Py_4NiBr_2	O	235	82
Py_4NiI_2	O	240, 223	82
β-Pic_4NiI_2	O	225, 210	82

(T = tetrahedral, O = octahedral, Py = pyridine,
Pic = picoline)

Table 3.1.

The metal - nitrogen stretching frequency, however, varies with the metal in a series of isostructural complexes.

This feature is illustrated in Table 3.2 for polymeric octahedral complexes.

Compound	ν(M-N) cms^{-1}	Reference
Py_2MnCl_2	212	82
Py_2FeCl_2	222	81
Py_2CoCl_2	235	81
Py_2NiCl_2	253, 235	81

Table 3.2

This order of frequencies is in agreement with the Irving - Williams[83] order of stabilities of complexes of bivalent ions of the first Transition Series, viz $Mn < Fe < Co < Ni < Cu > Zn$. Such an order is also found to hold for the pyridine ring deformation modes in a series of isostructural complexes. Thus, both bands increase in the expected order for the series of polymeric octahedral chloro complexes, of general formula Py_2MCl_2, detailed in Table 3.3

Compound	Deformation Mode (cms^{-1})	
	In-plane	Out-of-plane
pyridine	604	405
Mn	627	419
Fe	629	424
Co	631	429
Ni	634	439
Cu	644	441

(Only the metal atom is given for simplicity).

Table 3.3

The variations in these bands are parallel for a particular structure, but the shift in the 604cms^{-1} appears to be the more sensitive to changes in stereochemistry for a given metal, as is shown in Table 3.4

Compound	Structure	In-plane def(cms^{-1})	Out-of-plane def(cms^{-1})
Py_2CoCl_2	T	642	422
Py_2CoCl_2	P O	631	429
Py_4CoCl_2	O	625	422

(T = tetrahedral, P O = polymeric octahedral, O = octahedral)

Table 3.4

An Irving - Williams order has been found to hold for ring deformation modes, and also for metal - oxygen stretching vibrations in complexes of the type $[M(PyO)_6](ClO_4)_2$[84], Table 3.5. For simplicity, only the metal atom is given in the table.

Compound	Ring Skeletal Vibrations	ν(M-O)
Py	605 , 405	-
PyO	541 , 463	-
Mn	551 , 465	311
Fe	555 , 467	320
Co	556 , 468	331
Ni	557 , 464	342
Cu	560 , 464	363
Zn	553 , 465	319

(Py is pyridine, PyO is pyridine-N-oxide. Frequencies in cms^{-1}).

Table 3.5

The magnitude of shift for the ring skeletal vibrations is not as great in these complexes as it is for the pyridine complexes. This is to be expected, since, for the former, coordination is from an atom external to the ring, whereas for the latter coordination is from an atom in the ring system.

The stoichiometries and infrared spectra of these complexes of pyridine-N-oxide are in accord with ionic bonding between the perchlorate and the complexed cation. Since previous studies on metal - nitrogen vibrations had been confined to amine complexes of metal halides, it was thought relevent to conduct similar studies for a series of first row divalent Transition Metal ions in which the bonding between the metal and the anion could reasonably be expected to be ionic. Such a study should give unequivocal evidence as to the metal - nitrogen stretch in metal complexes.

Experimental.

The preparation of the complexes of the present work is relatively simple. The hydrated metal perchlorate was prepared by treating an excess of metal carbonate with 60% reagent grade perchloric acid, filtering off the excess carbonate and concentrating the filtrate on a steam bath to effect crystallisation. The hydrated metal salt was filtered and dissolved in absolute ethanol. To this solution was added a slight excess of the desired amine. This addition is an exothermic reaction and, in some cases, is accompanied by a change in colour. Thus, the green alcohol solution of nickel perchlorate turned blue on addition of pyridine or γ-picoline, whereas there was only slight darkening with addition of quinoline. The blue solution of the copper salt became purple on addition of pyridine, violet with γ-picoline and dark green with quinoline. No colour change was observed for either cobalt, manganese or zinc solutions on addition of the amines.

The pyridine and γ-picoline complexes of copper precipitated immediately on adding the ligand. The pyridine and γ-picoline complexes of cobalt, nickel and zinc and the quinoline complex of copper crystallised from solution after standing a few days in a refrigerator. The amine complexes of manganese, and the quinoline complexes of cobalt, nickel and zinc did not crystallise from solution, but were isolated by removing the solvent on a rotary evacuator, redissolving the residue in absolute ethanol and precipitating in anhydrous diethyl ether. These complexes were then redissolved in the minimum of hot ethanol and allowed to cool in a refrigerator. This treatment gave very small crystals of the complexes.

Removing the last traces of solvent from the complexes proved somewhat difficult, but was finally achieved by heating the solids to about 60°C in high vacuum. It was at this stage that a colour change was observed for the nickel -γ-picoline complex. The solid prior to this was a pale blue colour, which gradually became bright canary-yellow.

The general formulae for the complexes so prepared are $[ML_4(ClO_4)_2]$ and $[MQ_2(ClO_4)_2]$, where L is pyridine or γ-picoline, Q is quinoline and M is manganese, cobalt, nickel, copper or zinc. The analytical data obtained for these complexes is detailed in Table 3.1.

Compound	Colour	Analysis					
		Theory			Found		
		% N	% Cl	% M	% N	% Cl	% M
$MnPy_4(ClO_4)_2$	white	9.83	12.44	9.63	9.75	12.36	9.54
$CoPy_4(ClO_4)_2$	pink	9.75	12.34	10.21	9.68	12.29	10.23
$NiPy(ClO_4)_2$	blue	9.76	12.35	10.22	9.74	12.34	10.17
$CuPy_4(ClO_4)_2$	purple	9.68	12.25	10.97	9.64	12.31	10.93
$ZnPy_4(ClO_4)_2$	white	9.65	12.21	11.26	9.65	12.26	11.31
$Mn\gamma\text{-}Pic_4(ClO_4)_2$	white	8.95	11.32	8.77	8.77	11.30	8.65
$Co\gamma\text{-}Pic_4(ClO_4)_2$	pink	8.89	11.25	9.35	8.90	11.19	9.22
$Ni\gamma\text{-}Pic_4(ClO_4)_2$	yellow	8.89	11.22	9.32	8.89	11.20	9.30
$Cu\gamma\text{-}Pic_4(ClO_4)_2$	violet	8.82	11.16	10.01	8.84	10.98	10.14
$Zn\gamma\text{-}Pic_4(ClO_4)_2$	white	8.80	11.14	10.27	8.83	11.09	10.25
$MnQ_2(ClO_4)_2$	white	5.47	13.85	10.73	5.40	13.91	10.65
$CoQ_2(ClO_4)_2$	blue	5.43	13.74	11.42	5.36	13.66	11.40
$NiQ_2(ClO_4)_2$	yellow-green	5.43	13.74	11.38	5.42	13.52	11.36
$CuQ_2(ClO_4)_2$	dark green	5.38	13.61	12.20	5.40	13.58	12.19
$ZnQ_2(ClO_4)_2$	white	5.36	13.57	12.51	5.31	13.49	12.46

Table 3.6

General Discussion.

This investigation was initiated with a view to making unequivocal assignments for metal - nitrogen vibrations. However, the unusual nature of the infrared spectra obtained for the present complexes make necessary a discussion of the bonding between the anion and the complexed cation. It has been generally accepted that anionic association is minimal where the anion is a strong acid radical such as perchlorate. This ion was usually considered a very weak ligand since there were, until very recently, few known examples of perchlorato complexes. In the last year however, a large number of such complexes have been reported in the literature.

The perchlorate ion has a highly symmetrical structure. It is tetrahedral, having Td symmetry, and as such, has nine vibrational degrees of freedom giving rise to four fundamental vibrations, of which, only two, both triply degenerate, are infrared active; ν_3 the asymmetric stretch and ν_4 the asymmetric bend. In the unperturbed ion, the former is usually observed as a very broad strong absorption with a poorly defined maximum in the region 1050 - 1150cms^{-1}, while the latter is observed at about 630cms^{-1} as a sharp well-defined band. ν_1, the symmetric stretch, is theoretically infrared inactive, but is usually also observed as a very weak absorption at about 930cms^{-1}. It becomes very weakly allowed owing to distortion of the ion in a crystal field of lower symmetry than itself. A study of the effects of coordination upon the infrared spectrum of the perchlorate ion has been reported by Hathaway and Underhill[88]. These authors have shown that, as the perchlorate ion becomes involved in covalent bonding, its symmetry is lowered from Td to C_{3v} or C_{2v}, depending on whether one or two of its oxygen atoms are involved in bonding. Each of the two infrared active bands in Td symmetry are split into two components in C_{3v} symmetry, and into three components in C_{2v} symmetry. In addition, ν_1, the infrared inactive stretch in Td symmetry, becomes infrared active in perchlorato complexes, as does ν_2, the symmetric bend at 460cms^{-1} in Td symmetry, which gives one band in C_{3v} symmetry, and is split into two components in C_{2v} symmetry. It is therefore possible to distinguish between ionic, monodentate and bidentate perchlorate by means of infrared spectroscopy.

For convenience, part of the table, compiled by Hathaway and Underhill[88], where vibrations for ionic and monodentate perchlorate are assigned is reproduced in Table 3.7. The vibrations attributable to perchlorate observed in the present study are assigned according to this table. Other workers[90] disagree, in some instances, with the assignments of Hathaway and Underhill.

<u>State of ClO_4</u>	<u>Assignment.</u>					
ClO_4^-(Td)	ν_1	ν_2	ν_3		ν_4	
	A(R)	E(R)	F_2(I.R)		F_2(I.R)	
	sym.str	sym.bend	asym.str		asym.bend	
$-O^*-ClO_3(C_{3v})$	ν_2	ν_6	ν_1	ν_4	ν_3	ν_5
	A_1(I.R)	E(I.R)	A(I.R)	E(I.R)	A(I.R)	E(I.R)
	Cl-O^* str.	rocking	sym.str ClO_3	asy.bend Cl-O^*	sym.bend ClO_3	asy. bend ClO_3

(* coordinated oxygen, A - nondegenerate, E - doubly degenerate, F - triply degenerate, I - infrared active, R - Raman active).

Table 3.7

Harris et al[86], on the basis of conductivity experiments, postulated perchlorate coordination in $[M(phen)_2(ClO_4)_2]$ and $[Cu\ dipy_2(ClO_4)_2]$, where M is nickel or copper, phen is 1:10-phenanthroline and dipy is 2,2'-dipyridyl. McWhinnie[87], Quagliano et al[88] and Moore et al[89] reported the isolation and infrared characterisation of compounds of the type $[Cu\ en_2(ClO_4)_2]$, $[NiL_2(ClO_4)_2]$ and $[Ni\ x\text{-}Py_4(ClO_4)_2]$ respectively, where en is ethylene diamine, L is 3,4 or 3,5-lutidine and x-Py is a substituted pyridine. In each of these reports the infrared data indicate that the perchlorate ion is coordinated as a monodentate ligand. Very recently, Pavkovic and Meek[90] reported the synthesis of $[NiL_2(ClO_4)_2]$ complexes, where L is N-alkyl-ethylenediamine, in which the perchlorate group can be either mono or bidentate, depending on the number and size of the alkyl substituents on the nitrogen atoms. Thus, N-methyl and N,N'dimethyl derivatives form complexes containing monodentate perchlorate, whereas the N,N,N'-trimethyl ethylenediamine complex contains a bidentate perchlorate group. Wickenden and Krause[91] studied the coordination compounds of nickel(II)perchlorate with acetonitrile and obtained $[Ni(CH_3CN)_6](ClO_4)_2$, $[Ni(CH_3CN)_4(ClO_4)_2]$ and $[Ni(CH_3CN)_2(ClO_4)_2]$. The infra-red spectra of these complexes indicate the presence of ionic, monodentate and bidentate perchlorate respectively. Two other examples of a bidentate perchlorate group have been postulated in anhydrous $Cu(ClO_4)_2$[88], and Me_3SnClO_4[92]. Straub and Yung[93] have recently prepared the first anionic complexes containing only the perchlorate ion as the ligand. These are formulated $L_2[M(ClO_4)_4]$, where L is the tetra-butylammonium or methyl-triphenylarsonium ion and M is Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or UO_2^{2+}. The infrared spectra are not reported for these complexes.

A) Perchlorate vibrations.

1) The region 800 - 1300cms^{-1}.

In this region, the infrared spectra of the complexes of the present study clearly show the perchlorate moiety in two different environments. The strong absorption in the region 1060 - 1100cms^{-1} in the zinc complexes is assigned to the ν_3 mode in ionic perchlorates. Similarly, the absorptions at about 1100cms^{-1} in the quinoline complexes are also assigned to this asymmetric stretching vibration, although the peak contour is much sharper than that observed for potassium perchlorate[58] or for the present zinc complexes. However, the peaks at 1050^{-1} and 1100cms^{-1} in $CnQ_2(ClO_4)_2$ and 1063 and 1100cms^{-1} in $NiQ_2(ClO_4)_2$ may be due to coordinated perchlorate, but the presence of only a very weak absorption at 930 and 920cms^{-1} respectively suggests the contrary. Again, in Ni γ-pic$_4$(ClO$_4$)$_2$, the asymmetric stretching frequency appears to be slightly split, maxima at 1060 and 1105cms^{-1}, but the symmetric stretch at 934cms^{-1} in this complex is very weak, from which it is infered that ionic perchlorate is present. This also agrees with published[89] infrared data for this complex. The details of the infrared active vibrations of the present, and related, complexes are given in Table 3.8a.

The spectra of these complexes are in sharp contrast to those of the remaining pyridine and γ-picoline complexes. In these, the ν_3 mode of Td symmetry is clearly split into two sharp peaks at about 1030 and 1130cms^{-1}, the ν_1

and ν_4 modes of C_{3v} symmetry respectively. The ν_2 stretching mode of C_{3v} symmetry is also clearly observed as a strong band at about 930cms^{-1}. The complex $NiPy_4(ClO_4)_2$ recently prepared by other workers[93], has been studied spectroscopically, and the agreement with the present values is excellent. Details of the infra-red active vibrations observed in the present investigation, together with those reported by other authors for the same or similar complexes are given in Table 3.8b.

The present spectra were recorded as nujol mulls on potassium bromide plates, the mulls being prepared in a dry box since the complexes are very sensitive to atmospheric moisture.

Compound	Symmetry^{+} Assignment	Frequency cms^{-1} ν_1	ν_3	Reference
ClO_4^-	Td	935^{w}	$1050-1170^{s}$ b	58
$ZnPy_4(ClO_4)_2$	Td	945^{w}	$1060-1100^{s}$	
$Zn\gamma-Pic_4(ClO_4)_2$	Td	928^{w}	$1075-1095^{s}$	
$ZnQ_2(ClO_4)_2$	Td	925^{w}	$1085-1107^{s}$	
$CuQ_2(ClO_4)_2$	(Td)	930^{w}	$1050^{s}_{;}1100^{s}$	
$NiQ_2(ClO_4)_2$	(Td)	920^{w}	$1063^{s}_{;}1100^{s}$	
$Ni\gamma-Pic_4(ClO_4)_2$	Td	934^{w}	$1060^{s}1105^{s}$	
$Ni\gamma-Pic_4(ClO_4)_2$	Td	931^{w}	$1040-1130^{s}$	93
$CoQ_2(ClO_4)_2$	Td	920^{w}	$1095-1105^{s}$	
$MnQ_2(ClO_4)_2$	Td	937^{w}	$1090-1107^{s}$	

Table 3.8a

Compound	Symmetry^{+}		Frequency in cms^{-1}			Reference
		Assignment	ν_2	ν_1	ν_4	
$Cu(ClO_4)_2 2H_2O$	C_3v		920^s	1030^s	1158^s	85
$CuPy_4(ClO_4)_2$	C_3v		929^m	1040^s	1107^s	
$Cu\gamma$-$Pic(ClO_4)_2$	C_3v		930^m	1045^s	1120^s	
$NiPy_4(ClO_4)_2$	C_3v		932^s	1030^s	1130^s	
$NiPy_4(ClO_4)_2$	C_3v		929^s	1032^s	1133^s	93
$CoPy_4(ClO_4)_2$	C_3v		930^s	1030^s	1130^s	
$Co\gamma$-$Pic_4(ClO_4)_2$	C_3v		925^s	1020^s	1137^s	
$MnPy_4(ClO_4)_2$	C_3v		936^s	1030^s	1130^s	
$Mn\gamma$-$Pic_4(ClO_4)_2$	C_3v		929^s	1025^s	1135^s	

($^{+}$ refers to ClO_4, w = weak, m = medium, s = strong, b = broad. Spectra recorded on a Perkin-Elmer 125 Spectrophotometer).

Table 3.8b

The magnitude of splitting of the asymmetric stretching frequency, about 100cms^{-1} in the present complexes, has been interpreted[90] as indicative of strong perchlorato coordination. However, perchlorate coordination to a metal through an oxygen atom is not the equivalent of complete convalent bond formation, and possibly a better guide to the covalent character of the bond would be the shift observed for the infrared inactive symmetric stretch, ν_1 of Td symmetry. Coordination through a given oxygen atom would be expected to lower the bond order, and consequently, the vibrational frequency of the corresponding Cl-O* bond. The corresponding shift has been reported[85] for the sulphate ion, 981cms^{-1}(Td) to 970cms^{-1}(C_3v), and for the amine nickel perchlorato complexes[63], 935cms^{-1}(Td) to 925cms^{-1}(C_3v). The magnitude of shift observed for this band in the present complexes is about 6cms^{-1}. A much larger shift in this band would be expected if the bond were strongly covalent. Thus, ν_3 occurs at 739 and 715cms^{-1} in the spectra of anhydrous perchloric acid and perchloryl fluoride respectively[85], corresponding to shifts of 193 and 217cms^{-1} for the Cl-OH and Cl-F stretching vibrations respectively. The bands at 630 and 460cms^{-1}.

The zinc pyridine complex and the γ-picoline complexes of nickel and zinc exhibit spectra in accord with ionic perchlorate, (Table 3.9a). The spectra of the remainder of the pyridine and γ-picoline complexes confirm the presence of monodentate perchlorate, Table 3.9b. The magnitude of splitting observed when the ν_4 mode of Td symmetry is lowered to C_3v symmetry is about 10cms^{-1}. The spectrum of quinoline as a liquid film shows the presence of two weak and two strong bands, in this region, which make it rather difficult to assign unequivocally the peaks observed in the spectra of the complexes. If, as the spectra of the quinoline complexes in the region 800-1300cms^{-1} suggest, the bonding between metal and anion is ionic, only one peak attributable to the anion should be observed at about 630cms^{-1}. However, comparison with the pyridine and γ-picoline complexes suggests that there are two peaks which may be attributable to perchlorate at about 625cms^{-1}.

The expected band at about 460cms^{-1}, the ν_6 rocking mode of monodentate perchlorate, is not observed in the present spectra of the pyridine and γ-picoline complexes. A weak peak is present in this region in the quinoline complexes, the details of which are given in Table 3.9c.

Compound.	Symmetry.	Frequency (cms^{-1}) Assignment ν_4	Reference.
ClO_4^-	Td	626	58
$ZnPy_4(ClO_4)_2$	Td	622^s	
$Zn\gamma^2Pic_4(ClO_4)_2$	Td	622^s	
$Ni\gamma$-$Pic_4(ClO_4)_2$	Td	620^s	

Table 3.9a.

Compound	Symmetry	Frequency (cms^{-1})			Reference
	Assignment	ν_6	ν_5	ν_3	
$Cu(ClO_4)_2 2H_2O$	C_3v	430	620, 605	643	85
$CuPy_4(ClO_4)_2$	C_3v	(427)	619^{s}	625^{sh}	
$Cu\gamma\text{-}pic_4(ClO_4)_2$	C_3v	–	620^{s}	625^{sh}	
$NiPy_4(ClO_4)_2$	C_3v	–	614^{s}	623^{s}	
$CoPy_4(ClO_4)_2$	C_3v		615^{s}	623^{m}	
$Co\gamma\text{-}pic_4(ClO_4)_2$	C_3v	–	615^{s}	625^{m}	
$MnPy_4(ClO_4)_2$	C_3v	–	617^{sh}	625^{s}	
$Mn\gamma\text{-}Pic_4(ClO_4)_2$	C_3v	–	616^{s}	633^{s}	
$HClO_4$	C_3v	426	585	574	85
$FClO_3$	C_3v	405	589	549	85

Table 3.9b.

Compound	Symmetry	Frequency (cms^{-1})			Reference
	Assignment	ν_6	ν_5	ν_3	
$Cu(ClO_4)_2 2H_2O$	C_3v	430	620, 605	643	
$ZnQ_2(ClO_4)_2$	(C_3v)	433^{w}	624^{s}	635^{m}	
$CuQ_2(ClO_4)_2$	(C_3v)	492^{w}	620^{s}	633^{m}	
$NiQ_2(ClO_4)_2$	(C_3v)	467^{w}	616^{s}	624^{m}	
$CoQ_2(ClO_4)_2$	(C_3v)	463^{w}	623^{s}	634^{m}	
$MnQ_2(ClO_4)_2$	(C_3v)	484^{w}	622^{s}	633^{m}	

Table 3.9c

The band at $427 cms^{-1}$ in $CuPy_4(ClO_4)_2$ may be due to splitting of the ring deformation of the amine as a result of interaction between different pyridine molecules, either within a single molecule or between different molecules of the unit cell. This interpretation has been used by other workers[82] to explain a similar observation in complexes of the type Py_2CoX_2 where X is a halogen. Further, the ν_6 rocking mode of monodentate perchlorate occurs at 480cms^{-1} in $Cu(ClO_4)_2 2H_2O$. The lack of absorption in this region in the picoline complexes may be due to the fact that the amine ligand also absorbs at about this frequency and consequently would mask the perchlorato vibration. It is much more difficult to explain the lack of this vibration in the pyridine complexes. It may be masked by amine vibrations, although this is unlikely since it would mean quite large shifts in frequency. Alternatively, it may be that this vibration is only observed when there is extensive covalent interaction between perchlorate and metal.

The spectra of the quinoline complexes present an anomaly. Their spectra in the region 800 - 1300cms^{-1} suggests ionic perchlorate, whereas the region 400 - 800cms^{-1} suggests monodentate perchlorate. It is possible that the weak peak observed in these complexes at about 485cms^{-1} may be due to the amine, and that crystal interactions cause splitting of the ν_4 asymmetric bending vibration of Td symmetry at about 630cms^{-1}. The magnitude of splitting is about 10cms^{-1}, which is similar to that observed[95] in $Cu(ClO_4)_2 2H_2O$ and to a lesser extent in anhydrous $Cu(ClO_4)_2$. It has been suggested that the splitting may be due to the presence of ^{35}Cl and ^{37}Cl Chlorine isotopes. If this is so, the magnitude of splitting would be expected to be much less than that observed. It is therefore, not possible on the evidence so far presented, to decide whether ionic or monodentate perchlorate is present in the quinoline complexes. Other evidence, which will be presented help to resolve this problem. However, it is relevent, at this point to discuss the infrared active amine vibrations.

Amine Vibrations.

In general, the spectra of the complexes are not particularly different from those of the free amine in the region 1900 - 650cms^{-1}. The strong band at 1604 and 1580cms^{-1} in the spectra of γ-picoline and pyridine respectively move to slightly higher frequencies in the complexes. This agrees with the observations of other workers[72,82]. However, significant shifts are observed for the ring deformation modes when the amine is coordinated to the metal. The observed frequencies for these vibrations are detailed in Tables 3.10a, b and c. In compiling these tables further arguments have been anticipated.

Compound	Amine Ring Vibrations.			
Pyridine			405^{m}	600^{S}
$MnPy_4(Cl_4)_2$			414^{m}	609^{S}
$CoPy_4(ClO_4)_2$			415^{m}	610^{S}
$NiPy_4(ClO_4)_2$			431^{m}	630^{S}
$CuPy_4(ClO_4)_2$			440^{m}	637^{S}
$CuPy_2Cl_2$[82]			441	644
γ-picoline			433^{S}	513^{m}
$Mn\gamma\text{-}pic_4(ClO_4)_2$			491^{S}	537^{m}
$Co\gamma\text{-}pic_4(ClO_4)_2$			494^{S}	540^{m}
$Cu\gamma\text{-}pic_4(ClO_4)_2$			495^{S}	551^{m}
Quinoline	373^{W}	388^{m}	475^{S}	515^{W}
$MnQ_2(ClO_4)_2$	373^{W}	390^{m}	474^{S}	518^{W}
$CuQ_2(ClO_4)_2$	-	401^{m}	494^{S}	529^{W}

Table 3.10a

Compound	Amine Ring Vibrations.			
Pyridine			405^{m}	600^{S}
$ZnPy_4(ClO_4)_2$			419^{m}	644^{S}
$ZnPy_2Cl_2$[82]			422	639
γ -picoline			483^{S}	513^{m}
$Zn\gamma\text{-}pic_4(ClO_4)_2$			490^{S}	504^{m}
Quinoline	373^{W}	388^{m}	475^{S}	515^{W}
$ZnQ_2(ClO_4)_2$	377^{W}	395^{m}	481^{S}	528^{W} -
$CoQ_2(ClO_4)_2$	372^{W} ,	389^{m} ,	473^{S} ,	521^{m}

Table 3.10b

Compound	Amine Ring Vibrations.			
γ-picoline			483^{s}	513^{m}
$Ni\gamma\text{-pic}_4(ClO_4)_2$			509^{s}	572^{m}
Quinoline	373^{w}	388^{m}	475^{s}	515^{w}
$NiQ_2(ClO_4)_2$	373^{w}	390^{m}	475^{s}	522^{w}

(w = weak, m = medium, s = strong)

Table 3.10c

The spectra in the region 400 - 650cms^{-1} were obtained as nujol mulls on KBr plates using a Perkin-Elmer 125 Infrared Spectrophotometer. The spectra below 400cms^{-1} were obtained as nujol mulls on polythene plates and recorded on a Grubb-Parsons DM2 Far Infrared Spectrophotometer. Mulls were prepared in a dry box. All frequencies are in cms^{-1}.

Any shift observed in these vibrations must be attributed to either the stereochemistry of the complex, or to the particular metal or to both, since only metal perchlorates were used. Clark and Williams[82] have demonstrated that the shift observed for pyridine ring deformation modes in complexes of the type MX_2Py_2 or $_4$, where X is a halogen, is independent of the halogen, but follow the Irving-Williams order for a series of complexes of the same stereochemistry, differing only in the central metal (cf Table 3.3 p.85). Inspection of table 3.10a shows a similar order for the three series of complexes, viz the frequency increases in the order Mn < Co < Ni < Cu. This is the order of stability predicted by Irving and Williams[83].

Metal-Nitrogen Vibrations.

The most explicit publication to date on metal-nitrogen vibrations in aromatic amine metal complexes is due to Clark and Williams[82], although Sharp et al[76,81,84] have certainly examined a wider variety of complexes. Metal-nitrogen vibrations are strongly dependent on the ligand to which the nitrogen atom is attached, and their frequencies decrease as the mass of the ligand increases, as Table 3.11 illustrates.

Type of Complex.	ν(M-N)	Ref.
metal - ammonia	420-500	58
metal - hydrazine	306-440	95
metal - glycine	275-423	96
metal - anilines	350-400	94
metal - pyridines	200-300	82

Table 3.11

The basicity of the ligand will also influence the metal-nitrogen vibration. However, in the complexes of the present study, although the order of basicity is γ-picoline > pyridine > quinoline, it would appear that the basicity difference between γ-picoline and pyridine is not sufficient to overcome the mass effect as Table 3.12 illustrates.

Compound	ν(M-N)	Other Vibrations.
$MnPy_2Cl_2$[82]	212	–
$MnPy_4(ClO_4)_2$	222	233
$CoPy_4(ClO_4)_2$	233	246
$NiPy_4Cl_2$[82]	236	–
$NiPy_4(ClO_4)_2$	240	262
$CuPy_2Cl_2$[82]	263	–
$CuPy_4(ClO_4)_2$	264	283
$ZnPy_4(ClO_4)_2$	220	–
$ZnPy_2Cl_2$[82]	220	–
$Mn\gamma\text{-}pic_4(ClO_4)_2$	200	238
$Co\gamma\text{-}pic_4(ClO_4)_2$	227	249
$Cu\gamma\text{-}pic_4(ClO_4)_2$	241	291
$Zn\gamma\text{-}pic_4(ClO_4)_2$	200	–
$MnQ_2(ClO_4)_2$	200	–
$CoQ_2(ClO_4)_2$	210	–
$CuQ_2(ClO_4)_2$	220	–
$ZnQ_2(ClO_4)_2$	220	–

(frequency in cms^{-1})

Table 3.12.

The spectra in the region 200 - 400cms^{-1} were obtained as nujol mulls on polythene plates and recorded on a Grubb-Parsons DM2 Far Infrared Spectrophotometer using CsI optics, the mulls being prepared in a dry box. The complex $Ni\gamma\text{-}Pic_4(ClO_4)_2$ is not included in the table since it gives a spectrum which is not consistant with the other complexes. This complex will be discussed later.

The metal-nitrogen frequencies increase in the order $Mn < Co < Ni < Cu > Zn$ for each of the ligands. This again, is in accord with the Irving-Williams order, and is also in agreement with the observations of Clark and Williams[83].

The bands listed under the heading ''other vibrations'' may be due to metal-oxygen stretches. Quagliano et al[84] studied the far infrared spectra of complexes of the type $[M(PyO)_6](ClO_4)_2$, where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cr(III), Fe(III) or Al(III) and PyO is pyridine N-oxide. The bands assigned to $\nu(M-O)$ in these complexes are listed in Table 3.13, only the metal atom is given for simplicity.

Mn	Fe	Co	Ni	Cu	Zn	Central Metal.
311	320	331	342	363	319	Frequency cms^{-1}.

Table 3.13.

If there is bonding between the metal and the oxygen in the perchlorato complexes then infrared activity may be expected and the frequency of absorption should follow the Irving-Williams order. Such an order is observed in these other bands listed in Table 3.12, but it should be pointed out that these bands may also be attributed to metal-nitrogen vibrations, rather than metal-oxygen.

While the primary purpose of this investigation has not been achieved, viz the unequivocal assignment of metal-nitrogen vibrations, the physical measurements recorded demonstrate further proof of the coordinative nature of the perchlorate ion. Clark et al[82] were able to assign structures to the complexes they studied, on the basis of their infrared spectra, since they found that metal-halogen vibrations were quite sensitive to structural environment. On the basis of their observations, and on the observed vibrational frequencies for metal-nitrogen and amine ring deformation modes it is possible to postulate structures for the present complexes. It is for this purpose that Tables 3.10 a, b and c (pps. 104,105) were compiled in that particular manner. It is suggested that the complexes listed in Table 3.10a have an octahedral or distorted octahedral structure, that those in Table 3.10b conform to a tetrahedral structure and that those in Table 3.10c have a square planer arrangement of ligands round the central metal. To substantiate these postulated structures, the reflectance spectra in the region 50-10 kK, and magnetic moments, measured by the Gouy Method, were obtained.

Reflectance Spectra.

Tables 3.14 a, b, c, d and e give the assigned transitions and bands observed for the present and related complexes according to structural environment. Figures are in cms^{-1} x 10^{-3}, and the results of this examination are discussed for each element.

Manganese - octahedral environment.

Compound	${}^4T_1g(G)$	${}^4T_2g(G)$	${}^4A_1g(G)$	${}^4Eg(G)$	Reference
$[Mn(H_2O)_6]^{2+}$	18.9	23.1	24.95	25.3	97
$MnPy_2Cl_2$	16.7, 19.0	20.4	23.7		97
MnQ_2Cl_2	18.35	21.28	23.8		98
$MnAn_4I_2$	17.95	20.41			94
$MnPy_4(ClO_4)_2$	-	22.73	25.0		
$Mn\gamma$-$Pic_4(ClO_4)_2$		23.81	26.67		
$MnQ_2(ClO_4)_2$	17.33, 18.87	23.26	25.0		

(An = aniline, Py = pyridine, γ-Pic = γ-picoline,
Q = quinoline)

Table 3.14a

Copper - probably tetragonally distorted octahedron.

Compound.	Mixture of Transitions.	Reference
$CuPy_4(ClO_4)_2$	17.54	
$Cu\gamma\text{-}Pic_4(ClO_4)_2$	17.39	
$CuQ_2(ClO_4)_2$	16.94, 23.31	
CuQ_2Cl_2	16.13, 19.23	98

Table 3.14b.

Nickel - distorted octahedral environment.

Compound	$^3T_{2g}(F)$	$^3T_{1g}(F)$	$^1E_g(D)$	$^1T_{2g}(D)$	$^3T_{1g}(P)$	Ref
$NiPy_4Cl_2$	10.86	16.13	12.99	19.61	25.64	99
$NiPy_4(ClO_4)_2$	-	16.69	12.12	-	27.03	
$Ni\gamma\text{-}Pic_4I_2$	-	15.83	11.77	-	25.0	100
$Ni(3\text{-}BrPy)_4(ClO_4)_2$		16.2	12.0		26.9	89

Cobalt - distorted octahedral environment.

Compound.	$^4A_{2g}$, T_{1g} Mixture	Reference
$CoPy_4(ClO_4)_2$	18.7 22.2	
$Co\gamma\text{-}pic_4(ClO_4)_2$	20.0 25.0	
$Co\gamma\text{-}pic_4Br_2$	17.24 19.23 20.83	102

Table 3.14c

Cobalt - Distorted tetrahedral environment.

Compound.	$^4T_1$ $^2E_1$ $^2T_1$ Mixture	Reference.
$[CoCl_4]^{2-}$	14.4, 15.2, 15.5, 16.1, 16.4	97
CoQ_2Cl_2	15.33, 16.26, 17.45	98
$CoQ_2(ClO_4)_2$	16.92, 22.5	

Table 3.14d

Nickel - Distorted Planar environment.

Compound.	Transition observed.	Reference.
$Ni\gamma\text{-}Pic_4(ClO_4)_2$	22.73	
$NiQ_2(ClO_4)_2$	23.26	
$Ni\gamma\text{-}Pic_4(ClO_4)_2$	22.9	89
$Ni\text{-}(p\text{-}NH_2Py)_4(ClO_4)_2$	23.6	89

Table 3.14e

Manganese.

Bispyridinemanganese(II)chloride is known to have octahedral coordination about the metal atom[101]. Sharp et al[94,98] suggest that, by comparison with standard spectra, the complexes MnQ_2Cl_2 and $MnAn_4I_2$ also have octahedral environment about the metal atom. The spectra of the present complexes are very similar to those reported by these authors. The ground state for a d^5 atom in an octahedral field is ^6A_1g and the observed bands correspond to transitions to the electronic states given at the head of the columns. The reflectance spectra of the manganese complexes are, in general, poor. The d→d transitions of Mn(ll) are spin-forbidden and therefore of weak intensity. To account for octahedral coordination in $MnQ_2(ClO_4)_2$ it is suggested that the perchlorate group acts as a bridge between two or more metal atoms.

Cobalt.

The spectra of the cobalt compounds are quite characteristic of octahedral, for $L_4Co(ClO_4)_2$, L = pyridine or γ-picoline, and of tetrahedral, for $CoQ_2(ClO_4)_2$, environments. The ground state for the Co(ll) ion is ^4T_1g for octahedral coordination and $^4A_2$ for tetrahedral coordination. The transitions $^4T_1g \rightarrow {}^4A_2g(F)$ and $^4T_1g \rightarrow {}^4T_1g(P)$ occur at slightly lower energies in the present complexes, and the transition $4T_1g \rightarrow {}^2Eg$, which in regular octahedral environment usually occurs at about 11 kK is not observed in the present complexes, although the presence of a band is indicated. However, with the present apparatus it was not possible to obtain spectra below 10 k.K.

Table 3.14d compares the transitions observed for $CoQ_2(ClO_4)_2$ with those reported for the $[CoCl_4)^{2-}$ ion and CoQ_2Cl_2. The absorption bands between 20 and 15 kK correspond to transitions[27] to mixtures of the excited states $^4T_1$, $^4A_2$ and $^2T_1$ and confirm the proposed tetrahedral configuration about the cobalt atom.

Nickel.

From the spectroscopic evidence $NiPy_4(ClO_4)_2$ has octahedral configuration about the metal atom. The colour of the complex is a very pale blue and the visible spectra can be interpreted in terms of electronic transitions from a $^3A_2g(F)$ ground state to the excited states given at the head of the columns.

The complexes $Ni\gamma\text{-}pic_4(ClO_4)_2$ yellow and $NiQ_2(ClO_4)_2$, very pale yellow green give a single absorption maximum at about 23 kK which is typical of square planar nickel(II) complexes[103].

Copper.

No definite information can be deduced from the electronic spectra of the present complexes concerning their stereochemistry. As is general with copper(II) complexes, the transitions observed are in accord with distorted octahedral coordination about the central metal.

Zinc.

It is not possible to obtain information on the structure of the zinc complexes from their ultra-violet or visible spectra. However, bispyridinezinc(II)chloride and bromide, on the basis of partial structural determination[104], are considered to have tetrahedral coordination about the zinc atoms. By analogy, it is suggested that the complexes $L_4Zn(ClO_4)_2$, where L is pyridine or γ-picoline also have a tetrahedral arrangement of ligand molecules about the central metal, and that a distortion of this arrangement may describe the stereochemistry of the quinoline complex. Such an arrangement could be achieved by considering perchlorate groups acting as bridges.

Magnetic Moments.

The Gouy method was used to obtain the magnetic moments of the present complexes using a permanent magnet with a field strength of 7000gauss. Possibly the main source of error using this method arises from non-uniform packing of the tube. All of the complexes of the present investigation were finely ground in a dry box using an agate pestle and mortar and packed into a specimen tube, the dimensions of which were, overall length 19.5cms, external diameter 4m.m, internal diameter 3m.m. Where possible 13cms. of sample was gently and uniformly tapped into the specimen tube, corresponding to about 0.3 - 0.4gm of sample. The tube was standardised using $Hg[Co(CNS)_4]$[108], and the measurements carried out at room temperature. The observed values are recorded in Table 3.15.

Compound	$(\chi_m^{corr} \times 10^6)$c.g.s.	Temp °K	$\mu_{eff.}$ B.M.
$MnPy_4(ClO_4)_2$	14,290	297	5.85
$Mn\gamma\text{-}pic_4(ClO_4)_2$	13,832	297	5.77
$MnQ_2(ClO_4)_2$	14,634	297	5.91
$CoPy_4(ClO_4)_2$	10,360	297	5.10
$Co\gamma\text{-}pic_4(ClO_4)_2$	10,230	297	4.95
$CoQ_2(ClO_4)_2$	8,335	297	4.60
$NiPy_4(ClO_4)_2$	4,922	297	3.44
$Ni\gamma\text{-}pic_4(ClO_4)_2$	105	297	diamagnetic
$NiQ_2(ClO_4)_2$	112	297	diamagnetic
$CuPy_4(ClO_4)_2$	1,353	297	1.80
$Cu\gamma\text{-}pic_4(ClO_4)_2$	1,206	297	1.70
$CuQ_2(ClO_4)_2$	1,322	297	1.78
$ZnPy_4(ClO_4)_2$	-80	297	diamagnetic
$Zn\gamma\text{-}pic_4(ClO_4)_2$	-90	297	diamagnetic
$ZnQ_2(ClO_4)_2$	-103	297	diamagnetic

Table 3.15

The diamagnetic correction factors used in the calculation of the observed magnetic moments were taken from published data[406]. The moments are within the usually observed experimental values for spin free complexes in octahedral configurations for Mn(ll), Co(ll), Ni(ll) and Cu(ll) with the obvious exceptions of the complexes $CoQ_2(ClO_4)_2$, which is within the experimentally observed range of values for high spin tetrahedrally coordinated Co(11), and the nickel γ-picoline and quinoline complexes, the diamagnetism of which is, in accord with a square planar arrangement of ligands around the central metal.

The octahedral stereochemistry of the manganese, and copper quinoline complexes could be explained by Fig 3.1.

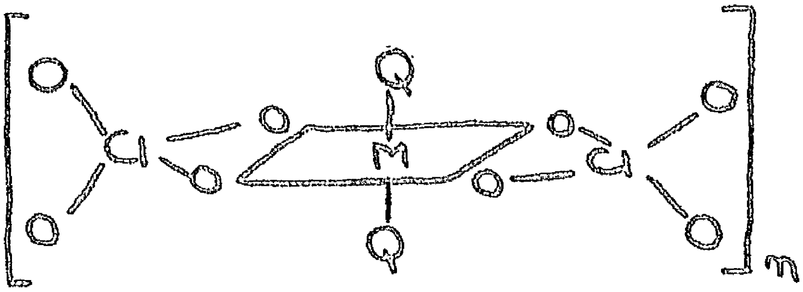
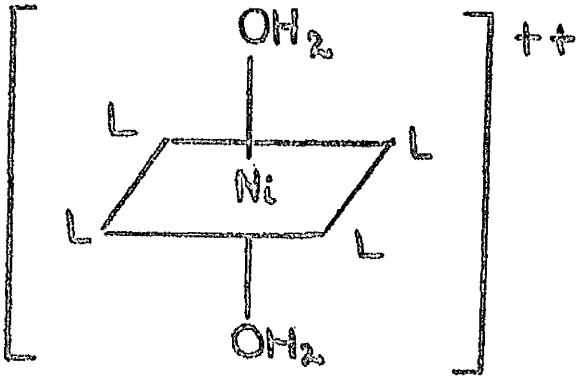


Fig. 3.1

Such an arrangement, it is suggested, could also explain the apparently anomolous infrared spectra obtained for these complexes. The structures of the other complexes are visualised as distortions of regular octahedral, tetrahedral and square planar arrangements since the perchlorate ligand is not expected to be as strongly bonded as the amine. This is substantiated by the marked difference in the spectra obtained when mulls of the complexes are prepared outwith the dry box. In every case the bands attributable to perchlorate, particularly the vibration in the region 1030 — 1130cms^{-1}, become very broad and have poorly defined maxima. The spectra in these instances are quite characteristic of ionic perchlorate. In one case, that of $Ni\gamma\text{-pic}_4(ClO_4)_2$, mulling in the open atmosphere resulted in the colour of the complex changing from yellow to blue. The spectrum obtained in the region 1030—1130cms^{-1} was much more diffuse than that for the yellow complex. It is suggested that this blue compound may be the dihydrate which would then confer octahedral symmetry on the central metal, Fig.3.2



(L = γ-picoline.)

Fig 3.2

The X-ray powder patterns of the anhydrous complexes are not particularly illuminating. They present a very complex pattern of lines indicative of low symmetry. As far as could be ascertained by visual inspection, the nickel and cobalt pyridine complexes are isomorphous.

Reproduction of a representative selection of infrared spectra obtained during this study are appended at the end of Chapter 4.

Chapter 4.

Amine Complexes of Transition Metal Tetrafluoroborates.

Introduction.

This study is a natural extension of that described in the previous chapter for two particular reasons. The tetrafluoroborate ion has the same symmetry elements, and therefore, essentially the same infrared spectrum, as that described for the perchlorate ion. It is also a strong acid radical in which the boron is covalently saturated by fluorine, and is usually considered a noncomplexing ion since fluorine does not often form bridges[107]. In this event, it should therefore have been possible to make unequivocal assignments for metal - nitrogen in amine - metal tetrafluoroborates. On the other hand, it was also of interest to investigate the possibility of preparing complexes in which tetrafluoroborate might be complexed, since, in this event, these would be among the first known examples of such behaviour for this ion. By analogy with the perchlorate ion, the infrared spectra of such complexes should be quite characteristic of the bonding between tetrafluoroborate and the complexed cation.

Greenwood[108] has studied isotope and crystal field effects in the vibrational spectrum of potassium tetrafluoroborate, and has shown that some of the structure observed in the infrared spectrum of this salt is due to isotopic doubling. The acid itself is known only in solution, but the metal salts are known, usually as hydrates. In some instances, attempts to prepare the anhydrous salt, particularly for the Transition Metals, by heating in vacuum results in loss of boron trifluoride with formation of the metal fluoride. It may be that some coordinated transition state is formed which decomposes with loss of boron trifluoride as a result of the greater lattice energy of the metal fluoride. There are, however, only two compounds reported in the literature containing coordinated tetrafluoroborate. Hathaway and Webster[54] reported the infrared characterisation of trimethyltin tetrafluoroborate, which contains bidentate tetrafluoroborate. The infrared spectrum of this, and related compounds, has also been discussed by Clark and O'Brien[109], in a more detailed publication. Quagliano et al[88] prepared tetrakis(3,5-lutidine)nickel(11)tetrafluoroborate, in which it is evident from infrared, electronic spectra and magnetic moment data, that the anion is acting as a monodentate ligand. These authors have made tentative assignments for the bands, attributable to tetrafluoroborate, observed in the infrared spectra of these two compounds.

It may be anticipated that the results of this investigation are in general, analogous to those discussed in the previous chapter, and consequently the arguments presented therein are equally applicable in the present study.

Experimental.

The method used for the preparation of the complexes in the present investigation is exactly analogous to that described for the perchlorates of Chapter 3. Excess metal carbonate was treated with 42% fluoroboric acid solution, the excess carbonate removed by filtration, and the filtrate concentrated on a steam bath to give crystals of the hydrated metal tetrafluoroborate, which was then filtered off and dissolved in absolute ethanol. The amine was added to this solution, and, in some instances was accompanied by a change in colour as shown in columns 3, 4 and 5 of Table 4.1. This addition is an exothermic reaction.

Salt.	Solution	Pyridine	γ-Picoline	Quinoline
$Mn(BF_4)_2$	colourless	colourless	colourless	colourless
$Co(BF_4)_2$	red	red	red	red
$Ni(BF_4)_2$	green	blue	blue	pale green
$Cu(BF_4)_2$	blue	purple	violet	dark green
$Zn(BF_4)_2$	colourless	colourless	colourless	colourless

Table 4.1

The copper pyridine and γ-picoline complexes precipitated on addition of the amine. The pyridine and γ-picoline complexes of cobalt, nickel and zinc, and the copper - quinoline complex crystallised from solution after standing about a week in a refrigerator. The quinoline complexes of manganese, nickel and zinc, and the manganese - pyridine complex were isolated by removing the solvent on a rotary evacuator, redissolving the residue in the minimum of absolute ethanol and precipitating in diethyl ether. The manganese complexes were particularly difficult to isolate, and the manganese-γ-picoline complex could only be obtained as a viscous liquid.

The complexes were dried by heating the solids to about 80-90 °C in high vacuum. During this treatment the pale blue nickel-γ-picoline complex turned a bright yellow colour, a change analogous to that observed during the similar treatment of the perchlorate complex. The quinoline complexes of cobalt, nickel and copper, on the basis of analytical data, are degraded by this process. The boron - fluorine ratio is 1:5, and these complexes analyse to the formulation $MQ_2F(BF_4)$, where Q is quinoline. The loss of boron trifluoride from tetrafluoroborate salts is not uncommon[107], as already indicated, but it is peculiar that only one ion should be broken down. It is, of course, likely that slightly more vigorous conditions would remove another molecule of boron trifluoride. Such a reaction would be particularly interesting since other workers[110] have attempted, without success, to prepare divalent metal-amine fluorides. The analytical data and colours of the present complexes are detailed in table 4.2.

Compound	Colour	Analysis							
		Theory				Found			
		% N	% B	% F	% M	% N	% B	% F	% M
MnL_4X_2	white	10.28	3.97	27.89	10.08	10.20	3.80	27.67	9.93
CoL_4X_2	pink	10.21	3.94	27.68	10.74	10.19	3.83	27.57	10.69
NiL_4X_2	blue	10.21	3.94	27.70	10.69	9.94	3.85	27.59	10.63
CuL_4X_2	purple	10.13	3.91	27.46	11.43	10.07	3.36	27.34	11.46
ZnL_4X_2	white	10.09	3.90	27.36	11.77	10.01	3.86	27.29	11.66
CoL'_4X_2	pink	9.26	3.58	25.11	9.74	8.96	3.47	24.97	9.65
NiL'_4X_2	yellow	9.27	3.58	25.13	9.71	8.90	3.58	24.96	9.70
CuL'_4X_2	violet	9.19	3.55	24.93	10.42	8.90	3.49	24.86	10.41
ZnL'_4X_2	white	9.16	3.54	24.85	10.69	3.95	3.50	24.79	10.58
MnQ_2X_2	white	5.80	4.43	31.48	11.40	5.76	4.29	30.93	11.19
CoQ_2FX	pink	6.85	2.64	23.22	14.41	6.76	2.59	23.09	14.29
NiQ_2FX	yellow-green	6.85	2.65	23.24	14.35	6.78	2.53	22.96	14.31
CuQ_2FX	dark-green	6.77	2.62	22.96	15.36	6.71	2.53	22.71	15.35
ZnQ_2X_2	white	5.68	4.39	30.81	13.25	5.65	4.26	30.05	13.19

(L = pyridine, L' = γ-picoline, Q = quinoline, X = tetrafluoroborate).

Table 4.2

Discussion.

The evidence obtained from the infrared spectra of the present complexes quite clearly shows that the regular Td symmetry of the free tetrafluoroborate ion has been reduced to $C_{3}v$ in most of the compounds prepared in the present investigation. This is particularly obvious since the lowering of symmetry splits the degenerate vibrations and activates infrared inactive vibrations, as shown in Table 4.3[58]

Point Group	ν_1	ν_2	ν_3	ν_4
Td	A_1(R)	E(R)	F_2(I.R.)	F_2(I.R.)
$C_{3}v$	A_1(I.R.)	E(I.R.)	A_1(I.R.)+E(I.R.)	A_1(I.R.)+E(I.R.)

(A,E,F. - non, doubly and triply degenerate respectively
I = Infrared active, R - Raman Active).

Table 4.3

On the basis of the infrared and analytical data, structural environments can be postulated for the metal atoms in these complexes, and these postulates are substantiated by electronic reflectance spectra and magnetic moment measurements.

Tetrafluoroborate Vibrations.

The Region 700 - 1300cms^{-1}.

The bands observed in this region show two different environments for tetrafluoroborate.

The triply degenerate stretching vibration, ν_3, in the free ion, is usually observed as a rather broad band with an ill-defined maximum at about 1100cms^{-1}. The symmetric stretch, ν_1, observed at 769cms^{-1} in the Raman spectrum, is infrared inactive, but is also often observed in the infrared as a very weak peak at about 770cms^{-1}. It is weakly permitted probably because of the perturbing influence of the crystal field on the tetrahedral BF_4^- ion. The absorptions listed in Table 4.4a are in accord with ionic tetrafluoroborate, although the intensity of the band observed at about 740cms^{-1} in the quinoline complexes requires explanation. It may be that the magnitude of the crystal field perturbation has caused a marked reduction in symmetry, in which case the intensity of this band would be expected to vary with the crystal field. However, if the symmetry of the ion is lowered from Td to C_3v, ie if the tetrafluoroborate becomes involved in forming a bond through one of its fluorine atoms to some other atom, then the ν_1, vibration of Td symmetry becomes the ν_2 infrared active vibration of C_3v symmetry, and will appear as a single intense band[108]. Such a band is observed in trimethyltin tetrafluoroborate[109] at 746cms^{-1}. By analogy with the perchlorate ion[85], the shift observed for this vibration, from that observed for the free ion, may be interpreted as giving some indication of the covalent nature of the bond. In the present complexes, the observed magnitude of shift is about 20cms^{-1}. The spectrum of pyridine measured on a liquid film, shows a single sharp peak at 745cms^{-1}. The analogous vibration in the perchlorate complexes occurs at about 750cms^{-1}. This band, at about 755cms^{-1}, in the present complexes, is rather broader of the order of 2-3cms^{-1}. It is possible that there are two unresolved bands in this region. Indeed in the copper-pyridine complex, a strong shoulder at 760cms^{-1} is just detectable.

The spectra in the region 950 - 1050cms^{-1} are quite definitive as to the state of the tetrafluoroborate. Two strong bands are observed in this region, (Table 4.4b), clearly showing that the degeneracy of the ν_3 mode of Td symmetry has been removed and that mono-dentate tetrafluoroborate is present.

Compound.	Frequency (cms^{-1}).		Reference.
BF_4^-	773^{w}	$1030-1160^{s}$ b	108
$ZnPy_4(BF_4)_2$	-	$1030-1075^{s}$	
$Zn\gamma$-$pic_4(BF_4)_2$	-	$1050-1075^{s}$	
$ZnQ_2(BF_4)_2$	770^{m}	$1060-1065^{s}$	
$Ni\gamma$-$pic_4(BF_4)_2$	764^{w}	$985-1050^{s}$ b	
$Ni(3,4$-$L)_4(BF_4)_2$	-	$1090-1100$	88
$NiQ_2F(BF_4)$	740^{m}	$1045-1060^{s}$	
$CuQ_2F(BF_4)$	744^{m}	$1030-1105^{s}$	
$CoQ_2F(BF_4)$	745^{m}	$1045-1055^{s}$	
$MnQ_2(BF_4)_2$	744^{m}	$1060-1065^{s}$	

Table 4.4a

Compound.	Frequency (cms^{-1})	Reference.
$Ni(3,5$-$L)_4(BF_4)_2$	$765^{m}, 925^{s}, (959), 1115^{s}$	88
$MnPy_4(BF_4)_2$	$+, 940^{s}, -, 1070^{s}$	
$CoPy_4(BF_4)_2$	$+, 925^{s}, (950), 1105^{s}$	
$NiPy_4(BF_4)_2$	$+, 922^{s}, (960), 1107^{s}$	
$CuPy_4(BF_4)_2$	$+, 975^{s}, -, 1070^{s}$	
$Co\gamma$-$pic_4(BF_4)_2$	$748^{s}, 920^{s}, (945), 1120^{s} (1163)$	
$Cu\gamma$-$pic_4(BF_4)_2$	$760^{s}, 953^{s}, -, 1100^{s}$	

(L = lutidine, Py = pyridine, γ-pic = γ-picoline,
Q = quinoline. +, pyridine absorbs here.)

Table 4.4b

Tentative assignments for these bands can be made by analogy with the perchlorate complexes, as suggested by other workers[88]. Thus, the band in the region 740-770cms^{-1} is assigned to ν_2, the B - F^* stretching vibration of C_3v symmetry, where F^* is the fluorine atom involved in bonding to the metal. The two bands at about 930 and 1100cms^{-1} are assigned to ν_1, the BF_3 symmetric stretch, and ν_4, the B - F^* asymmetric bend, respectively, of C_3v symmetry. The bands reported in brackets in Table 4.4b may be due to isotopic doubling.

The bands at 520 and 420cms^{-1}.

The band of particular interest in this region of the spectrum ν_4, the infrared active asymmetric bending vibration which occurs at about 520cms^{-1} in the free ion, the degeneracy of which is removed when the symmetry is lowered to C_3v, giving two bands, ν_5 the BF_3 asymmetric bending mode, and ν_3 the BF_3 symmetric bending mode. Tables 4.5a and 4.5b give the details of the observed absorptions.

Compound	Frequency (cms^{-1})
BF_4^-	525
$ZnPy_4(BF_4)_2$	515^m
$Zn\gamma\text{-pic}_4(BF_4)_2$	524^m
$Ni\gamma\text{-pic}_4(BF_4)_2$	510^m

Table 4.5a

Compound.	Frequency (cms^{-1})
$\mathrm{MnPy_4(BF_4)_2}$	520^m, 420^m
$\mathrm{CoPy_4(BF_4)_2}$	511^m, 420^m
$\mathrm{NiPy_4(BF_4)_2}$	513^m, 434^m
$\mathrm{CuPy_4(BF_4)_2}$	517^m, 437^m
$\mathrm{Co\gamma\text{-}pic_4(BF_4)_2}$	513^m, 420^m
$\mathrm{Cu\gamma\text{-}pic_4(BF_4)_2}$	516^m, 435^m
$\mathrm{MnQ_2(BF_4)_2}$	520^m, 420^m
$\mathrm{CoQ_2F(BF_4)}$	518^m, 419^m
$\mathrm{NiQ_2F(BF_4)}$	518^m, 420^m
$\mathrm{CuQ_2F(BF_4)}$	518^m, 423^m
$\mathrm{ZnQ_2(BF_4)_2}$	520^m, 464^m

Table 4.5b

The presence of only one band attributable to tetrafluoroborate in the complexes listed in Table 4.5a is taken as evidence of the ionic nature of the bond between the anion and the complexed cation, and is assigned to ν_4, the asymmetric bending mode of Td symmetry. The two bands observed for the complexes in Table 4.5b are, by analogy with the perchlorate complexes, assigned to the ν_3 and ν_5 modes of C_3v symmetry at about 520 and 420cms^{-1} respectively.

The magnitude of splitting is much greater than that observed for the analogous perchlorate complexes, but is of the order of splitting observed for the bands at about

930 and 1100cms^{-1}.

The band at 353cms^{-1}.

The infrared inactive symmetrical bending mode, in tetrahedral symmetry, which occurs as a weak Raman line at 353cms^{-1} in the spectrum of KBF_4, becomes infrared active when the symmetry is reduced to C_3v. Again by analogy with perchlorates this band in C_3v symmetry may be described by ν_6, a rocking vibration. It is rather difficult to be precise as to the presence or absence of this band in the present complexes. The spectra of pyridine and quinoline, measured on liquid films, both show a weak peak at 353 and 349cms^{-1} respectively. This peak also appears in the present complexes, but the band contour is somewhat broader. From this it may be infered that the fluoroborate rocking vibration is also present, and this premise is substantiated by the presence of a weak band in this region in the γ-picoline complexes. It must be stressed, however, that these bands may be amine ligand vibrations only, and that the band contour is merely a feature of the mull compared with a liquid film spectrum. The bands observed are listed in Table 4.6 and their relative intensities are weak to medium.

Compound.	Frequency (cms^{-1})
Pyridine	353
$MnPy_4(BF_4)_2$	355
$CoPy_4(BF_4)_2$	353
$NiPy_4(BF_4)_2$	353
$CuPy_4(BF_4)_2$	356
γ-picoline	-
$Co\gamma\text{-}pic_4(BF_4)_2$	352
$Cu\gamma\text{-}pic_4(BF_4)_2$	352
Quinoline	349
$MnQ_2(BF_4)_2$	358
$CoQ_2F(BF_4)$	353
$CuQ_2F(BF_4)$	353
$ZnQ_2(BF_4)_2$	357

Table 4.6

Amine Vibrations.

The only amine vibrations considered in this discussion are those which can be attributed to ring deformation modes. These vibrations, as was found for the perchlorate complexes, suffer significant shifts from those observed for the free base. The absorptions observed are detailed in Tables 4.7a, b and c.

Compound.	Frequency (cms^{-1})			
Pyridine			405^m	600^s
$MnPy_4(BF_4)_2$			410^m	609^s
$CoPy_4(BF_4)_2$			415^m	629^s
$NiPy_4(BF_4)_2$			427^m	632^s
$CuPy_4(BF_4)_2$			423^m	634^s
γ-picoline			433^s	513^m
$Co\gamma\text{-}pic_4(BF_4)_2$			492^s	545^m
$Cu\gamma\text{-}pic_4(BF_4)_2$			495^s	552^m
$Cu\gamma\text{-}pic_4(ClO_4)_2$			495^s	551^m
Quinoline	373^w	388^m	475^s	515^w
$MnQ_2(BF_4)_2$	375^m	386^m	472^s	515^w
$CoQ_2F(BF_4)_2$	377^m	390^s	485^s	525^w
$CuQ_2F(BF_4)_2$	379^m	397^s	492^s	527^m
$CuQ_2(ClO_4)_2$	-	401	494	529

Table 4.7a

Compound.	Frequency (cms^{-1})			
Pyridine			405^m	600^s
$ZnPy_4(BF_4)_2$			415^m	635^s
$ZnPy_4(ClO_4)_2$			419^m	644^s
γ-picoline			433^s	513^m
$Zn\gamma\text{-}pic_4(BF_4)_2$			437^s	517^m
Quinoline	373^w	383^m	475^s	515^w
$ZnQ_2(BF_4)_2$	373^m	386^m	488^s	525^w
$ZnQ_2(ClO_4)_2$	377^w	395^m	481^s	523^w

Table 4.7b

<u>Compound.</u>	<u>Frequency (cm^{-1})</u>			
γ-picoline			483^{s}	513^{m}
Niγ-pic$_4$(BF$_4$)$_2$			492^{s}	573^{m}
Niγ-pic$_4$(ClO$_4$)$_2$			509^{s}	572^{m}
Quinoline	373^{w}	333^{m}	475^{s}	515^{w}
NiQ$_2$F(BF$_4$)	372^{m}	396^{m}	438^{s}	525^{m}
NiQ$_2$(ClO$_4$)$_2$	373^{m}	390^{m}	475^{s}	522^{w}

(w = weak, m = medium, s = strong).

Table 4.7c

The agreement between the vibrations observed in the present investigation with those recorded in Tables 3.10a, b and c, for the analogous perchlorate complexes is very good. The increase in frequency observed for these vibrations is again in accord with the Irving - Williams order of stabilities of complexes. In both series of complexes the greatest shift is observed in the nickel - γ-picoline complexes, Table 4.7c. It will be recalled that the corresponding perchlorate complex [Ni(γ-Pic)$_4$](ClO$_4$)$_2$, was found to be diamagnetic, consistant with a square planer arrangement about the nickel atom. Evidence will be presented at the end of this chapter which shows that the analogous tetrafluoroborate complex is also diamagnetic. It is suggested that the magnitude of shift observed, for the ring deformation mode at 513cms^{-1} in the free base, about 60cms^{-1} in these complexes, may, in some measure, reflect the strength of the coordinate link between the metal and amine.

Metal - Nitrogen Vibrations.

The effect of ligand mass on the metal - nitrogen vibrations follows the order found by other workers[82], and is parallel to that observed for the perchlorates discussed in the previous chapter, ie the frequency of vibration decreases with increasing ligand mass. It is again observed that the slightly greater basicity of γ-picoline over that of pyridine is not sufficient to overcome the mass effect, as is illustrated in Table 4.8

Compound	ν(M-N)	Other Vibrations
$MnPy_4(BF_4)_2$	220	-
$CoPy_4(BF_4)_2$	235	254
$NiPy_4(BF_4)_2$	250	266
$CuPy_4(BF_4)_2$	264	285
$ZnPy_4(BF_4)_2$	210	-
$Co\gamma\text{-}pic_4(BF_4)_2$	230	256
$Cu\gamma\text{-}pic_4(BF_4)_2$	241	291
$Zn\gamma\text{-}pic_4(BF_4)_2$	200	-
$MnQ_2(BF_4)_2$	200	-
$CoQ_2F(BF_4)$	215	230
$CuQ_2F(BF_4)$	233	266
$ZnQ_2(BF_4)_2$	200	-

Table 4.8

The metal - nitrogen bands, in both series of complexes, are quite broad and intense. The frequency of vibration of the metal - nitrogen mode is again found to follow the Irving - Williams order. The bands listed under the heading ''other vibrations'' may be due to metal - fluorine stretches of the coordinated tetrafluoroborate. The frequency of these bands also follows the Irving - Williams order. The fact that the frequency of this band does not vary much in the present complexes for a particular metal is taken to support this suggestion. However, the data at present available is insufficient to warrent unequivocal assignments for these bands.

The mixed anion quinoline complexes of cobalt, nickel and copper are analogous to the chloro-perchlorate complexes of these metals, which can be prepared by reaction of the anhydrous metal chloride with silver perchlorate in anhydrous diethyl ether[111]. Peacock and Sharp[60] have studied the infrared vibrational spectra of alkali salts of a large number of complex fluoro-acids, and find that for the divalent metals cobalt, nickel and copper, the metal - fluorine vibration, as measured in perovskites, is observed at 439, 445 and 439cms^{-1} respectively. In the present complexes the spectra in this region is quite complex. However, peaks are observed at 413, 430 and

462cms^{-1} for the complexes of cobalt, nickel and copper respectively, which may be due to the metal - fluorine vibration, since these bands are absent in the corresponding perchlorate complexes.

The spectra studied in the present investigation were obtained as nujol mulls on KBr plates and recorded on a Perkin - Elmer 125 Infrared Spectrophotometer for the region 400 - 1900cms^{-1}. The region 200 - 400cms^{-1} was studied as nujol mulls on polythene plates and recorded on a Grubb - Parsons DM2 Far Infrared Spectrophotometer equipped with CsI optics. Redistilled, sodium dry, nujol was used, and the mulls were prepared in a dry box since the complexes, particularly those which exhibit splitting of the vibrations attributable to tetrafluoroborate, are very sensitive to atmospheric moisture.

Reproductions of some of the infrared spectra obtained for the present compounds are appended at the end of this chapter.

Reflectance Spectra.

The method adopted in Chapter 3 is followed in the present discussion. The observed bands, in cms^{-1} x 10^{-3}, are reported for each metal according to postulated structural environment. Compounds which proved to be strong absorbers were diluted with dry potassium chloride by grinding the complex and diluent together in an agate mortar in a dry box, the concentration of the mixture being regulated so that absorption was within the range of the instrument.

Manganese - octahedral environment.

Compound	$^4T_{1}g(G)$	$^4T_{2}g(G)$	$^4A_{1}g(G)^4Eg(G)$	Reference
$[Mn(H_2O)_6]^{2+}$	18.9	23.1	24.95 25.3	97
$MnPy_4(BF_4)_2$	-	22.73	25.0	
$MnPy_4(ClO_4)_2$	-	22.73	25.0	
$MnQ_2(BF_4)_2$	17.24, 18.35	23.54	24.69	
$MnQ_2(ClO_4)_2$	17.33, 18.37	23.26	25.0	

Table 4.9a

Copper - probably tetragonally distorted octahedron.

Compound	Mixture of Transitions	Reference
CuQ_2Cl_2	16.13, 19.23	98
$CuPy_4(BF_4)_2$	17.39	
$CuPy_4(ClO_4)_2$	17.54	
$Cu\gamma$-pic$_4(BF_4)_2$	18.7	
$CuQ_2F(BF_4)$	16.95	

Table 4.9b

Nickel - distorted octahedral environment.

Compound	$^3T_2g(F)$	$^3T_1g(F)$	$^1Eg(D)$	$^1T_2g(D)$	$^3T_1g(D)$	Reference
$NiPy_4Cl_2$	10.86	16.13	12.99	19.61	25.64	99
$NiPy_4(BF_4)_2$	-	15.75	12.82	-	25.98	
$NiPy_4(ClO_4)_2$	-	15.69	12.12	-	27.03	

Cobalt - distorted octahedral environment.

Compound	^4A_2g T_1g Mixture	Reference
$CoPy_4(BF_4)_2$	18.52, 21.28	
$Co\gamma\text{-}pic_4(BF_4)_2$	18.95, 23.54	
$Co\gamma\text{-}pic_4Br_2$	17.24, 19.23, 20.83	
$CoQ_2F(BF_4)_2$	18.37, 20.63	

Table 4.9c

Nickel - distorted planer environment.

Compound	
$Ni\gamma\text{-}pic_4(BF_4)_2$	22.22
$Ni\gamma\text{-}pic_4(ClO_4)_2$	22.73
$NiQ_2F(BF_4)$	24.34
$NiQ_2(ClO_4)_2$	23.26

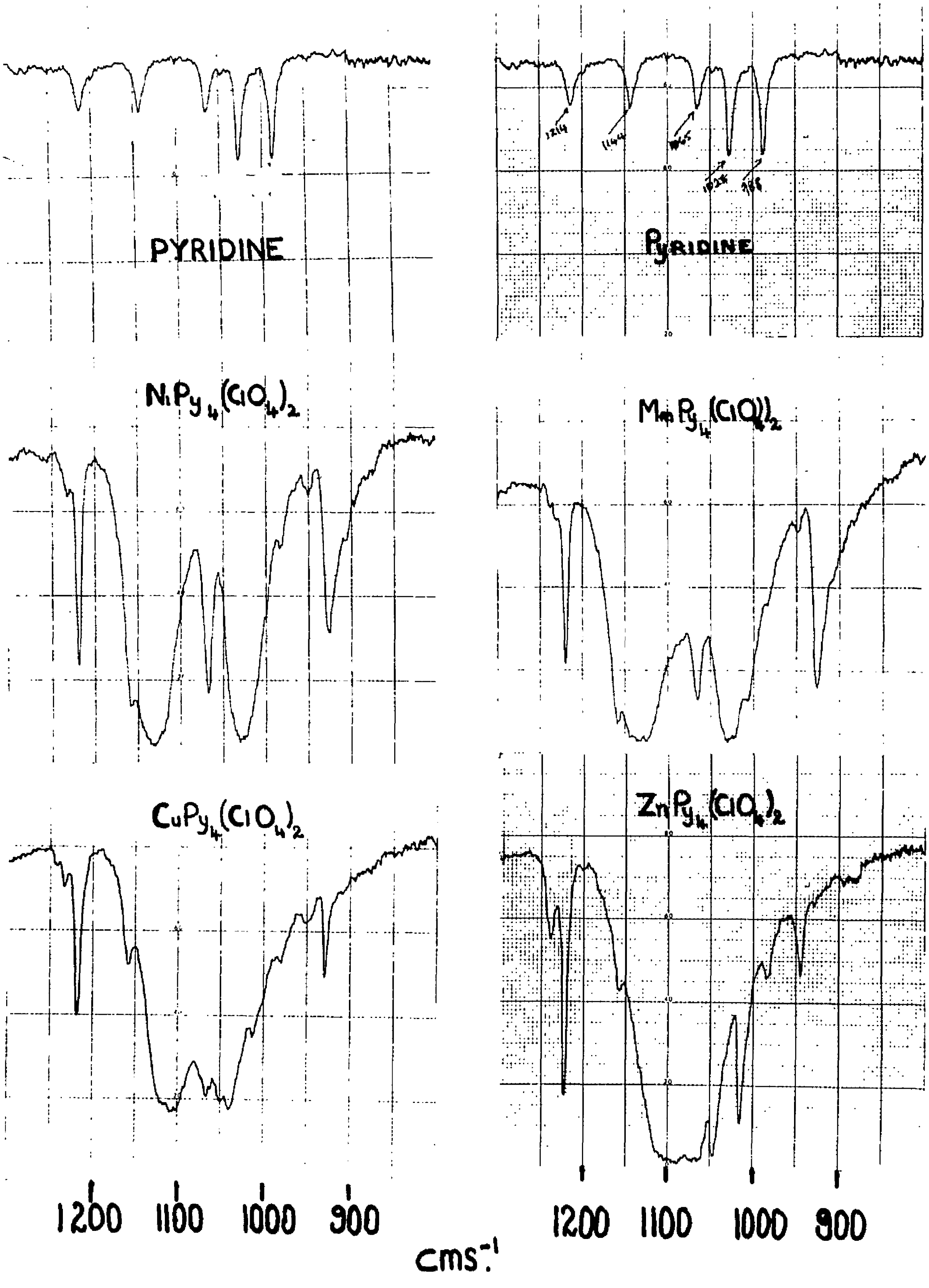
Table 4.9d

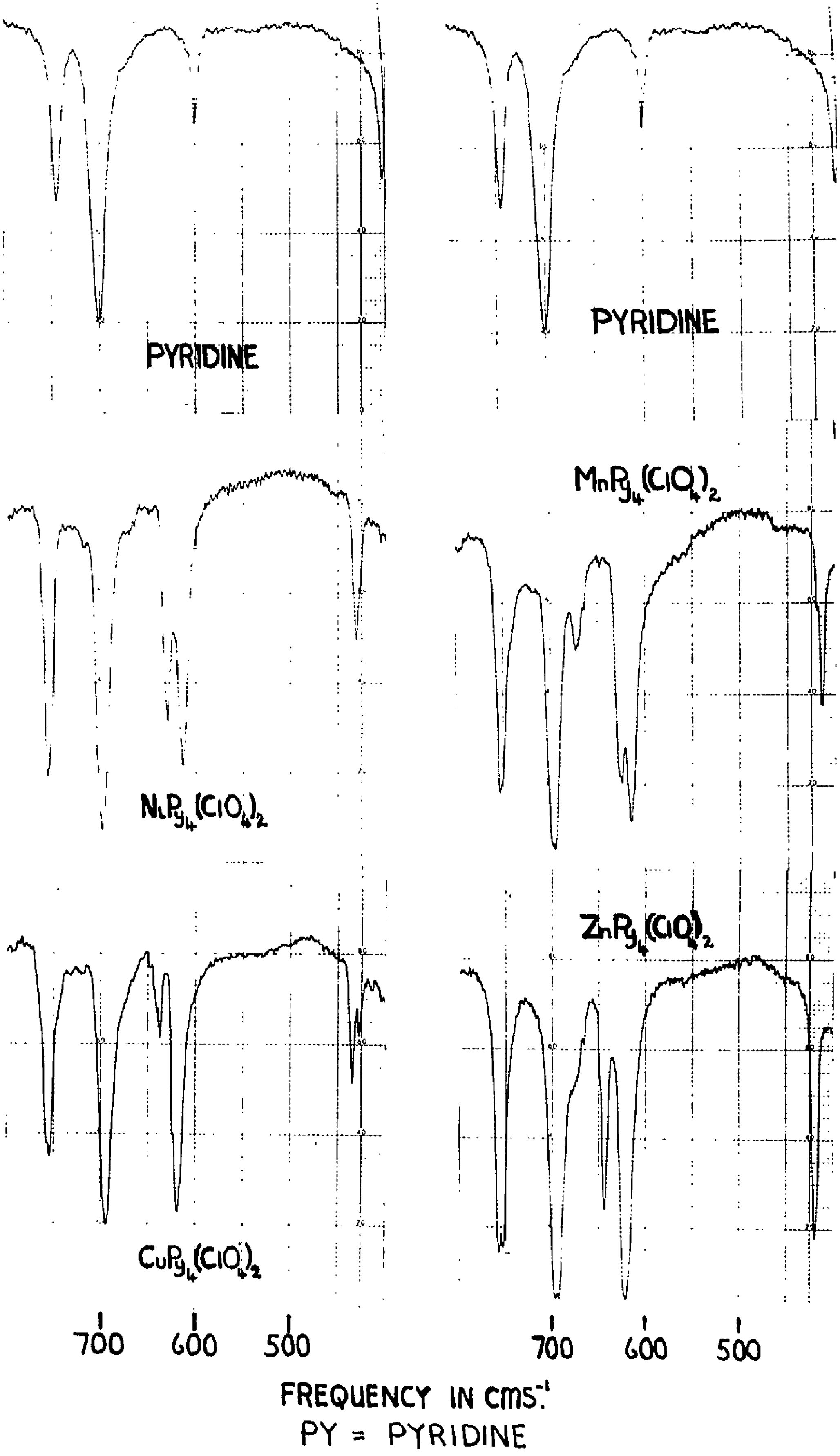
The reflectance spectra of the present complexes are in accord with those already reported for the perchlorates, and are in agreement with the environment suggested at the heading of Tables 4.9a, b, c and d. These proposed environments are further substantiated by the observed magnetic moments for the present complexes, which are recorded in Table 4.10 and were measured by the Gouy method.

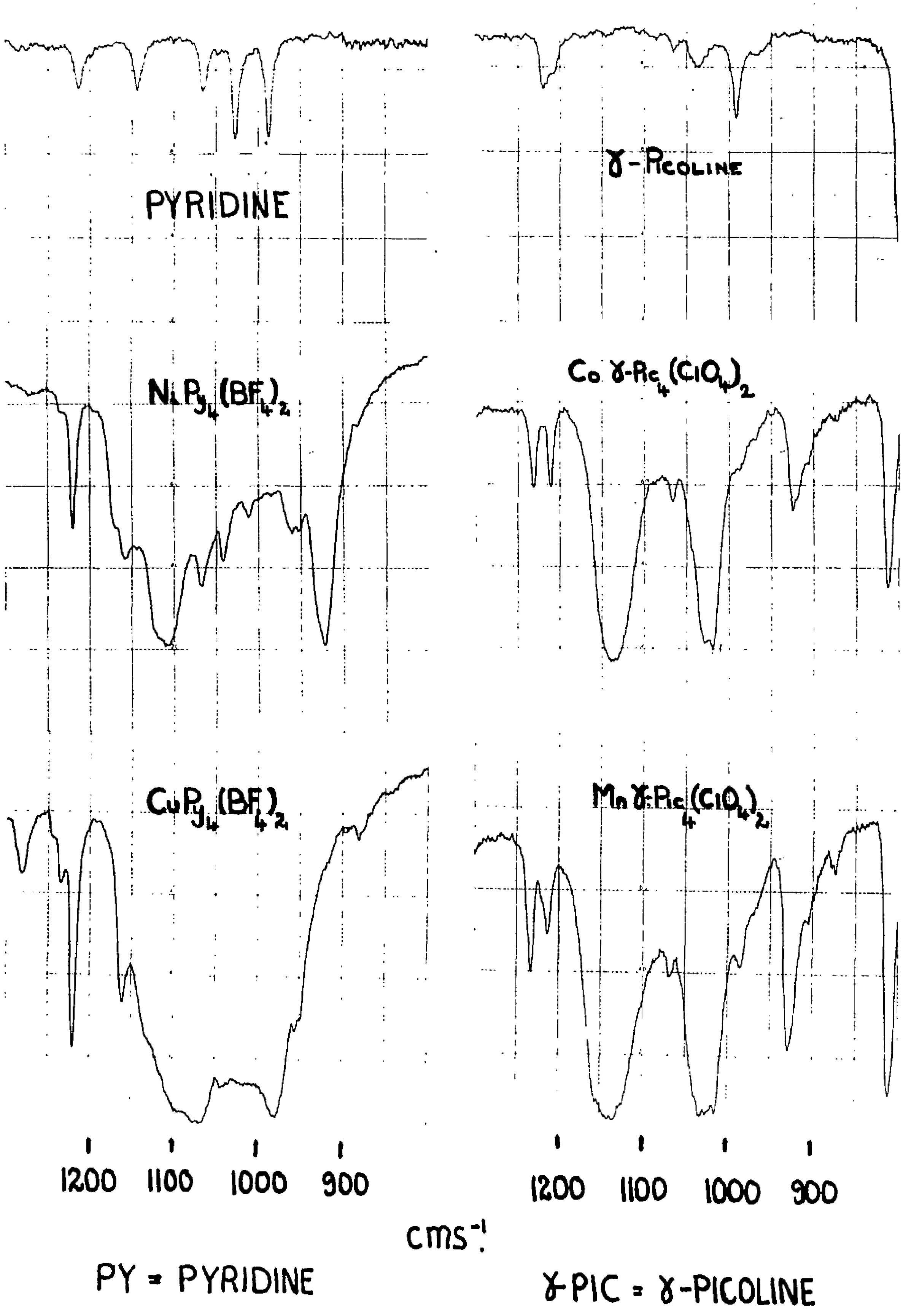
Compound	($X_M^{corr.}$ x 10^6)c.g.s.	Temp. °K	eff B.M.
$MnPy_4(BF_4)_2$	13637	293	5.68
$MnQ_2(BF_4)_2$	14531	293	5.90
$CoPy_4(BF_4)_2$	10582	293	5.0
$Co\gamma\text{-}pic_4(BF_4)_2$	10540	293	4.99
$CoQ_2F(BF_4)$	11439	293	5.2
$NiPy_4(BF_4)_2$	4393	293	3.4
$Ni\gamma\text{-}pic_4(BF_4)_2$	96	293	diamagnetic
$NiQ_2F(BF_4)$	106	293	diamagnetic
$CuPy_4(BF_4)_2$	1322	293	1.78
$Cu\gamma\text{-}pic_4(BF_4)_2$	1266	293	1.73
$CuQ_2F(BF_4)$	1356	293	1.79
$ZnPy_4(BF_4)_2$	-94	293	diamagnetic
$Zn\gamma\text{-}pic_4(BF_4)_2$	-93	293	diamagnetic
$ZnQ_2(BF_4)_2$	-98	293	diamagnetic

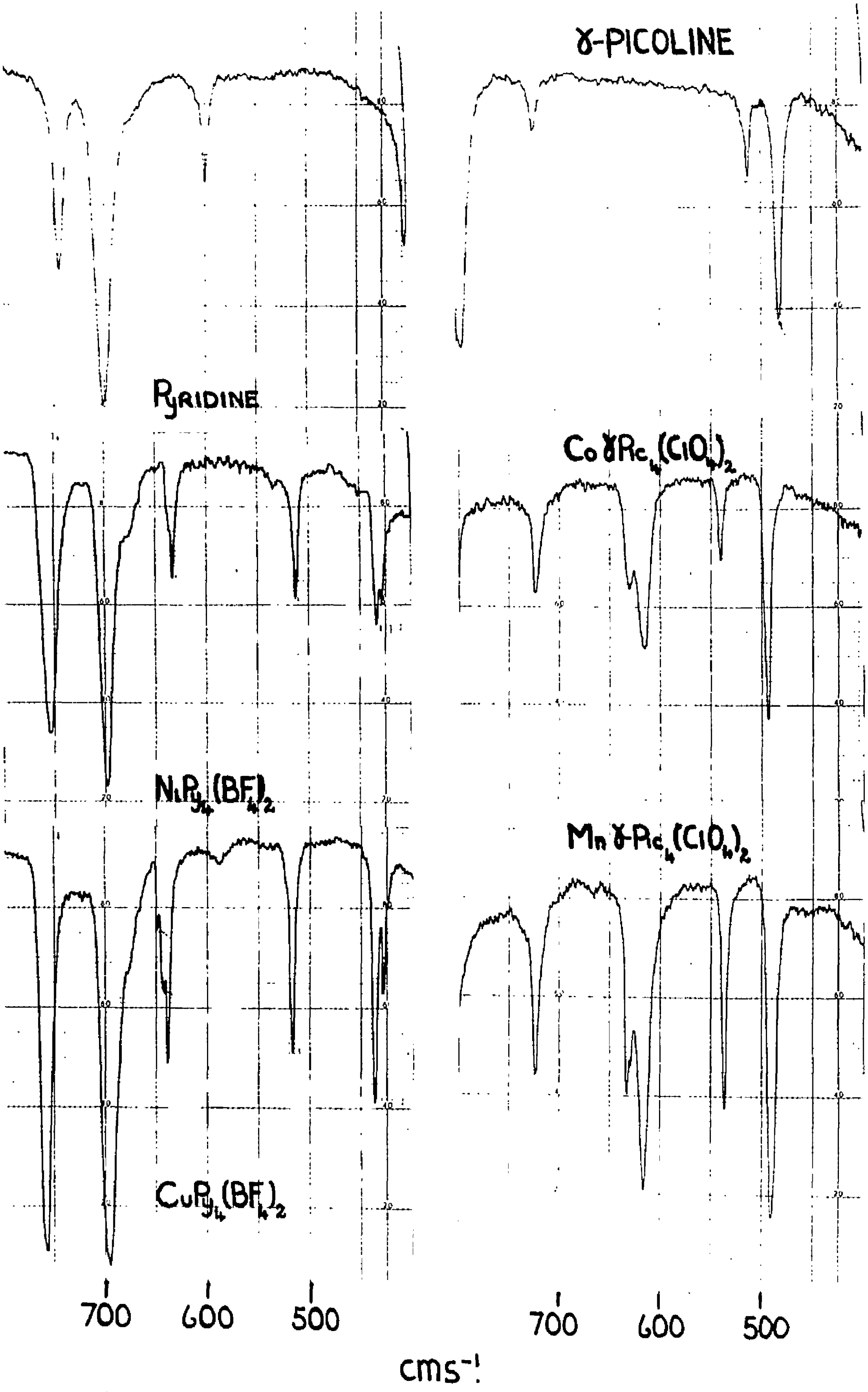
Table 4.10

The similarity observed between the tetrafluoroborate and perchlorate complexes is quite striking. The X-ray powder photographs of the compounds being studied show a complex pattern of lines, consistant with structures of low symmetry.


PYRIDINE
Pyridine
1214
1144
1065
1028
988
$NiPy_4(ClO_4)_2$
$MnPy_4(ClO_4)_2$
$CuPy_4(ClO_4)_2$
$ZnPy_4(ClO_4)_2$
1200
1100
1000
900
1200
1100
1000
900
cms.$^{-1}$

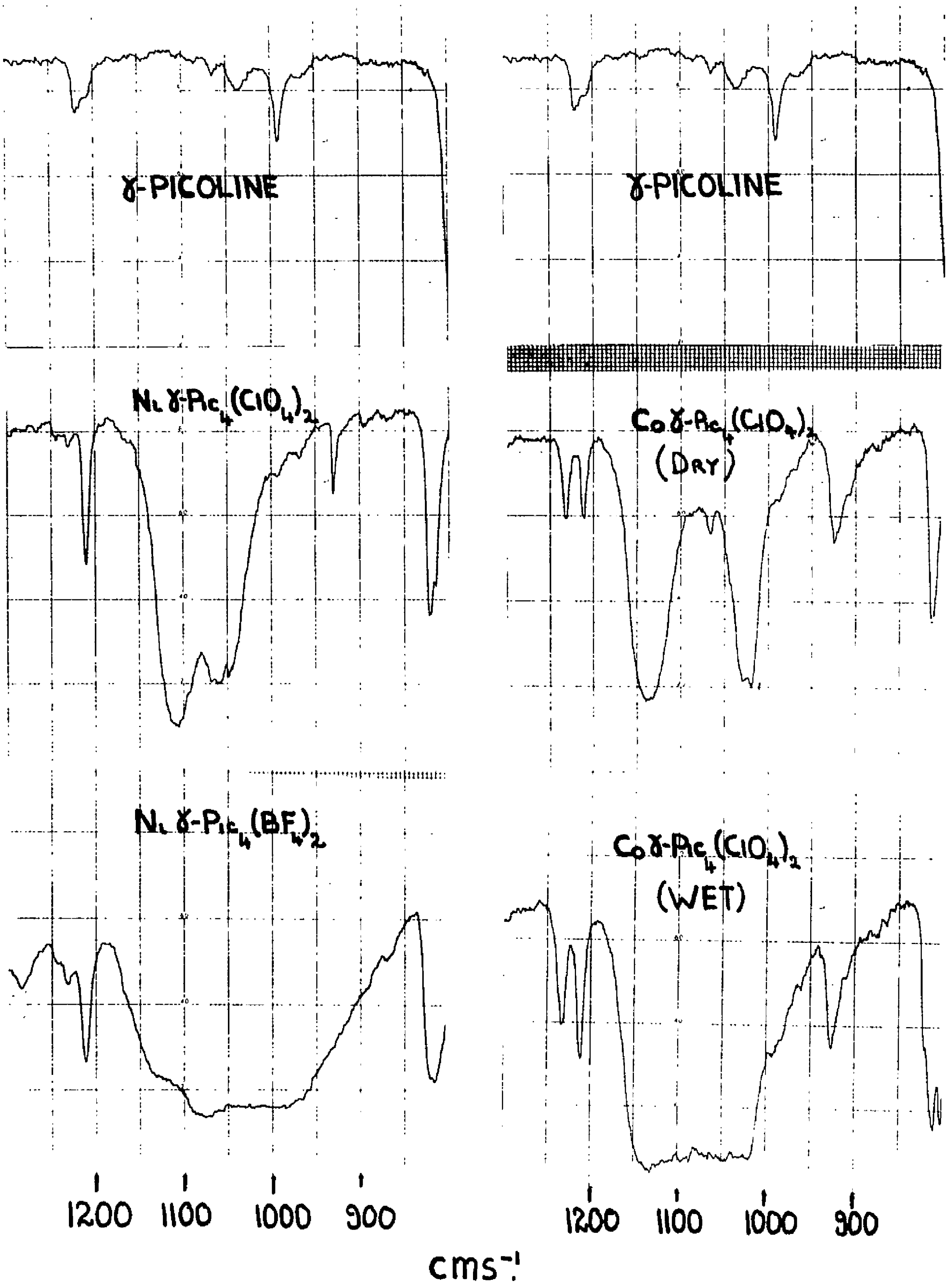

PYRIDINE
PYRIDINE
$NiPy_4(ClO_4)_2$
$MnPy_4(ClO_4)_2$
$CuPy_4(ClO_4)_2$
$ZnPy_4(ClO_4)_2$
700
600
500
700
600
500
FREQUENCY IN cms.$^{-1}$
PY = PYRIDINE


PYRIDINE
γ-PICOLINE
NiPy4(BF4)2
Co γ-Pic4(ClO4)2
CuPy4(BF4)2
Mn γ-Pic4(ClO4)2
1200
1100
1000
900
1200
1100
1000
900
cms-1
PY = PYRIDINE
γ-PIC = γ-PICOLINE

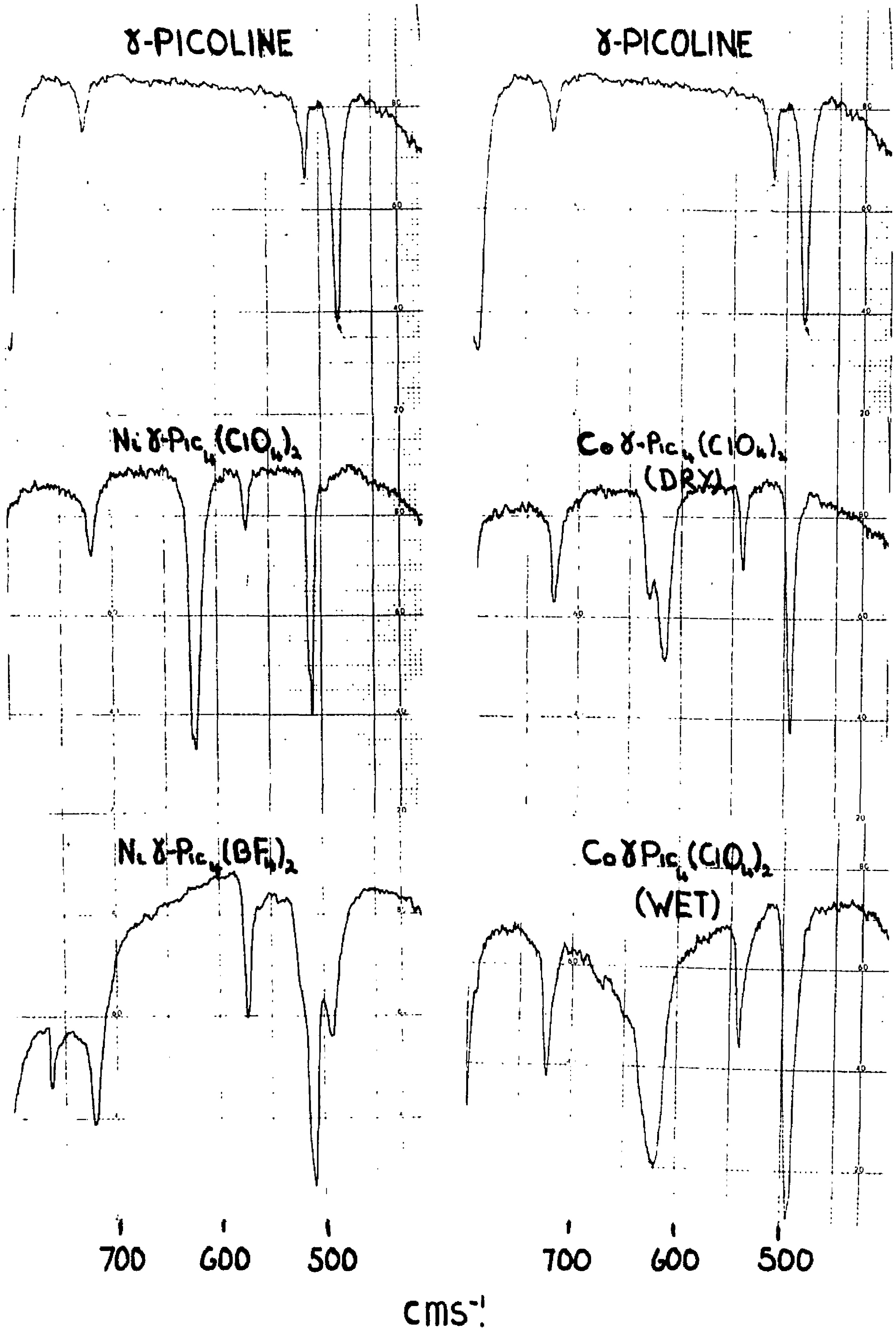


PY = PYRIDINE

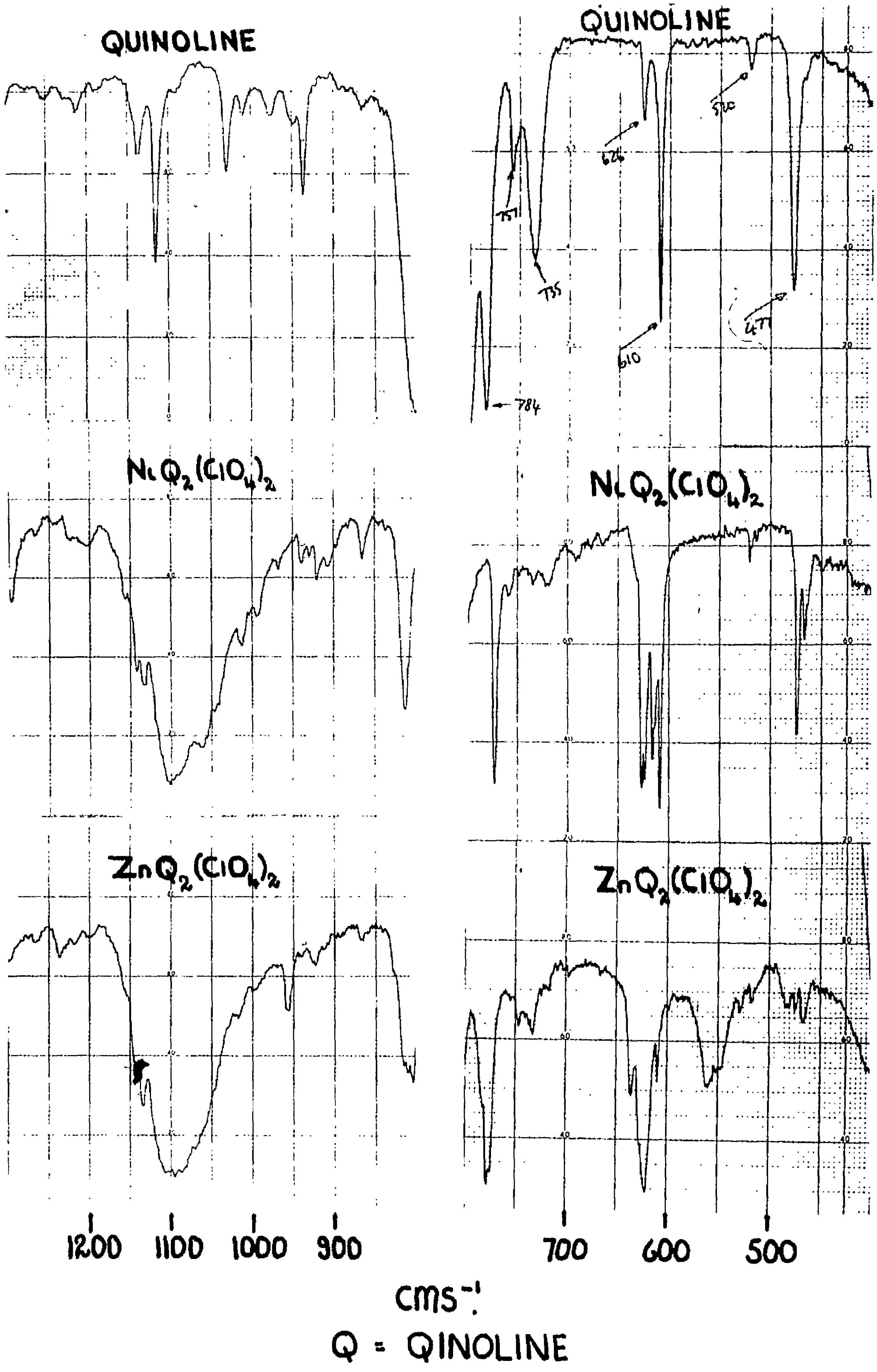
γ-PIC = γ-PICOLINE



γ-PIC = γ-PICOLINE



γ-PIC = γ-PICOLINE


QUINOLINE
QUINOLINE
757
735
784
626
610
510
477
NiQ2(ClO4)2
NiQ2(ClO4)2
ZnQ2(ClO4)2
ZnQ2(ClO4)2
1200
1100
1000
900
700
600
500
cms-1
Q = QINOLINE

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