STUDIES OF THE COORDINATION BEHAVIOUR OF SUBSTITUTED NITROGEN DONOR LIGANDS

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With one accompanying
leaflet.

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ABSTRACT

This work is concerned with metal-complexes of extensively conjugated heterocyclic nitrogen donor ligands.

Part I

Four-coordinate complexes of zinc(II), cadmium(II), mercury(II) and palladium(II) of general formula ML_2 have been prepared with the ligands 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene and 3,4'-dicarboxyethyl-5-chloro-3',4,5'-trimethyldipyrromethene. The complexes involve bidentate coordination of the dipyrromethene ligands. Those of the Group IIb metals are near regular tetrahedral while the palladium complex is shown in this work to be square planar. Complexes of palladium(II) of general formulae $Pd_2Cl_2L_2$ and PdX(L)(LH), where X is Cl^- and Br^-, and L is either of the dipyrromethenes have also been prepared. Both types are square planar four-coordinate complexes, the first being chloro-bridged with two bidentate dipyrromethene ligands, and the second having one monodentate and one bidentate dipyrromethene ligand.

The electronic absorption spectra of all the complexes have been measured and some of the observed bands have been assigned to intraligand $\pi \rightarrow \pi^*$ transitions and to metal→ ligand charge transfer transitions. The proton magnetic

resonance spectra of the complexes have been recorded and resonance peaks have been assigned to protons of particular groups substituted on the dipyrromethene ligands. The results of both these spectral studies are discussed with reference to the stereochemistry about the metal ion and the influence of ligand substituents on the metal-ligand bonding.

The crystal and molecular structure of bis-(4,4'-dicarboxyethyl-3,3'-5,5'-tetramethyldipyrromethenato)-palladium(II) has been determined from a single crystal X-ray diffraction study. The compound is "stepped" square planar and the dipyrromethene ligands are found to deviate considerably from planarity. The structure of this compound is compared with those of similar compounds which have been studied previously. The influences on stereochemistry of the metal ion (copper(II), nickel(II) and palladium(II)) and of bulky ligand substituents are discussed.

Part II

A number of o-phenanthroline complexes of iron(II) and ruthenium(II) have been prepared. These are all six-coordinate and have general formulae $M(phen)_3^{2+}$ and $M(phen)_2X_2$ where X is Cl^-, Br^-, I^-, SCN^- and CN^-, and phen is o-phenanthroline, 5-methyl-o-phenanthroline, 5-chloro-o-phenanthroline or 5-nitro-o-phenanthroline.

The electronic spectra of these complexes have been investigated in solution or in the solid state. Bands have been assigned to metal ⟶ ligand charge transfer transitions and intraligand $\pi \rightarrow \pi^*$ transitions from comparisons with the results of earlier studies. Energies of the electronic transitions are discussed with reference to both the influence of the ligands and of the substituents on the phenanthroline ligand on the metal - ligand π-interactions.

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PART I

THE COORDINATION CHEMISTRY OF DIPYRROMETHENES

FIGURE 1.1a

DIPYRROMETHENE SKELETON AND NUMBERING SYSTEM

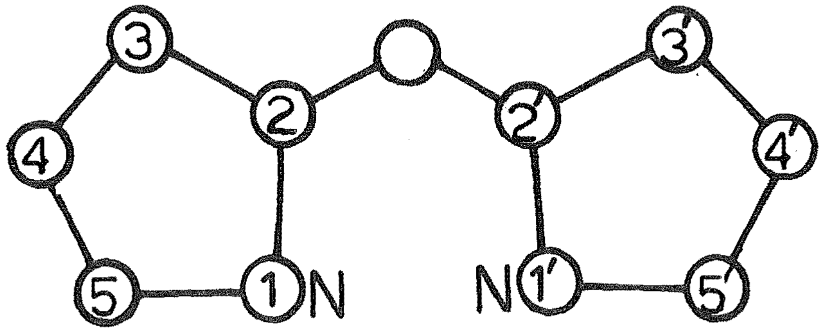
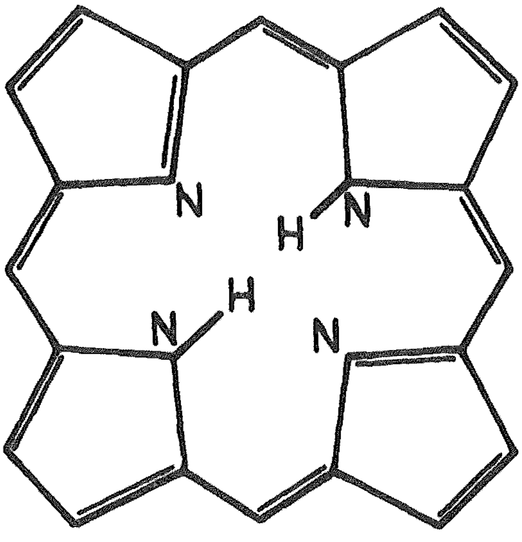


FIGURE 1.1b

PORPHYRIN SKELETON



CHAPTER 1

INTRODUCTION TO PART I

SECTION 1.1

Review of the Coordination Chemistry of Dipyrromethenes

INTRODUCTION:

The dipyrromethene (PMH) skeleton and numbering system is shown in Figure 1.1a. It is closely related to the porphyrin nucleus (Figure 1.1b) which can be regarded as two dipyrromethene molecules linked at the 5 and 5' positions by methine bridges. The dipyrromethene system is highly conjugated and consequently the two pyrrole rings are equivalent. The two main resonance forms are shown in Figure 1.12. In each resonance form the hydrogen atom can be regarded as being bonded to the nitrogen atom of one pyrrole ring, and hydrogen bonded to that of the other ring. It has been estimated that, for the porphyrin system, proton exchange between rings occurs within 5×10^{-3} seconds[1a].

The dipyrromethene skeleton can be protonated readily giving the cation PMH_2^+ where PMH represents the neutral molecule. Dipyrromethenes are very weak acids and the conjugate base PM^- has not been observed directly, although the equivalent porphyrin dianion P^{2-} is known[2].

Interest in dipyrromethenes as ligands arises from three main factors.

(a) The dipyrromethene skeleton can be made with a wide variety of different substituents at various positions on the pyrrole rings and therefore is suitable for studies of the effects of substituents on coordination behaviour.

(b) Molecular overcrowding occurs in some metal complexes if bulky groups are substituted in the 5 and 5' positions of the ligand.

(c) The similarity of the dipyrromethene skeleton to that of porphyrins leads to the possibility of comparison with biological systems.

Metal complexes of dipyrromethenes have a long history, but in comparison with other conjugated heterocyclic nitrogen ligands such as pyridine, 2,2'-bipyridyl and 1,10-phenanthroline their study has been largely neglected.

DIPYRROMETHENES AS LIGANDS:

Two main types of complexes of dipyrromethenes have been reported.

(1) Neutral bis-dipyrromethene complexes with divalent metals

(2) Complexes of dipyrromethenes containing other ligands.

FIGURE 1.12

DIPYRROMETHENE RESONANCE FORMS

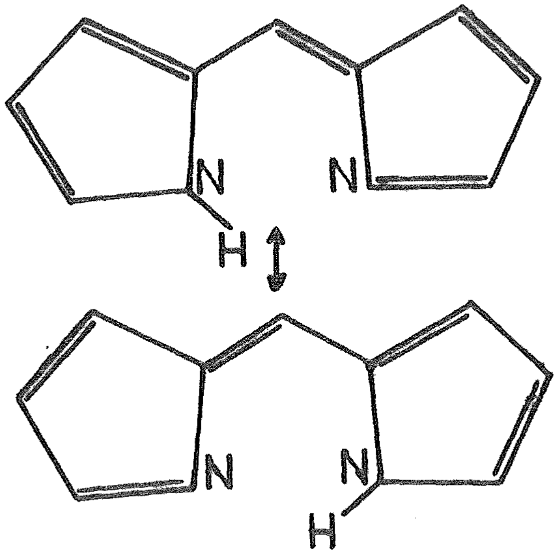
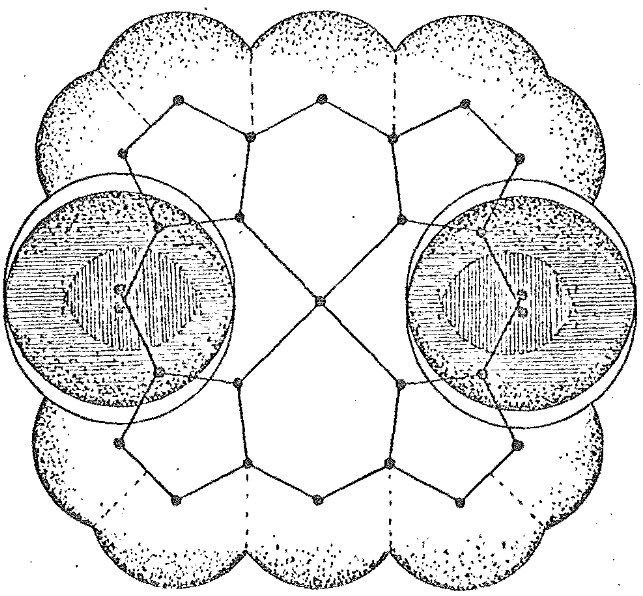


FIGURE 1.13

STERIC CROWDING IN SQUARE PLANAR
bis-DIPYRROMETHENATO COMPLEXES
(Mellor and Lockwood[8])



▤ Area of overlap of α-methyl groups

▥ Area of overlap of α-protons

(1) Neutral bis-dipyrromethene Complexes with Divalent Metals

The complexes of general formula $M(PM)_2$, with the conjugate base (PM^-) of the ligand acting as a bidentate ligand, are found for a wide range of metals. They are the most extensively investigated class of dipyrromethene complexes. Fischer et al (1924,1926)[3,4] reported the preparation of 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene (MMPMH) and 3,3',5,5'-tetramethyldipyrromethene, and the bis-complexes of these ligands with the divalent metal ions copper, nickel, cobalt, zinc and iron. Since then the preparation of complexes of these, and of other dipyrromethene ligands, have been reported for other divalent metals including cadmium, mercury, and palladium[5], and calcium and manganese[6].

Considerable stabilisation is achieved for these compounds by bidentate coordination of the ligand, forming a six membered chelate ring. Since the π-system of the ligand contains $4n + 2 = 10$ electrons, and is closed by coordination to a metal, the coordinated ligand may be regarded as a non-benzenoid aromatic system[7].

In 1938 Porter[5] calculated that complexes of this type with ligands containing methyl substituents at the 5 and 5' positions could not be planar (Figure 1.13), and proposed that such complexes would have tetrahedral stereochemistry.

He found that while the complexes of the first row transition metals could be decomposed in 3N HCl, Pd(MMPM)$_2$ could not be decomposed without breaking down the ligand. He postulated that this might be due to a difference in the metal-ligand bonding, or to a difference in stereochemistry around the metal ion. Mellor and Lockwood (1940)[8] measured the magnetic moments of the nickel(II) and palladium(II) complexes of MMPM. The former was found to be paramagnetic (μ = 3.2BM) while the latter was diamagnetic. They postulated that the nickel complex was tetrahedral, while the palladium complex might have a stereochemistry intermediate between the tetrahedral and square planar configurations.

Until the relatively recent development of sufficiently sophisticated physical methods of investigation, further serious stereochemical studies of these complexes were not possible. However the recent application of different methods of investigation to the problem has lead to conflicting results.

In 1952 West[9] studied the rates of exchange of radioactive cobalt with Co(MMPM)$_2$ in solution and concluded that the molecule was distorted square planar. Eley and Spivey (1962)[10] studied the semiconductor properties of several complexes in the solid state and concluded that while some (e.g. those of zinc(II)) appeared to be tetrahedral,

$Co(MMPM)_2$ was square planar.

Eaton and La Lancette (1964)[11] have analysed the NMR contact shifts of protons on dipyrromethene ligands in nickel(II) and cobalt(II) complexes in terms of unpaired electrons being in the t_2 orbitals of the metal ion. Their results therefore indicate a tetrahedral stereochemistry for these complexes.

More recently, Fergusson and Ramsay (1965)[12] carried out an investigation of the nickel(II), cobalt(II), copper(II) and zinc(II) complexes of 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene (MMPMH) and 3,4'-dicarboxyethyl-5-bromo-4,3',5'-trimethyldipyrromethene (MBrPMH). They confirmed Mellor and Lockwood's value for the magnetic moment of $Ni(MMPM)_2$[8] and found that those of $Ni(MBrPM)_2$ and of the cobalt complexes, together with the ligand field spectra of these complexes, indicated regular tetrahedral stereochemistries. These complexes were found to be isomorphous with the zinc complexes from X-ray powder photographs. The ligand field spectra of the copper complexes, on the other hand, were found to be similar to that of the $CuBr_4^{2-}$ ion, which is known to be a tetragonally distorted tetrahedron[13]. Couch (1965)[14] carried out similar studies on complexes of 3,4'-dicarboxyethyl-5-chloro-3,4',5'-trimethyldipyrromethene (MClPMH) which were in agreement with those of Fergusson and Ramsay. The crystal and molecular structure of $Cu(MMPM)_2$ has since been determined[15], confirming the structure to be as predicted, with an angle of 68° between the mean planes of the ligands.

Ferguson and West[16] studied the nickel(II) complexes of five dipyrromethenes, of which three had methyl substituents in both the 5 and 5' positions (type 1), one had one free 5 position (type 2) and one had both 5 and 5' positions unsubstituted (type 3). The complexes of type 1 ligands had ligand field spectra which were typical of tetrahedral complexes in the solid state and in solutions with different solvents. The complex with the ligand of type 2 gave a slightly different ligand field spectrum in the solid state from that in benzene solution. The latter spectrum indicated approximately regular tetrahedral stereochemistry, while the solid state spectrum, because of a shift to higher energy of one of the bands compared with the spectrum in benzene solution, was thought to indicate some tetragonal distortion. The complex of the ligand of type 3 showed similar effects on comparison of its solid state and solution spectra. Both the complexes of ligands of types 2 and 3 gave spectra in pyridine solutions which indicated some solvent coordination. This effect was more pronounced with the complex of the type 3 ligand. The authors inferred that as the number of substituents in the 5 and 5' positions in the ligand varied from 2 to 0 the reduction in steric hindrance permitted an increased amount of tetragonal distortion of the tetrahedral complexes.

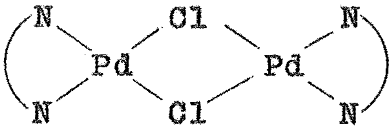
Murakami and Sakata[17] carried out a similar study to that of Ferguson and West with complexes of ligands of types 1 and 2 with cobalt(II), nickel(II) and copper(II). It was found that the ligand field bands of the nickel and copper complexes with type 2 ligands were at shorter wavelengths than those of type 1 ligands. They concluded that the cobalt complexes were tetrahedral, but that the stereochemistry of the nickel and copper complexes depended on the number of 5-substituents on the ligands.

Motekaitis[6] has studied complexes of 5,5'-dicarboxyethyl-3,4,3',4'-tetrahalodipyrromethenes with the divalent ions of calcium, manganese, nickel, copper and zinc in an attempt to find a suitable metal ion template for the synthesis of new porphyrins. He has reported the proton NMR, ultraviolet-visible and infra-red spectra of these complexes and has attempted to correlate the extent of tetragonal distortion of the tetrahedral complexes with variations of the intensity of bands in the visible spectrum. He concluded that the calcium, zinc and manganese complexes were essentially tetrahedral, but that those of the nickel and copper ions were tetragonally distorted to a considerable degree. In view of the findings of other workers, who have studied the complexes of ligands with considerably smaller groups in the 5 and 5' positions[16,17], his conclusions with respect to the nickel complex are in doubt.

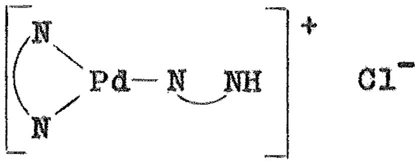
(2) Complexes of Dipyrromethenes Containing Other Ligands

A number of complexes have been reported in which halogen and other ligands are coordinated to a metal ion, along with dipyrromethene ligands. These can involve both monodentate and bidentate coordination of the dipyrromethenes. A tin complex $SnCl_4(PMH)$ has been reported in which the neutral dipyrromethene is said to coordinate as a bidentate[18]. Porter[5] reported the preparation of mercury(II) complexes, Hg(MMPM)X, X = $CH_3CO_2^-$ and Cl^-.

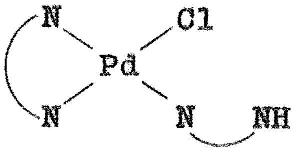
Porter also reported the preparation of the palladium(II) complexes $Pd_2Cl_2(MMPM)_2$ and PdCl(MMPM) (MMPMH). The first of these was postulated to be a four-coordinate bridged species



The second was thought to contain one bidentate and one monodentate dipyrromethene ligand. Porter proposed two possible structures:



and



Of these the four-coordinate formulation would appear to be the most likely. Both palladium complexes could be decomposed to give the neutral bis-complex $Pd(MMPM)_2$.

Ferguson and West[19] have reported the preparation of a series of monodentate complexes of dipyrromethenes of general formula $MX_2(PMH)_2$,
where M = Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) and $X = Cl^-$, Br^-, I^-, CNS^- and NO_3^-. Magnetic and ultraviolet-visible spectral results indicated that the cobalt complexes were tetrahedral. The nickel complexes had magnetic moments typical of tetrahedral complexes, but their ligand field spectra indicated that some degree of octahedral coordination might occur in solution. The stereochemistry of the copper complexes could not be assigned. A medium intensity band at 3220 - 3320 cm^{-1} in the infrared spectra of the complexes indicated that the N-H proton was present in the complexes, however changes in the position and intensity of the band on coordination indicated that the proton was involved in less hydrogen bonding in the complexes than in the free ligand.

SUMMARY OF THE COORDINATION CHEMISTRY OF DIPYRROMETHENES AND THE TYPES OF COMPLEXES FORMED

Table 1.11 lists the metal ions which have been found to form complexes with dipyrromethenes. Monodentate and bidentate coordination of the ligands are both possible, and

TABLE 1.11

METAL IONS REPORTED TO FORM DIPYRROMETHENE COMPLEXES.

Metal Ion	Type of Complex
Ca(II)	$Ca(PM)_2$
Sn(IV)	$SnCl_4(PMH)$ (*)
Mn(II)	$Mn(PM)_2$
Fe(II)	$Fe(PM)_2$ (*)
Ni(II)	$Ni(PM)_2$, $NiX_2(PMH)_2$
Co(II)	$Co(PM)_2$, $CoX_2(PMH)_2$
Cu(II)	$Cu(PM)_2$, $CuX_2(PMH)_2$
Zn(II)	$Zn(PM)_2$, $ZnX_2(PMH)_2$
Cd(II)	$Cd(PM)_2$
Hg(II)	$Hg(PM)_2$, $Hg(PM)X$ (*)
Pd(II)	$Pd(PM)_2$, $PdCl_2(PM)_2$, $PdX(PM)(PMH)$.

* The formulation of these complexes is uncertain.

in the case of some metal ions both types of coordination have been found.

Bidentate coordination of the ligands frequently involves problems of intramolecular overcrowding so that metal ions are sometimes forced to adopt stereochemistries other than those which would otherwise be preferred. For complexes of all the first row transition metal ions except copper(II), ligand field spectra and magnetic data indicate clearly that the stereochemistry of these complexes is basically tetrahedral, although in the case of the nickel(II) complexes tetragonal distortion of the tetrahedral environment appears to occur if the overcrowding is lessened. This is also found to occur in the copper(II) complexes.

Previous workers have not been able to assign a definite stereochemistry to the $Pd(PM)_2$ complexes, but have shown that they differ considerably in their magnetic properties, and perhaps in their bonding, from those of the nickel(II) and other first row transition metal ions. In view of the rather large number of complexes and different types of dipyrromethenes available it is rather surprising that few comparative ultraviolet-visible spectral studies have been made and interpreted in terms of the bonding between the metal and ligand. Until the present work only one X-ray crystallographic structure determination had been carried out.

SECTION 1.2

Scope of the Present Work in Part I

Chapters 2 to 4 in Part I of this thesis describe work carried out by the author on a number of dipyrromethene complexes.

In Chapter 2 the preparation and characterisation of a number of neutral bidentate complexes of general formula $M(PM)_2$, are described where M represents the divalent ions of zinc, cadmium, mercury and palladium, and PM is either 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene (MMPM) or 3,4'-dicarboxyethyl-5-chloro-3',4,5'-trimethyldipyrromethene (MClPM). Of these the zinc, cadmium and palladium complexes of MMPMH have been reported previously by Porter[5], and Mellor and Lockwood[8]. The ultraviolet-visible spectra of all these complexes are reported and compared with those of other complexes reported previously by Fergusson and Ramsay[12], and by Couch[14]. A metal oxidation charge transfer band in the near ultraviolet region of the spectrum has been assigned for the MMPMH and MClPMH complexes of cobalt, nickel, copper, zinc, palladium, and cadmium and for the MClPMH complex of mercury. The proton NMR spectra of the diamagnetic complexes of these ligands have been measured and are reported for the first time. Changes in the chemical shift of groups substituted onto the dipyrromethene skeleton are analysed and discussed in terms of changes in groups substituted in the ligands, coordination to a metal ion, and differences in the stereochemistry of the complexes.

In Chapter 3 the crystal and molecular structure determination of $Pd(MMPM)_2$ is described and discussed. The structure has been found to be "stepped" square planar with the palladium atom residing on a crystallographic centre of symmetry. The bonding at the nitrogen atoms of the ligand has been found to be distorted so that the chelate rings are not coplanar with the crystallographically required square plane of the nitrogen atoms about the metal ion. In addition the planarity of the ligands is destroyed. The determined structure is compared with other structures of closely related complexes, in particular those of $Cu(MMPM)_2$[15] and bis-(dipyridyliminato)palladium(II)[20].

The preparation and characterisation of the complexes $Pd_2Cl_2(PM)_2$ and PdX(PM)(PMH) is described in Chapter 4, where PMH is either MClPMH or MMPMH, and X is either Cl^- or Br^-. Of these the chloro-complexes of MMPMH have been previously prepared by Porter[5]. Porter's structure assignment has been confirmed for the bridged $Pd_2Cl_2(PM)_2$ complexes, and a structure has been assigned for the mixed monodentate and bidentate complexes PdX(PM)(PMH) from consideration of the proton NMR spectra of these complexes. The ultraviolet-visible spectra have been measured for these complexes and the positions of the bands and their assignments are considered in comparison with those of the $M(PM)_2$ complexes described in Chapter 2.

CHAPTER 2

Bis-(Dipyrromethenato) Metal(II) Complexes

SECTION 2.1

Introduction

Complexes of 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene (MMPMH) and 3,4'-dicarboxyethyl-5-chloro-3',4,5'-trimethyldipyrromethene (MClPMH) with the divalent ions of zinc, cadmium and palladium have been prepared and fully characterised. Dipyrromethene complexes of palladium (II), which also have coordinated halogen ligands, are discussed in Chapter 4. The MClPMH complex of mercury(II) has also been prepared and fully characterised. Attempted preparations of dipyrromethene complexes of ruthenium, rhodium, iridium and platinum were unsuccessful, and the preparation of $Hg(MMPM)_2$ previously reported by Porter[5] could not be confirmed. A silver(I) complex has been prepared but not fully characterised.

The preparations, and attempted preparations of these complexes are discussed in Section 2.2. Ultraviolet-visible spectra of the characterised complexes are reported and discussed in Section 2.3. The spectra are compared with those reported for complexes of these ligands with other metal ions. The proton NMR spectra of the fully characterised complexes of zinc, cadmium, mercury and palladium are reported and discussed in Section 2.4.

SECTION 2.2

Preparations

DISCUSSION:

The method of preparation for the complexes ML_2, ($M = Zn,Cd,Hg,Pd$) where simple salts of the divalent ions were available was to react an aqueous or ethanolic solution of the divalent metal halide, acetate or nitrate salt with a sodium acetate buffered solution of the ligand in ethanol. The use of the buffer assisted in the removal of the acidic proton of the neutral ligand before, or during, coordination according to the reaction:

$$2AcO^- + 2LH + M^{2+} \longrightarrow 2AcOH + ML_2$$

The presence of sodium acetate was not required for the coordination of MClPMH but on the other hand coordination of MMPMH was greatly assisted by the presence of the buffer. This difference in behaviour suggests that the chlorine substituent in MClPMH assists the formation of the L^- anion because of its electron withdrawing capacity. This corresponds to a reduction in the σ-donor capacity of the nitrogen atoms for this ligand in comparison with those of MMPMH. These complexes have been formulated as monomeric ML_2 complexes by elemental analysis, molecular weight determinations and NMR spectroscopy.

In the preparation of the silver(I) complex silver nitrate was used as a starting material. Trivalent chlorides were used in the attempted preparations of the rhodium and ruthenium complexes, and a tetravalent iridium salt ($(NH_4)_2IrCl_6$) was used in the attempt to obtain a complex with this metal. Attempts were also made to reduce the reaction mixtures of the rhodium, ruthenium and iridium salts with a variety of suitable reducing agents. One of the products obtained from some of the attempted preparations was identified only as "decomposed ligand". This was also obtained from a few of the preparations of the ligands, which for one reason or another, did not give the required product. The product of ligand decomposition was a deep purple colour, and was very soluble in chloroform. The proton NMR spectra of the "decomposition product" of both ligands showed two resonance peaks at 1.25ppm and 0.90ppm. Both resonances were broad and featureless. The ligands decomposed extremely readily in reaction mixtures containing ruthenium and rhodium salts.

The infrared spectra and proton NMR spectra of all reaction products were measured routinely. Infrared spectra proved rather unhelpful in characterisation of the complexes. The spectra of the ligands showed different intensities and positions for some bands from those obtained for the complexes. The spectra of the zinc, cadmium and mercury complexes with the same ligands were identical, while those of the palladium complexes differed in the intensities and positions of certain bands compared with the spectra of the other complexes. However, the infrared spectra of reaction products, which other methods of investigation such as elemental analysis and NMR showed to be largely mixtures of unidentifiable compounds, were often identical to those of the pure complexes. This indicated that the infrared spectra of these compounds were of little use for their characterisation. However the absence of absorptions above 3000 cm^{-1} indicated that the compounds were anhydrous.

Proton NMR spectra, on the other hand, were found to be very satisfactory for use in characterising complexes. The spectra readily showed if the complexes were free of organic impurities, particularly those due to ligand decomposition.

The molecular weights of some of the complexes were measured by osmometry and with the exception of $Pd(MClPM)_2$ were found to be normal for monomeric complexes. In retrospect the apparently very high experimental molecular weight in solution for $Pd(MClPM)_2$ can be explained in terms of some degree of association between molecules. This is possible because of the difference in stereochemistry between the palladium complexes and those of the other divalent metal ions. The molecular weight of $Pd(MMPM)_2$ in the solid state was obtained crystallographically.

With the exception of the silver(I) complex, all the compounds were extremely soluble in chloroform and were soluble to some extent in all common organic solvents but were insoluble in water.

EXPERIMENTAL

(a) Preparation of the Ligands

The preparations of the ligands have been reported elsewhere[8,21], however they are included here in full because some alterations have been made to the preparative methods.

2,4-dimethyl-3-carboxyethylpyrrole[8]

Acetoacetic ester (234mls) and glacial acetic acid (514mls) were placed in a 3 litre, 3 necked flask with a stirrer, dropping funnel and a thermometer dipping in the liquid. A solution of 64 gms of sodium nitrite in minimum water was added slowly while the temperature was kept below 0°C with a freezing mixture. The solution was kept at this temperature while stirring for 1 hour after all the sodium nitrite solution had been added. Zinc dust (120 gm) was then added at a rate sufficient to maintain continuous boiling, after which the mixture was heated for a further hour, and then poured into 6 litres of water. The diester, 2,4-dimethyl-3,5-dicarboxyethylpyrrole, was filtered off.

The diester (100gm) and potassium hydroxide (180gm) were dissolved in 1 litre of ethanol. The solution was heated under reflux for $1\frac{1}{2}$ hours and poured into 10 litres of water. It was filtered to remove any unchanged diester (about 10-20gms). Acetic acid was added to neutralise the solution and the mixture was left overnight. The monoester-carboxylic acid, 2,4-dimethyl-3-carboxyethyl-pyrrole-5-carboxylic acid was filtered and dried thoroughly under vacuum. (Yield approximately 80gm).

The acid-ester was heated in a Claisen flask (100ml flask for 100gms of acid-ester) until most of the carbon dioxide had been removed. It was then distilled under reduced pressure under a slow stream of dry nitrogen. The yield of α-free pyrrole, 2,4-dimethyl-3-carboxyethyl-pyrrole, was about 50gm.

4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene[8]

Finely divided 2,4-dimethyl-3-carboxyethylpyrrole was dissolved in minimum concentrated hydrochloric acid on a boiling water bath. A few drops of formaldehyde were added and heating was continued for about 10 minutes until a floculant yellow precipitate formed. The solution was cooled in an ice bath and filtered. The hydrochloride salt was washed and dried under vacuum.

The dry solid was finely ground in a mortar and pestle with a little concentrated ammonia before filtering, washing with water, and drying under vacuum. The neutral ligand was carefully recrystallised several times from chloroform/petroleum ether before final recrystallisation from acetone. The compound was obtained as bright red needle crystals.

Analysis: Calculated for $C_{19}H_{24}N_2O_4$ C, 66.3; H, 7.0; N, 8.1%. Found: C, 66.4; H, 7.0; N, 7.8%.

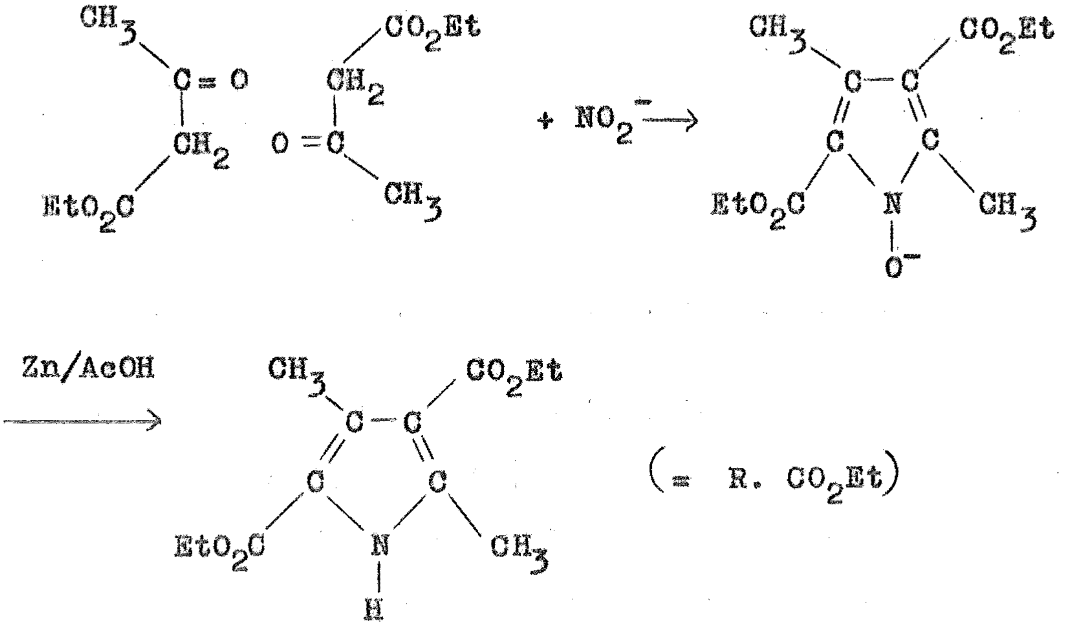
3,4'-dicarboxyethyl-5-chloro-3',4,5'-trimethyldipyrromethene[21]

The α-free pyrrole (2,4-dimethyl-3-carboxyethylpyrrole) (24gm) was dissolved in 400mls of dry ether and cooled to 0°C. Sulphurylchloride (24mls) was added dropwise with stirring. When nearly all of the sulphuryl chloride had been added an intense red precipitate separated out. After standing for a short time this precipitate was filtered and washed with ether. It was recrystallised several times from chloroform/petroleum ether before final recrystallisation from acetone. The compound was obtained as brown-red microcrystals.

Analysis: Calculated for $C_{18}H_{21}ClN_2O_4$: C, 59.3; H, 5.2; N, 7.7%. Found: C, 59.3; H, 5.7; N, 7.3%.

Equations:

(1) Preparation of 2,4-dimethyl-3-carboxyethylpyrrole:

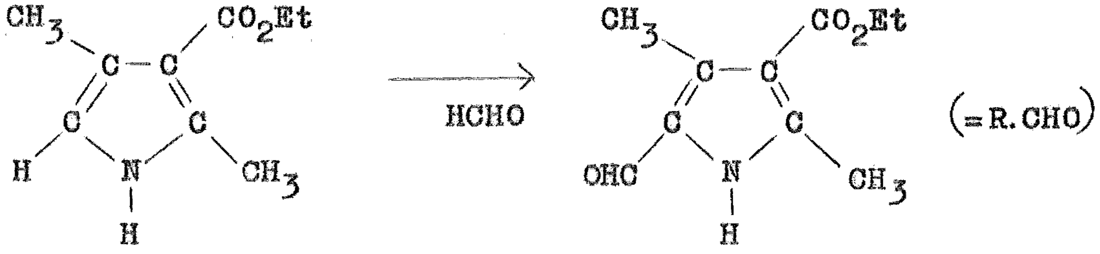


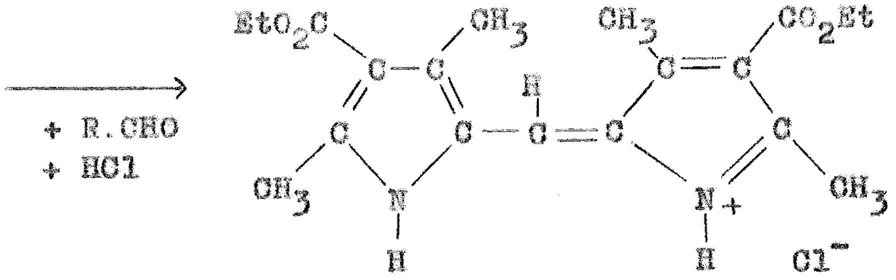
(2) Decarboxylation

$$R.CO_2Et \xrightarrow{KOH/EtOH} R.CO_2H$$

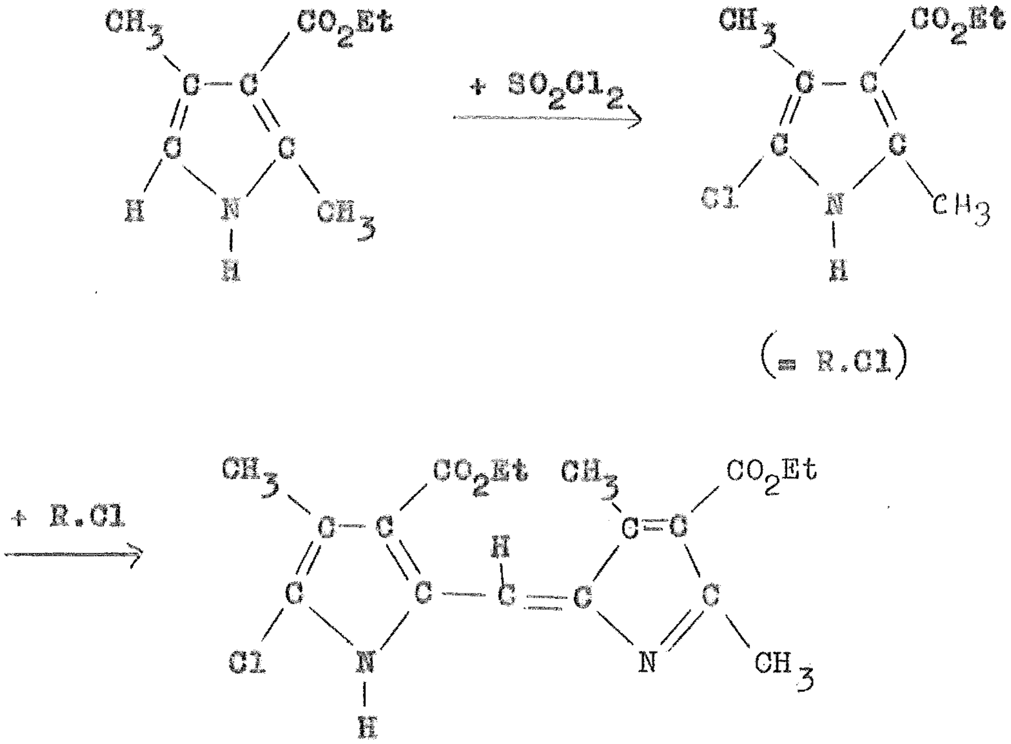
$$R.CO_2H \xrightarrow{\Delta} R\text{-}H + CO_2$$

(3) Preparation of $MMPMH_2Cl$ (formylation and condensation)





(4) Preparation of MClPMH



(b) Preparations of the Group IIb Metal Complexes

Several of these complexes have been prepared previously by Porter[5], and earlier workers[4]. The following abbreviations of the systematic name have been used for the ligands to avoid tedious repetition:

MMPMH : 5,5'-dimethyldipyrromethene
MClPMH : 5-chloro-5'-methyldipyrromethene.

(i) bis-(5,5'-dimethyldipyrrometheneato)zinc(II), Zn(MMPM)$_2$.[4]

A solution of A.R. zinc acetate dihydrate (0.2gm) in the minimum amount of water was added to a cold solution of the ligand (0.5gm) and an excess sodium acetate in minimum ethanol. The complex immediately precipitated as a finely divided orange solid, which was filtered and recrystallised from ethanol in the cold, and dried in vacuo.
Analysis: Calculated for $C_{38}H_{46}N_4O_8Zn$: C, 60.7; H, 6.1; N, 7.5%. Found: C, 59.3; H, 6.0; N, 7.3 %.

(ii) bis-(5-chloro-5'-methyldipyrromethenato)zinc(II), Zn(MClPM)$_2$.

The complex was prepared in a similar way to that outlined for Zn(MMPM)$_2$ in (i) above except that the complex was not immediately precipitated. A deep red solution of the complex was obtained which was evaporated to dryness on a water bath. The residue was recrystallised from ethanol and dried in vacuo.

Analysis: Calculated for $C_{36}H_{40}Cl_2N_4O_8Zn$: C, 54.5; H, 4.8; N, 7.1%. Found: C, 54.2; H, 5.0; N, 6.7%.

Molecular Weight: (See footnote). Calculated: 794.4, Found: 814 ± 20.

(iii) bis-(5,5'-dimethyldipyrromethenato) cadmium(II), $Cd(MMPM)_2$[5]:

The complex was prepared as outlined for $Zn(MMPM)_2$ in (i) above using cadmium nitrate as a source of cadmium ions. The complex was obtained as a yellow-orange finely divided precipitate, which was recrystallised from ethanol in the cold, and dried in vacuo.

Analysis: Calculated for $C_{38}H_{46}CdN_4O_8$: C, 57.2; H, 5.8; N, 7.0%. Found: C, 54.6; H, 5.7; N, 6.7%.

(iv) bis-(5-chloro-5'-methyldipyrromethenato) cadmium(II), $Cd(MClPM)_2$:

Cadmium nitrate was used as a source of cadmium ions and the method of preparation and recrystallisation was as outlined for $Zn(MClPM)_2$ in (ii) above.

Footnote: Unless otherwise stated molecular weights were determined in chloroform solutions by osmometry. The experimental procedure followed is outlined in Appendix A. Range estimates are derived from estimated errors in the experimental procedure.

Analysis: Calculated for $C_{36}H_{40}CdCl_2N_4O_8$: C, 51.3; H, 4.5; N, 6.7%. Found: C, 51.5; H, 4.7; N, 6.7%.
Molecular Weight: Calculated: 841.4 Found: 833 ± 40.

(v) Attempted preparation of bis-(5,5'-dimethyldipyrromethenato) mercury(II), Hg(MMPM)$_2$[5]

The preparation of this complex was attempted using mercuric nitrate as a source of mercuric ions, as outlined for Zn(MMPM)$_2$ in (i) above. Examination of the NMR spectra of those products of the reaction which were soluble in chloroform indicated that the ligand had decomposed. No evidence for the formation of Hg(MMPM)$_2$ as reported by Porter[5] was found. Products insoluble in chloroform appeared to be mainly unchanged mercuric nitrate.

(vi) bis-(5-chloro-5'-methyldipyrromethenato) mercury(II), Hg(MClPM)$_2$

Mercuric nitrate was used as a source of mercuric ions, and the complex was prepared as outlined for Zn(MClPM)$_2$ in (ii) above. A red powdery precipitate formed which was filtered and recrystallised from ethanol. The finely divided crystalline solid was dried in vacuo.

Analysis: Calculated for $C_{36}H_{40}Cl_2HgN_4O_8$: C, 46.6; H, 4.3; N, 6.0%. Found: C, 45.9; H, 4.2; N, 5.9%.

(c) Preparation of the Palladium Complexes

(i) Palladium nitrate

Approximately 1gm of bulk palladium metal was dissolved in 30mls of concentrated nitric acid to which 1 drop of concentrated hydrochloric acid had been added. The presence of a small amount of chloride ion catalysed the solution process, which was assisted by heating the mixture on a water bath for several hours. The dark-brown solution was evaporated to dryness and the residue was dissolved in 20 mls of concentrated nitric acid, which was also evaporated to dryness. The resulting crumbly brown compound was tested for chloride impurities by addition of a little silver nitrate solution to a solution of a small quantity of the palladium nitrate in water. If necessary the fuming process was repeated. The hygroscopic compound obtained was stored in the dark in a well sealed container. It was used as a source of palladium(II) ions without further investigation.

(ii) bis-(5,5'-dimethyldipyrromethenato) palladium(II), Pd(MMPM)$_2$[5].

A solution of palladium nitrate (0.17gm) in minimum ethanol was added to an ethanolic solution of the ligand (0.5gm) and excess sodium acetate. A red solution was obtained which was evaporated to a small volume under a

stream of compressed air. The complex was obtained as a finely divided orange-red solid which was recrystallised from ethanol and chloroform, and dried in vacuo. Crystals of a size suitable for single crystal X-ray diffraction studies could also be obtained, as outlined in Chapter 3.
Analysis: Calculated for $C_{38}H_{46}N_4O_8Pd$: C, 57.6; H, 5.8%.
Found: C, 57.5; H, 6.2%.
Molecular Weight: Found (Crystallographic Method) 792 ± 1
Calculated, 792.4.

(iii) bis-(5-chloro-5'-methyldipyrromethenato) palladium(II), $Pd(MClPM)_2$

The complex was obtained as a microcrystalline purple solid as outlined for $Pd(MMPM)_2$ in (ii) above.
Analysis: Calculated for $C_{36}H_{40}Cl_2N_4O_8Pd$: C, 51.7; H, 4.8; N, 6.7%. Found: C, 51.7; H, 4.9; N, 6.7%.
Molecular Weight: Found: 1017 ± 30, Calculated: 835.4.

Thin layer chromatography was used to try to separate out the cis and trans isomers of this compound. A partial separation was achieved, however attempts at using the process preparatively were unsuccessful. The NMR spectrum of the complex also indicated the presence of two isomers (see Figure 4.32, and discussion on page 100).

(d) Attempted Preparations of Complexes of Other Transition Metals

Unless stated otherwise the metal compounds used as starting materials are those available commercially. Only MClPMH was used in these preparations since previous experience had shown this ligand coordinated more readily than MMPMH.

Ruthenium

(i) potassium pentachloroaquoruthenate(III), $K_2RuCl_5H_2O$ [22]

This complex was used as one of the starting materials in the attempted preparation of a ruthenium(II) complex. It was also used in the preparation of a series of o-phenanthroline complexes (Chapter 5).

Potassium hydroxide pellets (6gm) were fused to a quiescent melt in a platinum crucible. Potassium chlorate (1.5gm) was finely ground and intimately mixed with ruthenium sponge (1gm). This mixture was added evenly in small portions over ½ hour to the fused potassium hydroxide while it was maintained at a sufficiently high temperature for scintillations to occur on the addition. The crucible was heated for a further ½ hour with occassional stirring with a silver wire. The cooled melt was removed by scraping, and any remainder was removed by swirling 30mls of water quickly around the crucible. These washings and the bulk of the melt were made up to 60 mls with sufficient hydrochloric acid solution to give a final acid concentration of about 2.5M. The acid solution was filtered and concentrated to about half the original volume. The product was filtered, and washed with a little cold dilute hydrochloric acid, followed by 80% aqueous ethanol with a few drops of dilute hydrochloric acid, and finally with ethanol followed by acetone. The yield of K_2RuCl_5OH was approximately 1.5gms.

The brown-black solid was dissolved in 30 mls of 1 N hydrochloric acid and 2 mls of 36% formaldehyde solution was added. The mixture was allowed to stand on a hot water bath (80^oC) for approximately 8 hours and was then evaporated to near dryness. Acetone was added and the product was filtered and dried in vacuo. The yield of $K_2RuCl_5 H_2O$ was about 1.3gm. This material was used as a source of ruthenium(III) without further investigation.

(ii) Attempted complex formation

The following reagents were used as starting materials: $RuCl_3.3H_2O$, $K_2RuCl_5.H_2O$, and $Ru(NH_3)_6Cl_3$. Of these only $K_2RuCl_5 H_2O$ reacted.

Several attempts were made to prepare a ruthenium(II) complex. Mole ratios of 1:2 and 1:3 of ruthenium(III) to MClPMH and excess sodium acetate in ethanol solution were used, and a number of reducing agents, including sodium dithionite, sodium thiosulphate, hydrazine hydrate, hypophosphorous acid, and gaseous sulphur dioxide were added to reaction mixtures. On heating a darkening was observed which suggested complex formation. The darkening occurred whether or not a reducing agent was present. When solutions were evaporated to dryness on a waterbath, a red powdery solid was obtained, which was dissolved in low boiling petroleum ether.

Chromatographic separation of reaction products was attempted using a column of 10% deactivated alumina. The red colouration in the petroleum ether was deposited on the alumina. Successive elutions were made with 5%, 10%, 20% and 50% mixtures of benzene in petroleum ether. The column was finally stripped, except for a dark brown residue at the head of the column, by elution with pure benzene. The remaining deposit was thought to be mainly metal residues. The following fractions were obtained:

(1) Unchanged ligand

(2) Ligand decomposition products.

In one preparation only (in which no reducing agents were used) about 10 mgs of a red product were obtained which may have been a ruthenium-dipyrromethene complex.

Analysis: Calculated for $C_{36}H_{40}Cl_2N_4O_8Ru$, $(Ru(MClPM)_2)$, C, 52.1; H, 4.8%. Found: C, 54.6; H, 5.4%

As the complex could not be formed reproducibly, and owing to the small quantity of the compound obtained, it was not investigated further.

Rhodium

1 mole of rhodium(III) trichloride trihydrate in ethanol was added to 2 moles of MClPMH with excess sodium acetate in ethanol. As for the reaction with ruthenium(III) a number of reducing agents were used for different preparations. Whether reducing agents were present or not a colour change from orange-red to a deep purple colour was observed after a few minutes in the cold. The solution was evaporated to dryness and the dark purple residue was recrystallised from ethanol and chloroform, and dried in vacuo.

Analysis: Calculated for $C_{36}H_{40}Cl_2N_4O_8Rh$, $(Rh(MClPM)_2)$ C, 52.0; H, 4.8; N, 6.7%. Found: C, 51.7; H, 4.9; N, 6.5%.

Magnetic Measurements: The complex was diamagnetic both in the solid state; $10^6\chi g$ $(20^{o}C) = -0.13$ cgs units (Gouy method), and in solution (NMR).

Although the complex was extremely soluble in chloroform, the NMR spectrum gave only a few very weak resonance peaks. The highest peaks were those of ligand decomposition products.

Thin layer chromatography on silica gel gave a continuous band covering two thirds of the plate suggesting a mixture of compounds.

It must be concluded that the analysis obtained is entirely fortuitous and that the "complex" is in fact a mixture of a number of compounds which may contain some complexed ligand. Because of the results obtained with NMR spectroscopy and with TLC experiments the product of the reaction was not further investigated.

Platinum, Iridium and Gold

Complex formation was attempted with potassium tetrachloroplatinite(II), K_2PtCl_4; ammonium hexachloroiridate(IV), $(NH_4)_2IrCl_6$; and sodium tetrachloroaurate(III), $NaAuCl_4$, with MClPMH under similar conditions to those described previously for other metals. In each case the ligand was always obtained unchanged from the reaction mixtures. There was no evidence of ligand decomposition in these cases.

Silver

Silver nitrate (0.05gm) in aqueous solution was added slowly to an ethanolic solution of MClPMH (0.2gm) and excess sodium acetate. A deep red floculant precipitate immediately formed, which was filtered and dried in vacuo. The complex was insoluble, or nearly insoluble in all common solvents including water, methanol, ethanol, n-butanol, chloroform, benzene, carbon tetrachloride, dimethylformamide and dimethylsulphoxide.

Analysis: Found: C, 32.6; H, 3.3; N, 3.7%. Atomic ratios: C_{36}: H_{44}: $N_{3.5}$. Required for: $C_{36}H_{40}AgCl_2N_4NaO_8$,

$(NaAg(MClPM)_2)$, C, 50.4; H, 4.7; N, 6.5%. Required for: $C_{18}H_{20}AgClN_2O_4$, (Ag(MClPM)), C, 45.8; H, 4.2; N, 5.9%. Required for: $C_{20}H_{23}Ag_2ClN_2O_6$, $(Ag_2(CH_3CO_2)(MClPM))$, C, 36.7; H, 3.51; N, 4.3%.

Magnetic measurements: The solid was diamagnetic, $10^6\chi_g$ (20°C) = -0.10 cgs units (Gouy method).

The atomic ratios C:H:N found by elemental analysis indicate that the ligand may be largely unchanged in the complex. On the assumption that the compound was a salt attempts were made to prepare salts with tetramethylamine and tetra-n-propylamine cations, in the hope of producing a more soluble compound, without success. The infrared spectrum of the complex was similar to those obtained for the other metal complexes. No evidence was found for the presence of coordinated acetate. Because of the insolubility of the complex measurement of its conductivity and NMR spectrum was not possible.

SECTION 2.3

Ultraviolet-Visible Spectra

INTRODUCTION

The main features of the ultraviolet-visible spectra of dipyrromethenes are well known[6,12,14,17]. Ligand field spectra have been used extensively, with reasonable success, in attempting to determine the stereochemistry of the ML_2 complexes of the transition metals[12,14,16,17]. An attempt has been made to use the extinction coefficients of one of the bands of the non-ligand field spectra of some complexes to extract information about their stereochemistry[6].

The spectra of the MMPMH and MClPMH complexes of zinc(II), cadmium(II), mercury(II) and palladium(II) in chloroform solution are reported here, and are compared with spectra of complexes of these ligands, and those of 3,4'-dicarboxyethyl-5-bromo-3',4,5'-trimethyldipyrromethene (MBrPMH) with the metal ions cobalt(II), nickel(II) and copper(II), which have been reported previously[12,14]. An attempt is made to explain the origin of some bands in the non-ligand field spectra of these complexes.

The non-ligand field spectra are similar for all of the complexes studied so far whose spectra have been reported, and can be divided into three main regions.

(1) <u>22,000 - 18,000 cm^{-1}</u>: A band is found in this region, often with one or more shoulders. The extinction coefficient

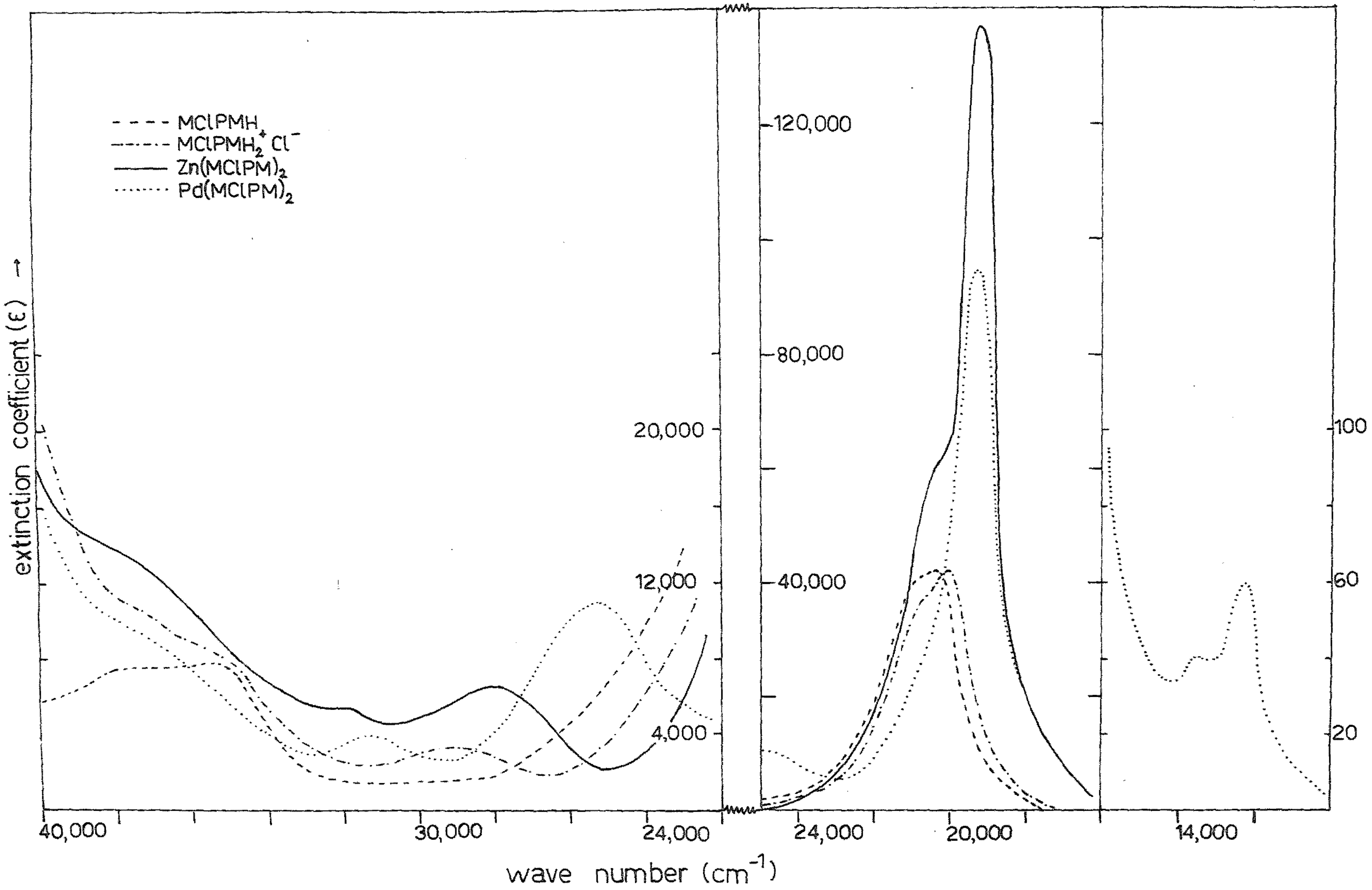
is of the order of 10^5. This band is also found in the spectra of the neutral and protonated ligands. It is therefore considered to be due to a low energy intraligand $\pi \rightarrow \pi^*$ transition and has been described by Fergusson and Ramsay[12] as being similar to the Soret band of porphyrins since it is of about the same intensity, and behaves in a similar manner on coordination of the ligand. The band is generally found to intensify and to move to lower energy when the ligand coordinates to a metal ion.

(2) <u>30,000 - 25,000 cm^{-1}</u>: In this region a band is often found with an extinction coefficient of between 10^3 and 10^4, for metal complexes, but is not found in the spectra of the free ligand. This band is tentatively assigned to a metal $\rightarrow \pi^*$ charge transfer transition. It does not seem probable that it is a ligand $\rightarrow$ metal charge transfer since it is observed for both transition metal complexes, and for zinc(II), cadmium(II) and mercury(II) complexes.

(3) <u>Above 30,000 cm^{-1}</u>: A number of bands are found in this region. The spectra vary from complex to complex, but bands observed are probable due to high energy intra-ligand $\pi \rightarrow \pi^*$ transitions.

(4) <u>Below 18,000 cm^{-1}</u>: Ligand field bands are observed for transition metal complexes outside the region dominated by the low energy $\pi \rightarrow \pi^*$ band. However these are not

FIGURE 2.31



- - - MClPMH
-·-·- $MClPMH_2^+Cl^-$
—— $Zn(MClPM)_2$
······ $Pd(MClPM)_2$
extinction coefficient (ε) ↑
20,000
12,000
4,000
120,000
80,000
40,000
100
60
20
40,000
30,000
24,000
24,000
20,000
14,000
wave number (cm^{-1})

found for complexes of the d^{10} metals and will not be discussed in detail.

The spectral data obtained for the complexes of zinc, cadmium, mercury and palladium are listed in Table 2.31. Table 2.32 lists the wave numbers and extinction coefficients of the low energy $\pi \rightarrow \pi^*$ transition as measured for a number of complexes and reported by several authors. Table 2.34 lists the wave numbers and extinction coefficients of the charge transfer bands of a number of MClPMH and MMPMH complexes. Figure 2.31 illustrates the ultraviolet-visible spectra of MClPMH, $\mathrm{MClPMH_2Cl}$, $\mathrm{Zn(MClPM)_2}$ and $\mathrm{Pd(MClPM)_2}$ as typical examples of the spectra obtained.

It has been found that the solution spectra of the ligands are strongly dependent on the nature of the solvent[14], although those of the complexes are only slightly affected by solvent changes[12]. All the spectra reported and compared here have been measured in chloroform. Hence solvent effects may be considered as constant throughout the series.

Figure 2.32 illustrates a molecular orbital bonding scheme for the regular tetrahedral complexes and the square planar palladium complexes. This diagram is greatly simplified, but illustrates the electronic transitions observed for these complexes.

FIGURE 2.32

SCHEMATIC REPRESENTATION OF MOLECULAR ORBITALS OF TETRAHEDRAL AND SQUARE PLANAR DIPYRROMETHENE COMPLEXES

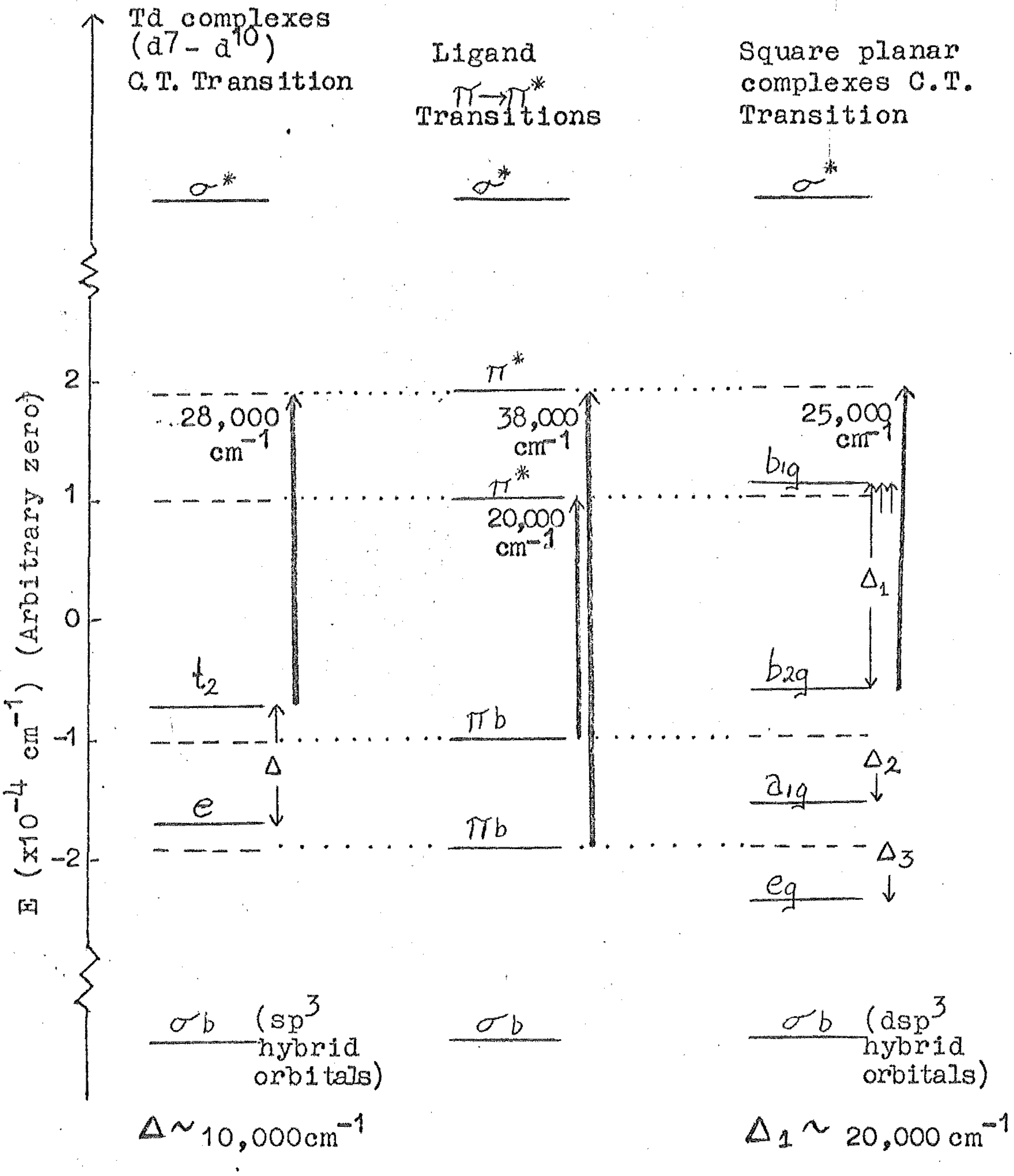


TABLE 2.31 continued

Pd(MCIPM)$_2$	ν	12,300; (13,600)	19,300	25,300	No resolved bands.
	ε	60	$9.5x10^4$	$11.0x10^3$	
	ν	12,100			

a Shoulders in parentheses. b Wave number (ν) in cm^{-1}. c. Solid state reflectance spectrum.

TABLE 2.31

ULTRAVIOLET - VISIBLE SPECTRA OF THE ML_2 COMPLEXES[a].

Compound	b	Ligand Field Bands (?)	Low Energy $\pi \rightarrow \pi^*$ Band	Charge Transfer Band	High Energy $\pi \longrightarrow \pi^*$ Bands
MMPMH	ν		20,400; (21,300)	-	38,600; (30,000; 36,500)
	ε		8.7×10^4		7.0×10^3
MCIPMH	ν		20,300; (21,000)	-	37,300; (36,400)
	ε		4.2×10^4		7.8×10^3
$MMPMH_2^+$	ν		21,100	-	29,000; (35,300; 38,500)
	ε		12.8×10^4		3.57×10^3
$MCIPMH_2^+$	ν		20,080; (20,800)	-	28,900; (36,500)
	ε		4.15×10^4		2.3×10^3
$Zn(MMPM)_2$	ν		20,400; (22,400)	28,300	37,700
	ε		21.5×10^4	4.86×10^3	16.0×10^3
$Zn(MCIPM)_2$	ν		19,200; (20,000)	2.82	(32,300; 33,300; 35,700; 37,000
	ε		13.6×10^4	6.55×10^3	
$Cd(MMPM)_2$	ν		20,400; (22,400)	28,650	37,800
	ε		24.0×10^4	5.1×10^3	15.5×10^3
$Cd(MCIPM)_2$	ν		19,300; (20,000)	28,400	37,000; (32,200; 36,100)
	ε		19.3×10^4	6.27×10^3	33.6×10^3
$Hg(MCIPM)_2$	ν		19,100; (20,000)	28,100	32,000; 37,200; (36,300; 37,900
	ε		17.0×10^4	7.24×10^3	5×10^3 10.4×10^3
$Pd(MMPM)_2$	ν		20,500	25,700	(37,900)
	ε		16.4×10^4	11.7×10^3	

TABLE 2.32 - THE LOW ENERGY $\pi \rightarrow \pi^*$ BAND

Metal	Ligand	Reference	ν (cm^{-1})	ε
-	MMPMH	a	20,400	8.7×10^4
	MClPMH	a	20,300	4.2×10^4
	MBrPMH	12	20,200	4.4×10^4
Zn	MMPM	a	20,400	21.5×10^4
	MClPM	a	19,200	13.6×10^4
	MBrPM	12	19,300	17.0×10^4
Cd	MMPM	a	20,400	24.0×10^4
	MClPM	a	19,300	19.3×10^4
Hg	MClPM	a	19,100	17.0×10^4
Co	MMPM	12	20,400	22.9×10^4
	MClPM	14	19,200	9.0×10^4
	MBrPM	12	19,200	15.0×10^4
Ni	MMPM	12	20,200	9.7×10^4
	MClPM	14	18,900	5.9×10^4
	MBrPM	12	19,100	6.8×10^4
Cu	MMPM	12	20,200;22,200	11.2×10^4;8.7×10^4
	MClPM	14	18,700;20,600	12.7×10^4;8.6×10^4
	MBrPM	12	15,600;18,700;20,200	2.3×10^4;9.4×10^4;6.9×10^4
Pd	MMPM	a	20,500	16.4×10^4
	MClPM	a	19,300	9.5×10^4

a. This work.

DISCUSSION

(1) The Low Energy $\pi \rightarrow \pi^*$ band:

Table 2.32 lists a number of complexes of different dipyrromethene ligands whose spectra have been measured in the present work, and by others[12,14]. The band arises from the first allowed transition between a π-bonding orbital of the ligand and a π^*-antibonding orbital. It appears to have two components since a shoulder is observed on the high energy side of the main band for the ligands, and for most of the complexes. The composite nature of the band makes comparisons of the differences in position and intensity of the band from one complex to another difficult, since small differences in the relative intensities of the two components can have a considerable influence on the position of the dominant band. The spectra of the copper(II) complexes of MMPMH, MClPMH and MBrPMH reported by Fergusson and Ramsay[12], and by Couch[14], have multiple bands in this region. With the exception of the palladium complexes, whose spectra have a single band in this region, the spectra of the remaining complexes have one dominant band with a prominent shoulder.

For the free ligands there is little difference in the position of the band whether substituents in the 5-position are methyl, chloride or bromide. The substitution of a halogen for a methyl group would be expected to lower the energy of a $\pi \rightarrow \pi^*$ transition in a conjugated system[23].

An increase in intensity might also be expected[23]. However these effects are not observed to any great extent for these compounds, and in fact the extinction coefficients of the bands for MClPMH and MBrPMH are approximately half that for MMPMH. The spectra of the protonated ligands are similar to those of the neutral species. In the case of $MMPMH_2^+$ the band is at a slightly higher energy than for the neutral ligand, while the band is at a lower energy than for the neutral ligand in the case of $MClPMH_2^+$.

When the ligand coordinates to a metal ion an increase in the intensity of the band occurs. Generally this increase in intensity is greater than would be expected on the basis of 2 moles of ligand per 1 mole of complex, indicating that there may be an interaction between the conjugation systems of the two ligands through the metal ion[24a]. For the MClPMH and MBrPMH complexes the band moves to lower energy by about 1000 cm^{-1} on coordination, but this is not found for the complexes of MMPMH where the energy of the band for $Pd(MMPM)_2$ is in fact slightly higher than for that of the free ligand.

The energy of the band is found to vary as follows:

(i) $MClPMH \gg Cd(MClPM)_2 = Pd(MClPM)_2 > Zn(MClPM)_2 = Co(MClPM)_2 > Hg(MClPM)_2 > Ni(MClPM)_2$

(ii) $MBrPMH \gg Zn(MBrPM)_2 > Co(MBrPM)_2 > Ni(MBrPM)_2$.

(iii) $Pd(MMPM)_2 > MMPMH = Zn(MMPM)_2 = Cd(MMPM)_2 = Co(MMPM)_2 > Ni(MMPM)_2$.

Differences in energy between the bands for different complexes is not great, and as has been pointed out previously, the presence of two components in the band envelope makes comparisons unreliable.

The decrease in energy for the transition noted for two of the three ligands on coordination has also been found for other systems involving halogen substituted dipyrromethene ligands[6]. The reason this shift is not observed for MMPMH complexes is not readily apparent, since in all other respects the MMPMH complexes are similar to those of the other ligands. It has been pointed out (page 15) that MMPMH may be a better σ-donor ligand than MClPMH. However, because of the inductive effect of halogen substituents, ligands such as $MClPM^-$ and $MBrPM^-$ should be better π-acceptor ligands than $MMPM^-$. Since the lowest $\pi \rightarrow \pi^*$ transition occurs at about 20,000 cm^{-1} for the dipyrromethene ligands, the highest π-bonding molecular orbital and the lowest π^*-antibonding molecular orbital of the ligands are very close together (Figure 2.32). Under these circumstances it is very difficult to predict what effect bonding will have on the relative positions of the π and π^* orbitals with respect to each other. It may be that metal – ligand π-bonding decreases the difference in energy of these orbitals for the two halogen substituted ligands. However the very small differences in energy of the bands between complexes of different metals do not justify an extension of this argument to the relative ability of the metals to participate in π-bonding. In the case of complexes of phenanthroline and bipyridyl the lowest $\pi \rightarrow \pi^*$ transition generally decreases in energy on coordination to a metal ion. This effect is considered to be due to the influence of the charge of the metal ion, rather than any π-bonding between the metal and the ligand. (Chapter 6). This does not seem to hold for MMPMH since the protonated species, $MMPMH_2^+$, and the palladium complex, $Pd(MMPM)_2$, both show an increase in the energy of the band compared with the free ligand.

The position of the band, besides being rather insensitive to changes in the coordinated metal ion, and to ligand substituents, does not appear to be influenced greatly by the stereochemistry about the metal ion. There can be little doubt that the zinc, cadmium, mercury, cobalt and nickel complexes are regular or near regular tetrahedral. The copper complexes have been established as having tetragonally distorted tetrahedral stereochemistry. The palladium complexes have square planar configurations, while the planarity of the ligand is destroyed by a "butterfly" folding of the ligand at two points on the skeleton (Chapter 3).

The copper complexes show differences in their spectra

TABLE 2.33. PREDICTED INTENSITIES FOR THE LOW ENERGY $\pi \longrightarrow \pi^*$ BAND[6]

Complex	θ_i = angle between ligands in complex	Predicted intensity $\frac{\mathcal{E}_i}{\mathcal{E}_{90}} = \sin^2\theta$	Intensity observed
Zn(MMPM)$_2$	90°	-	21.5×10^4
Cu(MMPM)$_2$	68°	18.5×10^4	8.7×10^4, 11.2×10^4
Pd(MMPM)$_2$	0°	0	16.2×10^4

from those of the other complexes which seem to be too great to be explained in terms of stereochemical effects, since the deviation from tetrahedral stereochemistry in these cases is relatively small. On the other hand, the palladium complexes, which not only have square planar configurations, but also have the ligand planarity disturbed, have spectra very similar to those of the tetrahedral complexes. The decrease in π-delocalisation in the ligand expected because of the distortion found would be expected to decrease the $\pi \rightarrow \pi^*$ transition energy[24b] but, in fact, the energy of the band is found to be higher for the palladium complexes than for the others.

An attempt has been made by Motekaitis[6] to correlate the intensity of the low energy $\pi \rightarrow \pi^*$ transition with stereochemistry. He has based his argument on the work by Braude and Sondheimer on substituted benzene systems[25]. He has proposed that for the regular tetrahedral complexes this band will be fully allowed, but that the intensity of the band will fall off as the complexes tend towards a square planar stereochemistry. It is difficult to see any theoretical justification for his proposals or how it is related to the work of Braude and Sondheimer. The two complexes whose configurations have been determined as being non-regular tetrahedral by single crystal X-ray studies ($Cu(MMPM)_2$ and $Pd(MMPM)_2$) do not show the decrease

TABLE 2.34 - CHARGE TRANSFER BAND

Ligand	Metal	Reference Number	Wave number (cm^{-1})	ε
MMPM	Cd	a	28,650	5100
	Zn	a	28,300	48600
	Co	26	27,800	~ 5000
	Ni	26	27,500	~ 5000
	Cu	26	26,800	b
	Pd	a	25,700	11,700
MClPM	Cd	a	28,400	6270
	Zn	a	28,200	6550
	Hg	a	28,100	7240
	Co	14	27,000	5400
	Ni	14	26,300	12,200
	Cu	14	26,300	9000
	Pd	a	25,300	11,000

a. This work.

b. Shoulder.

of intensity that his theory would predict. (Table 2.33)

(2) <u>The Charge Transfer Band</u>:

A well resolved band has been observed in the region between 28,000 - 25,000 cm^{-1} in the spectra of the MMPMH and MClPMH complexes studied by the author and those reported by Ferguson and co-workers[12,14]. A broad unresolved shoulder is apparent in the spectra reported by Motekaitis in this region[6]. Data are not available in this region from the spectra reported by Fergusson and West[16]. An unresolved shoulder is found in this region for complexes of MBrPMH[26]. Since this band is not observed in spectra of the free ligands it may be postulated that it is due to a charge transfer between the metal and the ligand. Table 2.34 lists the wave numbers and extinction coefficients of this band for the MMPMH and MClPMH complexes of cobalt, nickel, copper, zinc, cadmium, mercury and palladium. The order of metal ions with respect to the energy of the band is the same for each ligand:

$$\text{Cd} > \text{Zn} > \text{Hg} > \text{Co} > \text{Ni} \geqq \text{Cu} \gg \text{Pd}.$$

The band is assigned as being due to metal ⟶ ligand charge transfer since it is in much the same position for the complexes of all the metal ions. The reverse charge transfer is unlikely as the metal ions would require suitable available acceptor orbitals, which is probably not the case for metal ions with the d^{10} configuration. The decrease in energy for the band in going from cadmium, zinc and mercury in the right of the above sequence, to the transition metals on the left, is that expected on the basis of ease of oxidation of the metal ions.

(3) The High Energy $\pi \rightarrow \pi^*$ Transitions

All the complexes show a band with an extinction coefficient of about 10^4 at roughly 38,000 cm^{-1}. However this band is often not resolved. In addition a number of poorly resolved bands of lesser intensity are also found for many of the complexes in this region of the spectrum. These bands are all probably due to transitions between the π-bonding orbitals and π^*-antibonding orbitals of the ligands. Because it is not possible to give more meaningful assignments to these bands at this stage, they will not be discussed further.

(4) Ligand Field Bands

A band is observed at about 13,000 cm^{-1} for $Pd(MClPM)_2$ which would appear on the basis of its extinction coefficient to be a ligand field band. The lowest energy transition expected for square planar palladium(II) is of the order of 20,000 cm^{-1} [27], and would be masked by the intense $\pi \rightarrow \pi^*$ transition in this region. In addition, the band is not observed for $Pd(MMPM)_2$. At this stage the band appears to be anomalous. There is no reason to suppose that it is due to impurities since other physical measurements, including NMR spectroscopy, which is extremely sensitive to small quantities of organic containing impurities, indicate that the compound is pure.

SECTION 2.4

Nuclear Magnetic Resonance Spectra

INTRODUCTION

The ligands which have been studied are particularly suitable for examination by the technique of proton NMR spectroscopy. Their spectra are comparatively simple since, apart from the ethyl ester side chains, there is no observable coupling between groups of protons, and virtually no overlap of resonances occurs.

The diamagnetic complexes of zinc, cadmium, mercury and palladium with MMPMH and MClPMH, as well as the ligands themselves, and their protonated species (LH_2^+) have been studied by this method. The spectra of the bis-complexes (ML_2) will be discussed here, and those of the other palladium complexes will be discussed separately in Chapter 4.

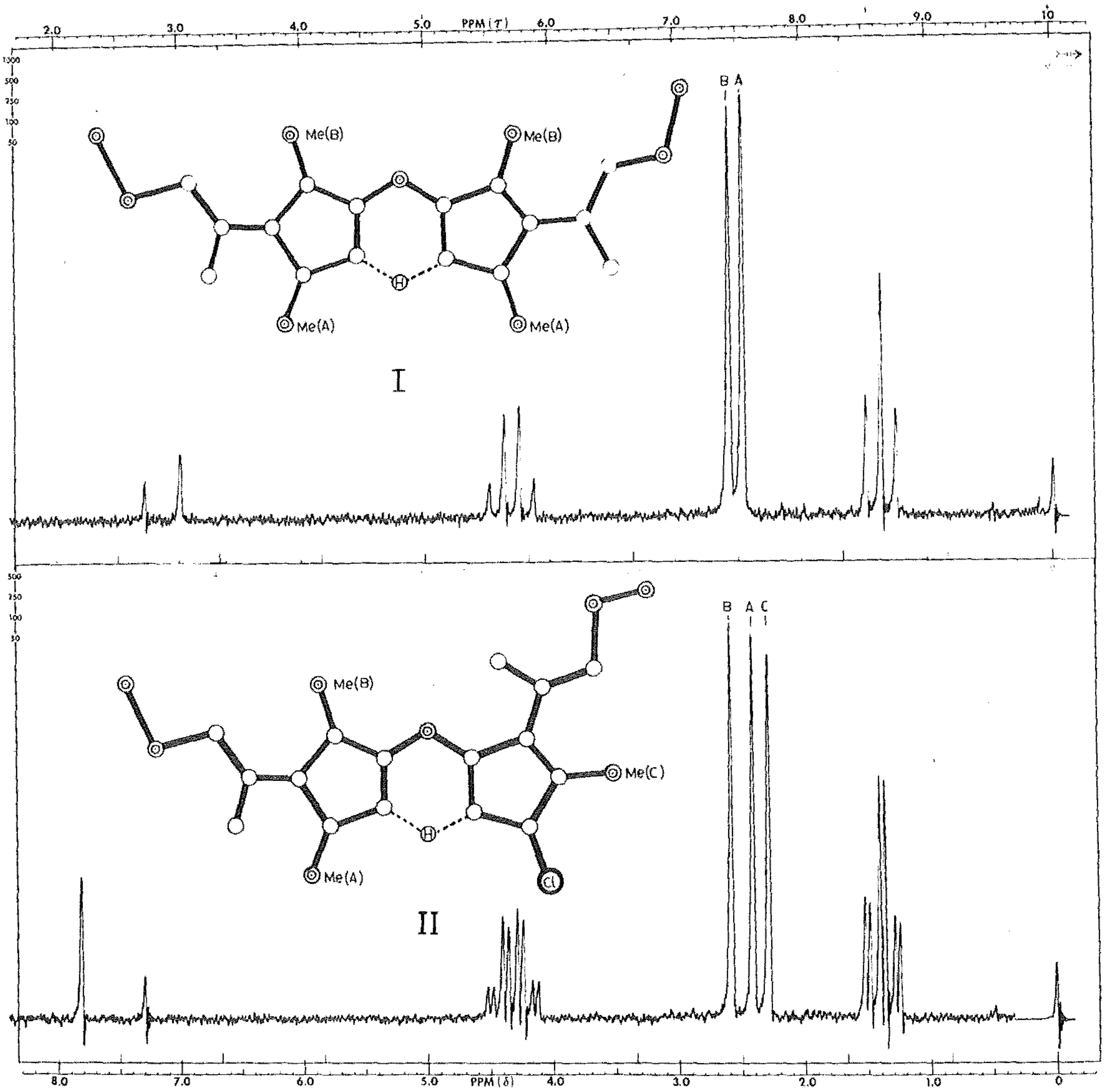
As a result of the work presented here it has been possible to assign resonances to the different types of methyl groups substituted in the ligands (Figure 2.41), and to study their chemical shifts for the series of complexes.

All spectra were run in deuterochloroform at a probe temperature of 35°C. In each case a concentration of approximately 50mg in 0.25mls of solvent was used. Small shifts were noted in the position of resonance peaks with different concentrations, however it is considered that

FIGURE 2.41

NMR SPECTRA OF THE NEUTRAL LIGANDS

I MMPMH II MClPMH



◎ protonated carbon atoms

these can be neglected since the relative positions of the resonances remained the same. Chemical shifts unless otherwise stated are given in parts per million (ppm) down field from T.M.S.

DESCRIPTION OF SPECTRA

(i) Ligands

The spectra of the neutral ligands are shown in Figure 2.41. They can be divided into four sections with integral ratios of 1:4:12:6 and 1:4:9:6 for MMPMH and MClPMH respectively. These correspond to the methine proton (1), the methylene group of the ethyl side chain (4), the ring substituted methyl groups (12 and 9) and the terminal methyl groups of the ethyl side chains (6) respectively. The resonance of the hydrogen bonded to the nitrogen atom has not been observed.

The Methine Proton: This gives rise to a resonance at 7.00 ppm for MMPMH and 7.88 ppm for MClPMH. Its integral is assigned a value of 1 in order to calculate the integral ratios of the resonances due to the other protons.

The Methyl Group Protons: The protons of the methyl group substituted on the pyrrole rings give rise to a set of resonances between 2.0 ppm and 3.0 ppm. The integral ratio of the methyl groups is 6:6 for MMPMH and 3:3:3 for MClPMH. The assignments of these resonances are shown in

Figures 2.41 and 2.42. The reasons for the assignments are discussed below.

The Ethyl Side Chain Protons: The quartet centered at about 4.25 ppm and the triplet centered at about 1.32 ppm are assigned to the ethyl side chains on the basis of splitting patterns and integral ratios. The chemical shifts observed for the methyl and methylene protons are normal for ethyl esters. In the case of the spectrum of MClPMH the two ethyl groups are not equivalent and two overlapping patterns are observed.

(ii) The Complexes and the Protonated Ligands

The Methine Proton: This is deshielded considerably on protonation or coordination of the ligand, its resonance being shifted well down field.

The Methyl Protons: These are not as greatly affected by protonation or coordination of the ligand as is the methine proton. However their chemical shifts with respect to each other vary from one complex to another. In the case of $Zn(MClPM)_2$ two of the three methyl group resonances exactly overlap giving an integral ratio of 3:6 for the two peaks.

The Ethyl Ester Side Chains: The coupling constant between the methylene and methyl protons of the ethyl group is 0.13 ± 0.02ppm for both ligands, and for the range of complexes studied. Over the range of complexes a small

TABLE 2.41

SUMMARY OF NMR DATA.

Compound	Chemical Shift downfield from T.M.S. (PPM).			
	Methine	Me (A)	Me (B)	Me (C)
MMPMH	7.00	2.45	2.58	
$MMPMH_2^+$	7.63	2.98	2.73	
$Zn(MMPM)_2$	7.43	2.22	2.62	
$Cd(MMPM)_2$	7.38	2.35	2.62	
$Pd(MMPM)_2$	7.38	1.93	2.57	
MCIPMH	7.88	2.46	2.62	2.33
$MCIPMH_2^+$	8.54	2.90	2.65	2.32
$Zn(MCIPM)_2$	8.41	2.27	2.62	2.27
$Cd(MCIPM)_2$	8.41	2.38	2.62	2.28
$Hg(MCIPM)_2$	8.38	2.48	2.63	2.27
$Pd(MCIPM)_2$	8.28	1.98	2.57	2.20

TABLE 2.42

RELATIVE CHEMICAL SHIFTS

Compound	Methine (w.r.t. free ligand)	Me (A) (w.r.t. Me (B))	Me (B) (w.r.t. free ligand)	Me (C) (w.r.t. Me (B))
MMPMH	-	-0.13	-	
$MMPMH_2^+$	0.63	0.25	0.16	
$Zn(MMPM)_2$	0.43	-0.40	0.04	
$Cd(MMPM)_2$	0.38	-0.27	0.04	
$Pd(MMPM)_2$	0.38	-0.63	-0.01	
MCIPMH	-	-0.16	-	-0.29
$MCIPMH_2^+$	0.66	0.25	0.03	-0.33
$Zn(MCIPM)_2$	0.53	-0.35	0.00	-0.35
$Cd(MCIPM)_2$	0.53	-0.23	0.00	-0.33
$Hg(MCIPM)_2$	0.49	-0.15	0.02	-0.37
$Pd(MCIPM)_2$	0.38	-0.58	-0.05	-0.37

difference in relative chemical shift was observed between the two non-equivalent ester groups of MClPMH. In the case of the zinc complex this difference was found to be equal to the coupling constant (0.12ppm) giving rise to a pseudo quintet and quartet. Generally this set of resonances was found to vary little from one compound to another and is of little further interest.

DISCUSSION

The chemical shift data obtained for these compounds are summarised in Tables 2.41 and 2.42, and in Figure 2.42. Table 2.42 lists the chemical shifts observed for the complexes with respect to the neutral ligand, and of some of the methyl groups with respect to each other.

In the course of this discussion comparisons are made between the closely related acetylacetone, porphyrin and dipyrromethene systems. The effects of metal coordination, protonation and ligand substituents on the chemical shifts of different groups of protons are summarised in Table 2.43.

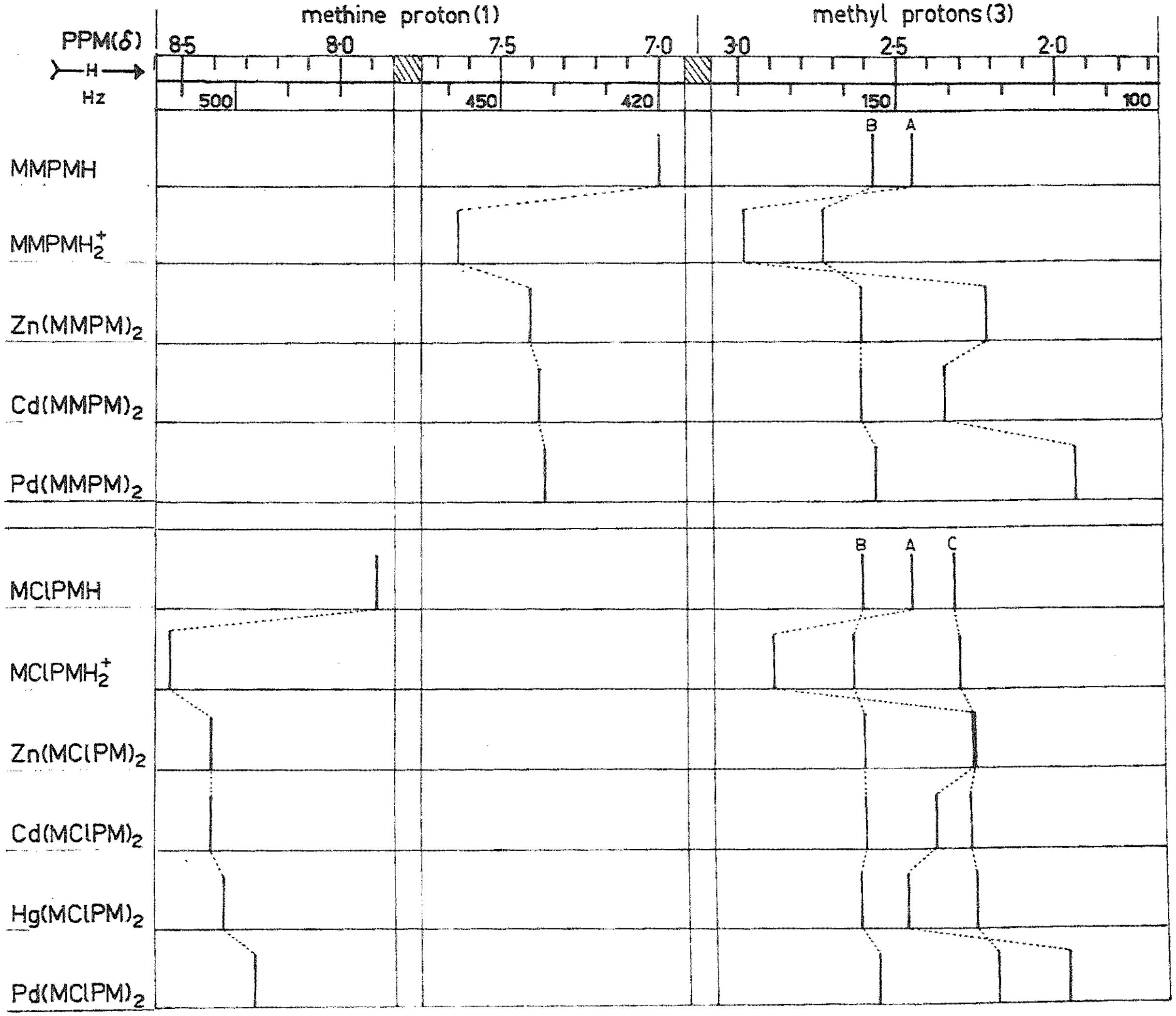
(i) Assignment of the Methyl Group Resonances

The methyl resonances have been assigned to groups (A) and (B) for MMPMH and to groups (A), (B) and (C) for MClPMH, as shown in Figure 2.41, by comparison of the relative shifts of each group from one compound to another on the basis of the following trends.

(1) The spectra of complexes of MClPMH show two resonances

FIGURE 2.42

SUMMARY OF NMR CHEMICAL SHIFT DATA



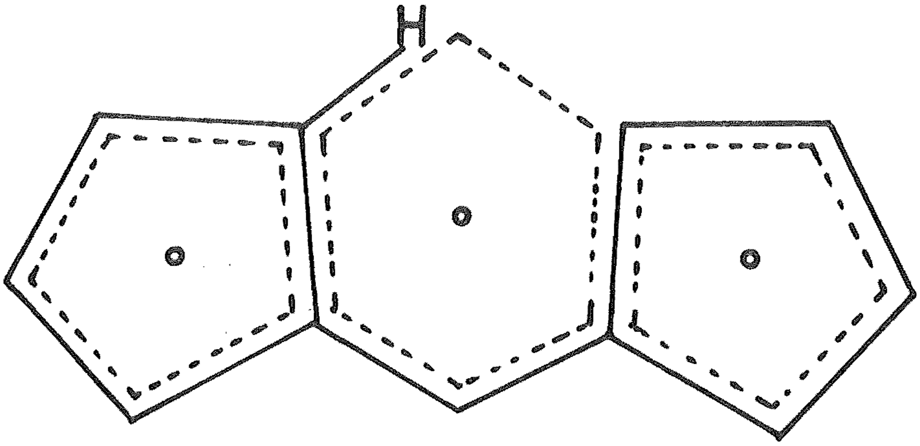
which are observed to remain virtually constant in absolute chemical shift at about 2.6 ppm and 2.3 ppm respectively for the whole series (Table 2.41). The relative chemical shift of one with respect to the other remains nearly constant for the series at 0.35 ± 0.02 ppm (Table 2.42). These resonances are assigned to methyl groups (B) and (C) on this basis alone since, of the three methyl groups, these should be the least influenced by the species coordinated to the nitrogen atoms.

(2) By comparison of the spectra of complexes of MMPMH and MClPMH one resonance at about 2.6 ppm is observed to be in much the same position for both ligands, and for the complexes of both ligands. The resonance is assigned to group (B) since this is present in both ligands. The other resonance noted under (1) above is now assigned to group (C) for MClPMH.

(3) The remaining resonance is assigned to methyl group (A). As this group is closest to the nitrogen atom of the pyrrole ring it would be expected to be very much more sensitive to changing the species attached to the nitrogen atoms than the other methyl groups. In addition a comparison of the chemical shift of (A) with respect to that of (B) for both series in Table 2.42 indicates a close similarity between complexes of the same metal ion. This is to be expected assuming the stereochemistries of the

FIGURE 2.43

RING CURRENT RINGS FOR THE DIPYRROMETHENE SYSTEM (after Abraham[30])



complexes of each ligand to be the same for a particular metal.

(ii) Ring Current Effects

While some work has been carried out on the NMR spectra of diamagnetic dipyrromethene complexes[6], very little interpretation of spectra has been attempted. However, a considerable amount of work has been carried out on the very similar porphyrin system[1b,28,29,30]. Abraham (1961)[30] has calculated the effect of ring currents in the porphyrin nucleus on chemical shifts of protons and methyl groups substituted at various positions on the skeleton. Attempts have been made to apply his calculations to other porphyrin systems with varying degrees of success[28,29]. However ring currents are a useful means of explaining observed NMR chemical shifts in a systematic manner.

It has been observed that a decrease in ring current occurs if an electron withdrawing group is substituted on to the porphyrin system[29], or if a metal ion such as palladium(II), nickel(II) or zinc (II) is coordinated[28,29]. This is reflected in a shielding of groups substituted on the porphyrin nucleus. The degree of shielding for chelate complexes of porphyrins has been found to increase in order of decreasing π-bonding tendency of the coordinating metal ion[29].

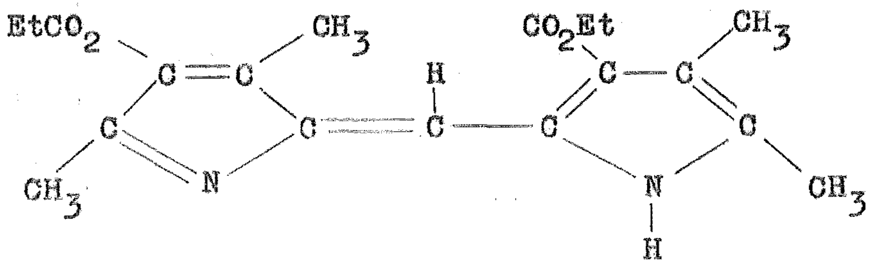
It would seem that provided account is taken of the likely effects of a smaller degree of π-delocalisation due to a less extensive conjugated system, a similar approach in terms of ring current effects should be useful in consideration of the dipyrromethene compounds. The dipyrromethene system can be divided into three separate ring systems as outlined by Abraham[30], as shown in Figure 2.43, giving two five membered pyrrole rings and one "six membered" ring which, in the case of the metal chelates, will be the chelate ring. An increase in ring current in the chelate ring will result in deshielding of the methine proton. The chemical shift of the methine proton therefore should give a sensitive indication of any change in conjugation of the dipyrromethene ligand on coordination.

(iii) Comparison of Spectra of the Two Ligands MClPMH and MMPMH:

In the porphyrin system substitution of electron withdrawing groups results in shielding of all methine protons and ring substituted methyl groups[29]. This is attributed to a decrease in ring current[29,30].

In the dipyrromethene system the methine proton of MClPMH is, in fact, deshielded by 0.88 ppm with respect to that of MMPMH, which cannot be explained in terms of ring current changes. The large shift may be attributable to an intramolecular dipole interaction between the methine proton and the 3-carboxyethyl-group. This could occur if free rotation of the ester group was hindered by overlap with the dipyrromethene π-orbital system so that it was positioned as shown in Figure 2.41. The degree of deshielding found in this case is similar to that observed in other systems under similar circumstances[31].

For the ring substituted methyl groups, the effect of the 5-chloro- substituent in the dipyrromethene MClPMH is only strictly comparable with the compound:



However it is not unreasonable to assume that the 4-methyl group (i.e. group (C)) in the above compound would have a similar chemical shift to group (B) in MClPMH. Therefore, in MClPMH group (C) is probably shielded by about 0.25ppm on the substitution of a halogen at the 5 position. Methyl groups on the other ring are less affected, both being slightly deshielded. It is doubtful if these smaller effects mean very much.

(iv) The Effect of Protonation of the Ligand:

With the exception of the deshielding of methyl group (A) the effect of forming the cation LH_2^+ is similar to that of coordination of the ligand to a metal ion. For both ligands the methine proton is deshielded by more than 0.6 ppm. Methyl groups (B) and (C) remain virtually unchanged, the (B) group of $MMPMH_2^+$ being deshielded by 0.17 ppm with respect to that of MMPMH, while the (B) and (C) groups of $MClPMH_2^+$ are rather less affected. These observations can be interpreted in terms of increased ring currents and are similar to those observed for protonation of coproporphyrin(I) where formation of the dication (PH_4^{2+}) leads to shifts roughly twice those observed for the protonated dipyrromethenes[30].

The effect of protonation on the (A) methyl group is rather larger (deshielded by 0.53 ppm and 0.44 ppm for $MMPMH_2^+$ and $MClPMH_2^+$ respectively) and may indicate a build up of positive charge on the α-carbon atom, rather than reflect changes in ring currents. The smaller effect observed for the chloro-substituted ligand is consistent with this interpretation, since the presence of a chlorine may be expected to assist the dispersal of the positive charge over the whole molecule.

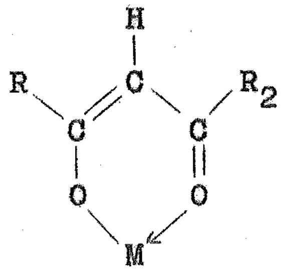
(v) The Effect of Metal Ion Coordination and Relation to Structure

For the dipyrromethene complexes the deshielding of the methine proton on coordination of the ligand to a metal ion is not as great as for protonation and decreases in the order Zn > Cd > Hg > Pd. This effect is, however, the

TABLE 2.43 - RELATIVE CHANGES IN CHEMICAL SHIFT OF GROUPS SUBSTITUTED ON LIGANDS RESULTING FROM CHANGES IN COORDINATION OR SUBSTITUTION.

Substituent or Group Coordinated	Group Affected	Porphyrin	acetylacetone	dipyrromethene
electron withdrawing group (e.g. Cl) on skeleton	methine	shielded	-	deshielded
	methyl	shielded	-	shielded
proton at hetero/atom	methine	deshielded	-	deshielded
	methyl	deshielded	-	deshielded
metal ion coordinated (complex formation)	methine	shielded	shielded	deshielded
	methyl	shielded	deshielded	no change or shielded

opposite to that found for porphyrin complexes of palladium (II), nickel(II) and zinc(II)[29], where the methine protons are found to be shielded. The methine protons are also found to generally be shielded or unaffected when acetylacetone and related ligands coordinate to metal ions[32,33] (Table 2.43).



This lack of deshielding has been used as evidence for a lack of aromaticity in the chelate ring for the acetylacetone complexes[34]. In the few cases where the proton is found to be deshielded, the effect has been attributed to molecular dipole effects[33] rather than ring current changes in the chelate ring.

The dipyrromethene ligands studied in this work, and by Motekaitis[6], all have the methine proton deshielded by about 0.5ppm on coordination to a metal ion irrespective of the stereochemistry of the complex. The effect cannot be explained by molecular dipoles in these cases, and the best explanation appears to be that the chelate ring, in the case of dipyrromethenes, has considerable aromatic character. The reason this does not apply to acetylacetonates or to porphyrins is not readily apparent at this stage.

In principle the degree of deshielding found for the methine proton in the dipyrromethene system should be dependent on the extent to which the metal can influence the π-delocalisation of the ligand, and as a result, on the degree of metal ⟶ ligand π-bonding in the complex. However the range of metal ions whose complexes can be studied by the NMR technique is severely limited by the requirement that the complexes be diamagnetic. Consequently attempts at correlating the shift of the methine proton with the extent of ligand field stabilisation and bonding are not likely to be very meaningful at this stage.

Changes in the positions of the methyl groups on coordination are found to be somewhat different to those observed for the acetylacetone and porphyrin systems also. However these differences can be explained in terms of the increase in ring current already noted for the dipyrromethene system on coordination, or in terms of the stereochemistry of the metal ion.

Except in the case of the palladium complex the (B) methyl protons are deshielded slightly, or not changed, while the (C) methyl protons are shielded in all the MClPMH complexes by 0.04 - 0.13 ppm. The (A) methyl protons are shielded in the order Pd $\gg$ Zn $>$ Cd $>$ Hg.

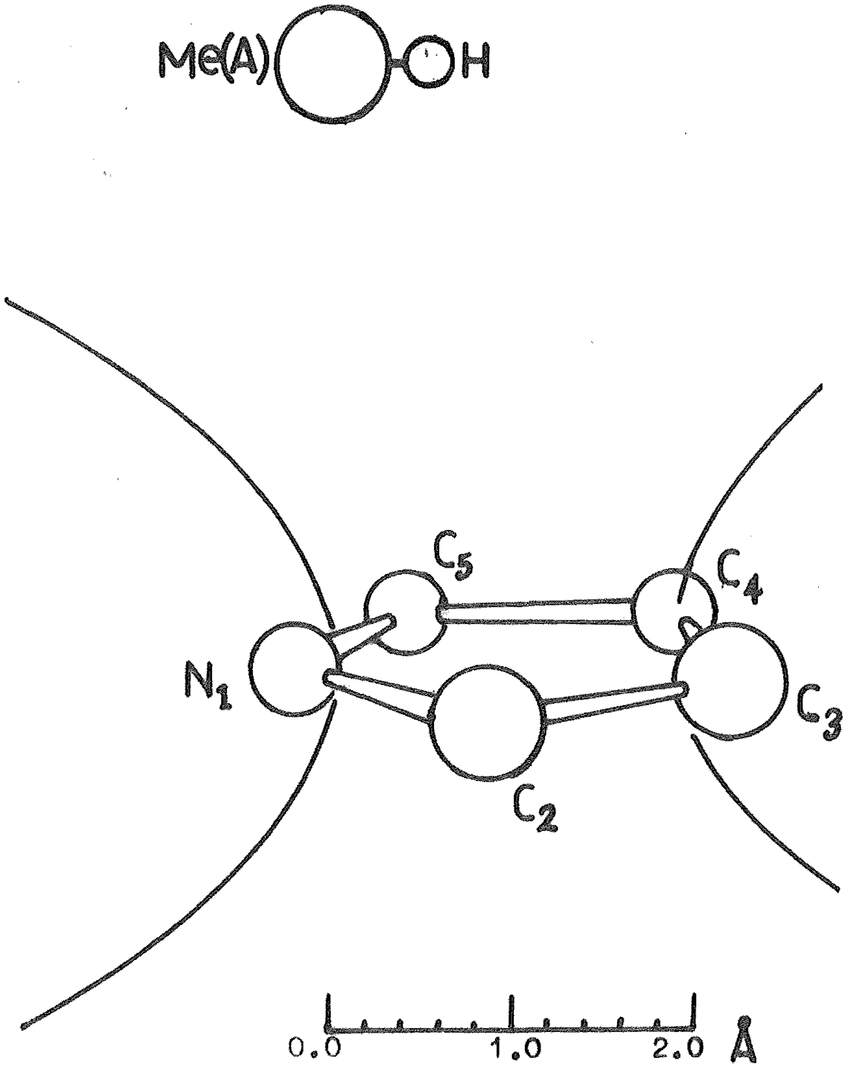
The zinc, cadmium and mercury complexes can be regarded as approximately regular tetrahedra. The shifts observed for these complexes for the (C) methyl protons are similar to those found for the porphyrin and acetylacetone systems with methyl group substituents. The (B) methyl protons are not shielded on coordination, however changes in the position of the (B) methyl resonance are small and probably unimportant. The reason for the change in position of the (A) methyl protons may be explained by interaction of these groups with the shielding cones of the pyrrole rings (see below).

The large upfield shift of the (A) methyl resonance in the case of palladium complexes can be readily explained in terms of the structures of these compounds. The molecular structure of $Pd(MMPM)_2$ has been determined to be "stepped" square planar (Chapter 3). Because of the similarity of its chemical behaviour $Pd(MClPM)_2$ undoubtably has much the same configuration. In these complexes the chelate ring is severely distorted from planarity with the palladium atom lying about 1 Å from the mean plane formed by the other atoms of the ring. This must result in reduced overlap between the nitrogen donor atoms and the metal orbitals. This probably explains the smaller deshielding of the methine proton, and the small shielding observed for the (B) and (C) methyl groups, with respect

FIGURE 2.44

RELATIONSHIP BETWEEN METHYL GROUP (A) AND THE SHIELDING CONE OF AN ADJACENT PYRROLE RING

Approximate mean position of the methyl protons is shown.



to what is observed for the other complexes studied.

The anomalously large shift of the (A) methyl protons for the palladium complexes is unlikely to be due to interaction between the (A) methyl groups of the two ligand in the complex, since these are found to be 3.65 Å apart in the case of $Pd(MMPM)_2$. Nor can this effect be ascribed to the distortion of the methyl group away from the plane of the pyrrole ring, which results from intramolecular contacts, since this is comparatively small (0.2Å). The best explanation appears to be that the groups are overlapping with the shielding cone of the pyrrole rings of the other ligand. Figure 2.44 illustrates the relationship between the pyrrole ring, and its shielding cones, and the (A) methyl group in the determined structure. Table 2.44a lists the averaged distances between the atoms of the ring and the carbon of the methyl group. The shielding observed in the complex, with respect to the free ligand, is 0.48ppm which is about one third of the value calculated for protons about the same distance from a benzene ring[10].

Table 2.44b lists the averaged non-bonding contacts less than 4.0Å between the (A) methyl groups and the pyrrole rings for the distorted tetrahedral complex $Cu(MMPM)_2$ [35]. It can be seen that in this case the methyl protons also enter the shielding cone of the pyrrole ring, but not to the same extent as for the "stepped" square

TABLE 2.44

AVERAGED NON-BONDING CONTACTS BETWEEN THE METHYL (A) CARBON ATOM AND THE ADJACENT PYRROLE RING

(Combined vander Waals Radii 3.7Å)

(a) Pd $(MMPM)_2$ (this work)

Atoms	Distance (Å)
Me (A) - C(5)	3.15
- C(4)	3.58
- C(3)	3.93
- C(2)	3.73
- N(1)	3.22

(b) Cu $(MMPM)_2$ 35

Atoms	Distance (Å)	
	Ring 1	Ring 2
Me (A) - C(5)	*	3.6
- C(4)	*	*
- C(3)	*	*
- C(2)	3.7	3.6
- N(1)	3.4	3.4

planar or distorted tetrahedral complexes.

The shielding of this methyl group would seem to be potentially a sensitive indication of the extent of tetragonal distortion of tetrahedral complexes. However, as has already been pointed out, only diamagnetic complexes can be compared by NMR methods.

CHAPTER 3

The Crystal and Molecular Structure of bis-(4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethanato) palladium(II)

SECTION 3.1

Introduction

Porter[5] pointed out that, because of steric requirements, bis- complexes of 5,5'-substituted dipyrromethenes could not be square planar, with the chelate rings coplanar with the plane of the metal-ligand bonds (Section 1.1, Figure 1.13). He proposed that the structure of Pd(MMPM)$_2$ was tetrahedral, or distorted tetrahedral. Similar conclusions, also justified in terms of molecular overcrowding, were reached by Mellor and Lockwood[8].

Freeman and Snow[20] have determined the structure of bis-(bipyridylimino) palladium(II) and found that a square planar conformation is retained with the ligand distorted from planarity. They pointed out that this type of distortion was also possible for the dipyrromethene complex, and that it need not necessarily be tetrahedrally distorted.

Chemical evidence is little help in deciding the metal stereochemistry. Ligand field spectra are difficult to observe because of the intense transition in the visible region. The ultraviolet-visible spectra generally reveal that little, if any, delocalisation energy is lost when the ligand coordinates to divalent palladium compared with other divalent metal ions such as copper, nickel, cobalt, zinc, cadmium and mercury (Section 2.2). Differences were apparent in the proton NMR spectra of the palladium complexes of MMPM and MClPM compared with those of the other diamagnetic complexes studied (Section 2.3). Because of the non specific nature of the available chemical data a crystal structure determination seemed desirable.

Throughout this chapter it will be convenient to distinguish between chemically equivalent, but crystallographically non-equivalent atoms. The numbering scheme which achieves this is illustrated in Figure 3.31.

SECTION 3.2

Structure Determination

EXPERIMENTAL

Single crystals of Pd(MMPM)$_2$, suitable for X-ray diffraction, were difficult to obtain. Two forms were found.

Form 1: Orange needle-shaped crystals were obtained by slow cooling of an ethanolic solution of the complex. Weissenberg photographs indicated possible tetragonal symmetry with approximate cell dimensions a = 14.0, c = 29.1 Å. The photographs indicated that there might be considerable disorder within the crystalline lattice. For this reason it was decided not to use this crystal form for further study.

Form 2: Orange plate-like crystals were obtained by slow cooling of a solution of the complex in a 50% mixture of ethanol and chloroform. Preliminary precession and Weissenberg photographs indicated monoclinic symmetry. The systematic absences oko for k odd and hol for l odd uniquely indicated space group P2$_1$/c. Accurate cell dimensions determined are a = 10.94(1), b = 22.49(2), c = 8.00(1)Å; β = (67.42 ± 0.08) at 20°C (room temperature), using CuK$_\alpha$ X-radiation (λ = 1.5418 Å) (see footnote).

Footnote. Throughout this chapter figures quoted in parentheses are estimated standard deviations (esd's) in the

These values were obtained by least-squares refinements of the setting angles of 31 reflections accurately aligned using a pinhole collimating system on a Supper equi-inclination diffractometer. Eighteen 2θ values were measured on the hko layer and the remaining 13 values were obtained from the $\bar{h}kh$ layer off a crystal mounted about the [101] diagonal. Beta was measured as the difference between spindle angle settings for accurately aligned hko and okl layers on a Supper precession camera.

The formula weight, calculated for $C_{38}H_{46}N_4O_8Pd$ is 792.4, giving a calculated density of 1.45 g/cm^3 for two molecules to the unit cell. This agrees perfectly with the measured value of (1.45 ± 0.01) g/cm^3 obtained by floatation in aqueous $AgNO_3$ solutions. The densities of these solutions were measured by weighing a known volume of the solutions at 20° ± 2°C.

Since the general multiplicity of space group $P2_1/c$ is 4 the palladium atom must lie on a crystallographic center of symmetry. This deduction is confirmed by the observed systematic weakness of the k+l odd reflections to which the Pd atom does not contribute.

Two crystals were used for the data collection.

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least significant digits derived from the inverse matrix in non-linear least-squares refinement procedures.

Range estimates due to errors in experimental procedures are indicated by the symbol ± before the estimated range.

Crystal I was an approximate rectangular prism with dimensions (0.1 x 0.1 x 0.05)mm^3, and a volume of 5.4×10^{-4} mm^3. Crystal II had an approximately hexagonal cross section with a volume of 4.8×10^{-4} mm^3. For absorption correction purposes the crystals were defined by 6 and 8 intersecting planes respectively. Crystal dimensions were measured to an accuracy of ±0.01mm using a calibrated graticule in a binocular microscope. The linear absorption coefficient for the CuK$_\alpha$ radiation used is 47.5cm^{-1}. Transmission coefficients ranged from 0.79 to 0.65 for crystal I and from 0.79 to 0.69 for crystal II.

Intensity data were collected in a Buerger single crystal diffractometer manufactured by the Charles Supper Company. Data collection procedures for this diffractometer have been outlined[36].

Machine settings are given in Table 3.21.

TABLE 3.21

scan rate	1.66.. deg/min
Receiving aperture (RA) radius	2.1mm
RA distance from crystal	64 mm
Take-off angle	4.5deg (This is the angle the counter arm makes with the direction of the X-ray beam).
Increments of azimuthal angle (Υ)	3 deg
Maximum value of Υ	146 deg

The pulse height analyser was set to pass 85% of the CuK_{α} radiation at the given take-off angle. Each intensity (I) was corrected for background using the formula:

$$I = CT - 0.5\,(B_1 + B_2).$$

The estimated standard deviation ($\sigma(I)$) was given by

$$\sigma(I) = \left[(CT + 0.5(B_1 + B_2) + (pI)^2\right]^{\frac{1}{2}}$$

where: CT is the total integrated count

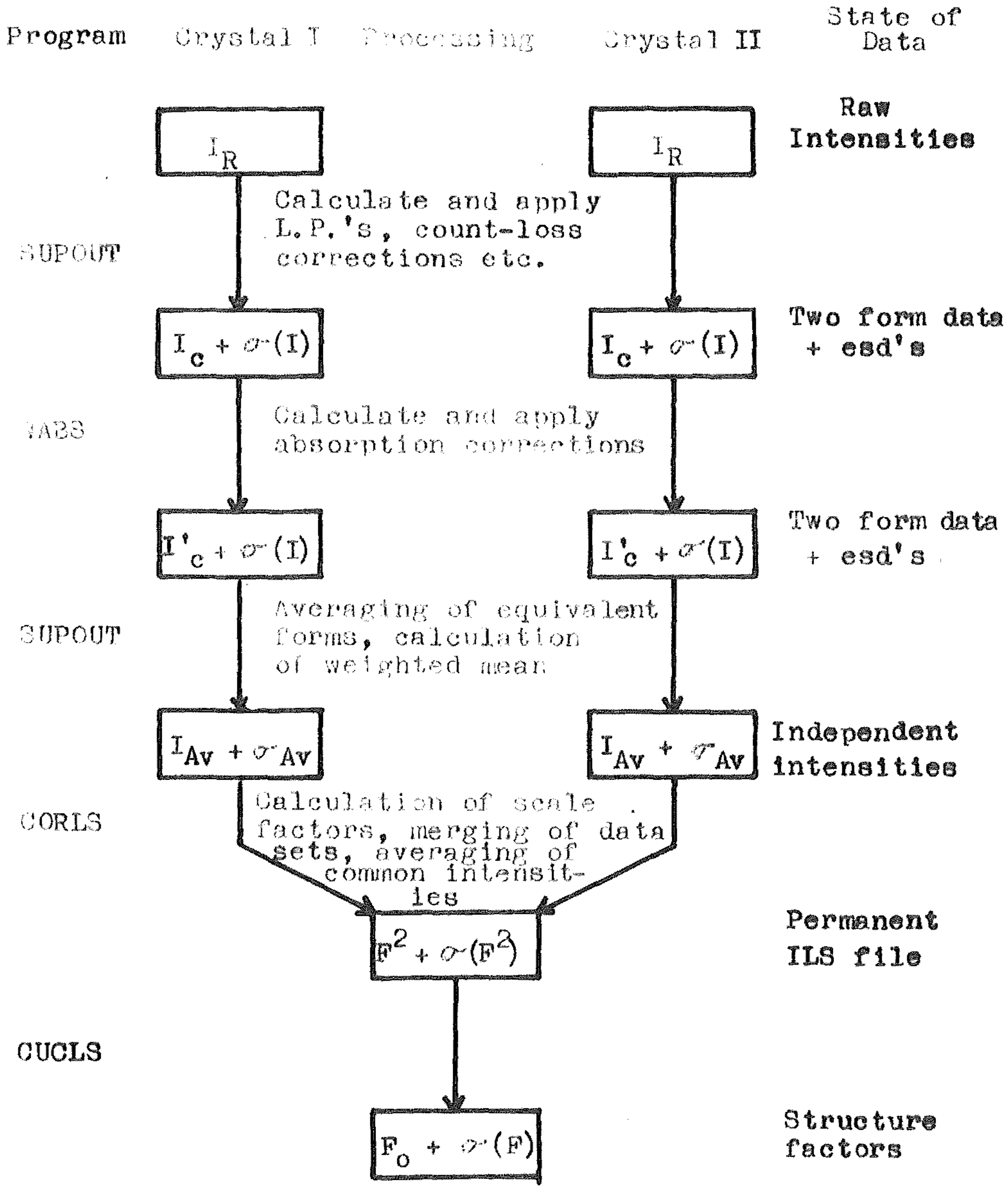
B_1 and B_2 are two integrated background counts on either side of the peak.

p is a factor introduced to avoid overweighting the intense reflections.

Several values were assigned to p at various stages of the refinement. A value of 0.06 was found to give the most constant value of $\sum w(|F_o| - |F_c|)^2$ for all ranges of intensity during the final stages of the refinement. A total of 31 reflections, well separated in reciprocal space, were monitored as standards every day during the data

FIGURE 3.21

PROCESSING OF RAW DATA



collection. A gradual fall-off in these standards was noticed over the whole time of the data collection for each of the crystals used, however variation within each layer was never greater than 5 - 10% and no corrections were applied.

Crystal I was used to collect the layers hkl, $o \leqslant l \leqslant 2$. For the zero layer two of the four equivalent forms were collected and averaged, but only one form was collected for each of the other two layers. In all 1232 independant reflections were measured, of which 252 had intensities less than their estimated standard deviations.

Crystal II was inadvertently mounted about the [101] diagonal which is of similar length to the *a* axis. The layers $\overline{(h+n)}kh$, $o \leqslant n \leqslant 3$, were measured. Two form data were collected for all layers giving a total of 1334 independent reflections of which 359 had intensities less than their esd's.

The data sets from the two crystals were combined and each of the seven layers were put into a common scale using the linear least squares method of Rae[59] to calculate the scale factors for each layer. The weighted mean for each of the common reflections was calculated and used subsequently. The processing of the raw data is outlined in Figure 3.21. A total of 2190 independent reflections were obtained, of which 1533 were greater than their esd's. Only those reflections greater than one esd were used in the solution and refinement of the structure.

STRUCTURE SOLUTION AND REFINEMENT

The palladium atom is uniquely placed on a center of symmetry, since there are two molecules to the unit cell, and contributes to the k+l even reflections only. It was initially placed at the cell origin, but once the structure had been solved was moved to the center of the unit cell $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for convenience. Two cycles of full-matrix least-squares refinement on F (with $\sigma(F) = 0.5\sigma(F^2)/F$) for the k+l even data only, gave an unweighted residual $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and a weighted residual $R_2 = (\sum\omega(F_o - F_c)^2/\sum\omega F_o^2)^{\frac{1}{2}}$ of 34.7% and 37.3% respectively. In all calculations of F_c the atomic scattering factors tabulated by Ibers[37] were used for carbon, nitrogen and oxygen. The scattering factors, and effects of anomolous dispersion given by the values of f' and f", for Pd(o) were those given by Cromer, Larsen and Waber[38].

A difference Fourier was computed using only the k+l even data. The resulting map had a psuedo-mirror plane across the y axis. Light atoms were placed on peaks in chemically sensible positions. After a number of cycles of refinement, interspersed with difference Fourier syntheses, all non-hydrogen atoms were located, giving a value for R_1 of 17.7% which fell to 16.3% when the Pd atom was allowed to vibrate anisotropically. At this stage a number of defects were apparent in the model. Light atom temperature factors ranged from 0.8 to 6.7, and a number of bond lengths and angles did not appear to be chemically reasonable. In addition the k+1 odd data, by itself, gave a value for R_1 of 42.8%, compared with 10.9% for the k+1 even data set.

It was decided to attempt to remove the Pd contributions from the k+1 even intensities, and then to apply direct methods to the whole data set. With the Pd atom assigned an artificially low isotropic temperature factor of 0.3, and its calculated intensity contribution subtracted from the data, 43 k+1 odd reflections appeared amongst the highest 150 normalised structure factors (E's).

Three reflections were designated as origin defining vectors with signs of +1. Symbols A,B,C, and D were assigned to 4 further reflections. Of these, indications were overwhelmingly in favour of A,B, and C having values of +1, but no sign could be assigned to D. D was arbitarily given a value of -1. In all 173 reflections with E's greater than 1.5 were given tentative signs in this way. The resulting E-map revealed peaks on which 20 out of 25 non-hydrogen atoms could be placed in chemically sensible positions. After two cycles of least-squares refinement a difference Fourier was plotted, which revealed the remaining 5 non-hydrogen atoms amongst the top 7 peaks.

The two highest peaks on the map were within 0.6Å of the Pd atom and were indicative of considerable anisotropic vibration.

The new isotropic model was refined to give values of R_1 and R_2 of 13.1% and 19.2% respectively. Corrections to the data set necessitated by punching errors, together with an improvement in the weighting scheme achieved by altering p to its final value of 0.06 (page 62b) gave R_1 and R_2 values of 12.7% and 13.7% respectively. At this stage it was felt that allowing the Pd atom to vibrate anisotropically was justified on the grounds that the highest peaks on the last difference Fourier (both 6.4 electrons/$Å^3$) were within 0.6Å of the Pd atom. In addition the predicted weighted R-factor obtained from the averaging of equivalent forms was less than that obtained from the isotropic refinement.

Refinement of the model with the Pd atom anisotropic resulted in convergence with values of R_1 and R_2 of 10.6% and 11.3% respectively. In the final refinement cycle shifts in all parameters were never greater than 90% of their esd's. The estimated error in an observation of unit weight is 1.34. A structure factor calculation for the reflections previously rejected as being less than their esd's revealed 7 reflections whose F_c's exceeded $3\sigma(F_o)$. In each case, on checking against film intensities, the diffractometer derived values for these

TABLE 3.22

FINAL ATOM STRUCTURAL PARAMETERS

Atom	x	y	z	B (Å^3) [a]
Pd	0.5000(00)	0.5000(00)	0.5000(00)	b
N(1)	0.4885(13)	0.5885(05)	0.5408(19)	2.4(2)
N(11)	0.3046(11)	0.5003(07)	0.4543(17)	2.2(2)
C(2)	0.5843(16)	0.6257(06)	0.6462(25)	2.0(3)
C(3)	0.5492(16)	0.6858(06)	0.5694(23)	1.7(3)
C(4)	0.4262(20)	0.6805(08)	0.4234(28)	3.2(4)
C(5)	0.3914(17)	0.6218(07)	0.4105(24)	2.3(3)
C(6)	0.2683(16)	0.5982(07)	0.3091(25)	2.4(3)
C(7)	0.2207(14)	0.5422(06)	0.3324(21)	1.5(2)
C(8)	0.0875(16)	0.5225(06)	0.2756(23)	1.9(3)
C(9)	0.0939(17)	0.4700(07)	0.3712(26)	2.7(3)
C(10)	0.2310(17)	0.4585(07)	0.4843(26)	2.9(3)
C(21)	0.6965(19)	0.6043(08)	0.8229(28)	3.5(4)
C(11)	0.2860(17)	0.4107(07)	0.6233(25)	3.0(3)
C(41)	0.3517(16)	0.7320(07)	0.3097(26)	2.8(3)
C(81)	-0.0268(16)	0.5568(06)	0.1421(24)	2.5(3)
C(31)	0.6295(19)	0.7380(08)	0.6295(29)	3.6(4)
O(32)	0.6016(14)	0.7887(06)	0.6040(19)	4.8(3)
O(33)	0.7610(13)	0.7223(05)	0.7379(18)	3.9(3)
C(34)	0.8573(22)	0.7713(09)	0.8019(32)	5.0(5)
C(35)	0.9978(22)	0.7391(10)	0.8831(32)	5.3(5)
C(91)	-0.0160(17)	0.4297(07)	0.3580(26)	2.7(3)
O(92)	-0.0014(14)	0.3843(05)	0.4452(19)	4.0(3)
O(93)	-0.1343(12)	0.4461(05)	0.2330(18)	3.2(2)
C(94)	-0.2412(20)	0.4053(08)	0.2112(29)	3.9(4)
C(95)	-0.3700(22)	0.4349(10)	0.0803(33)	5.1(5)

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a. The B values are the parameters in the isotropic temperature factor expression $\exp(-B(\sin\theta)^2/\lambda^2)$

b The anisotropic temperature factor coefficients (β) for Pd in the expression $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$ are as follows

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}
0.00312(12)	0.00079(02)	0.01176(51)	0.0061(08)	0.00127(24)

β_{23}
0.00032(14)

data were found to be in error. A final difference fourier, based on the 1533 "observed" reflections, showed no density greater than 0.82 electrons/ $\mathring{A}^3$, roughly 30% of the height of a carbon atom in the structure.

Correction of the intensities for absorption effects did not produce any significant changes in atomic positional or temperature parameters, and did not improve the agreement factors. This is not surprising in view of the small range of transmission coefficients found for each of the two crystals used in the data collection.

The value of R_1 for the k+1 odd intensities is 7.5% compared with 26.0% for that of the k+1 even intensities. However values found within each of 10 ranges of intensity for each set of data were found to be in close agreement. This apparent difference in the overall value is explained by the larger number of small intensities in the k+1 odd data set. Values of $\left(\sum\omega(|F_o| - |F_c|)^2/(NO - NV)\right)^{\frac{1}{2}}$ for 10 ranges of intensity over the whole data set ranged from 1.1 to 1.7 indicating that the relative weighting scheme was reasonable.

Table 3.22 presents the final atomic positional and thermal parameters together with their esd's. The orientation of the vibrational ellipsoid of the Pd atom is reasonable, being directed at approximately 60° to the plane of coordination of the ligands and between the bulky methyl groups C(11) and C(21). (Figure 3.33). In

Appendix C the final values of F_o and F_c (in electrons) are listed for all reflections included in the least squares refinements. Cases where $|F_o| - |F_c|$ exceed $3\sigma(F_o)$ are marked with an asterisk. There are 15 such reflections.

Computer programs used for all calculations in this structure determination are listed in Appendix B.

TABLE 3.32 - SELECTED INTRAMOLECULAR NON-BONDING CONTACTS

Atoms	Distance(Å)	Combined van der Waals radii [40](Å)
C(21)-Pd	3.54	4.2
C(11)-Pd	3.50	4.2
C(21)-C(11) (different ligands)	3.66	4.0

CLOSEST INTERMOLECULAR CONTACTS

Atoms	Distance(Å)	Combined van der Waals radii [40](Å)
N(11)-C(94)	3.69	3.7
C(8)-C(91)	3.48	3.6
C(8)-C(81)	3.62	3.7
C(9)-C(91)	3.46	3.6
C(81)-C(21)	3.30	4.0
C(81)-C(81)	3.62	4.0

TABLE 3.33

AVERAGE OF CHEMICALLY EQUIVALENT BOND LENGTHS

Bond Type	Number	Average[a]	Expected[51]	Found for $Cu(MMPM)_2$ [15a]
Pd—N	2	2.028(03)	2.00	-
C—CH_3	4	1.52(2)	1.52	1.53(3)
N --C (type 1)	2	1.34(2)	1.35	1.41(2)
N --C (type 2)	2	1.40(2)		
C --C (type 1)	6	1.39(2)	1.40	1.41(2)
C --C (type 2)	2	1.46(2)		
C - CO_2Et	2	1.46(3)	1.47	b
C = O	2	1.20(2)	1.23	1.20(3)
C - OEt	2	1.38(3)	1.36	1.36(3)
O - Et	2	1.46(2)	1.43	1.48(4)
CH_2 - CH_3	2	1.57(3)	1.54	1.40(5)

a. Averages were calculated from the expression $d_{av} = \sum_i di/M$ and the esd's by the expression

$$\sigma_{av} = \left(\sum_i (d_i - d_{av})^2 / (M-1)\right)^{\frac{1}{2}}$$

where M is the number of bonds being averaged.

b. This figure is not available.

SECTION 3.3

Description and Discussion of the Structure

The structure consists of well separated monomeric $Pd(MMPM)_2$ units with a Pd-Pd distance of 11.94Å. Closest intermolecular interactions are listed in Table 3.32. Some of these are within the combined van der Waals radii of the groups concerned, and may give rise to intermolecular interactions. A summary of bond distances and angles is listed in Table 3.31. Figure 3.31 shows the molecule viewed normal to the PdN_4 plane. Figure 3.32 shows the molecule rotated 46° about the N(1) - N(11) vector from the position in Figure 3.31.

Because the palladium atom is on a center of symmetry, the coordination of the 4 nitrogen atoms is necessarily square planar. Impossibly short intramolecular contacts between methyl groups C(11) and C(21) of opposite ligands do not occur because the chelate ring is not coplanar with the PdN_4 plane, giving the complex a "stepped" configuration. In addition the ligand is not planar. The nature of the deviation of the chelate ring from planarity with the PdN_4 plane is best seen in Figure 3.33. Each ligand is folded 44° out of this plane about the N(1) - N(11) vector. The deviation of the ligand from planarity is also seen in Figure 3.32. Folding of the two 5 membered pyrrole rings away from the plane of the chelate ring occurs along the

TABLE 3.34 continued

Plane 3						Plane 4					
W(1)	0.016(15)	1.0	C(21)	-0.224(21)	10.5	N(11)	0.017(14)	1.3	C(21)	-1.972(20)	99.0
C(2)	-0.023(19)	1.2	C(11)	-1.690(19)	87.6	C(7)	-0.017(15)	1.1	C(11)	-0.162(18)	9.0
C(3)	0.013(18)	0.7	C(41)	-0.017(19)	0.9	C(8)	0.011(17)	0.6	C(41)	-1.509(18)	82.1
C(4)	0.000(23)	0.0	C(81)	-1.495(19)	79.8	C(9)	0.004(18)	0.2	C(81)	0.008(17)	0.4
C(5)	-0.016(19)	0.8	C(31)	0.107(22)	4.9	C(10)	-0.022(19)	1.2	C(31)	-2.522(21)	122.4
			O(32)	-0.120(15)	7.8				O(32)	-3.067(14)	213.9
			O(33)	0.525(15)	36.3				O(33)	-2.490(13)	186.5
Pd	0.686(00)	-	C(34)	0.738(25)	29.8	Pd	0.576(00)	-	C(34)	-3.076(23)	133.1
N(11)	-0.658(13)	51.7	C(35)	1.474(25)	58.7	N(1)	-0.791(14)	57.6	C(35)	-2.627(24)	111.2
C(6)	-0.282(19)	14.9	C(91)	2.479(20)	127.0	C(2)	-1.518(17)	87.9	C(91)	0.080(18)	4.4
C(7)	-0.662(16)	41.4	O(92)	2.809(15)	184.1	C(3)	-1.857(17)	110.7	O(92)	0.085(19)	6.2
C(8)	-1.335(18)	74.5	O(93)	2.671(14)	194.1	C(4)	-1.346(20)	66.1	O(93)	0.214(13)	16.8
C(9)	-1.770(20)	88.8	C(94)	-3.294(23)	146.2	C(5)	-0.726(18)	41.6	C(94)	0.366(21)	17.4
C(10)	-1.352(20)	67.8	C(95)	-3.578(25)	142.3	C(6)	-0.305(18)	17.4	C(95)	0.339(24)	14.2

* Probability (P) that X^2 exceeds a if atoms are planar (2 degrees of freedom)[39]

a	P
5.99	0.05
9.21	0.01

TABLE 3.34 continued

Atom	Distance(P) (Å)	P (P)	Atom	Distance(P) (Å)	P (P)	Atom	Distance(P) (Å)	P (P)	Atom	Distance(P) (Å)	P
		Plane 1							Plane 2		
Pd	0.000(00)	-	C(21)	-1.735(20)	84.8	N(1)	-0.003(15)	0.2	C(21)	-0.679(21)	32.7
N(1)	0.000(14)	-	C(11)	-1.670(18)	90.7	N(11)	0.013(13)	1.0	C(11)	-0.620(19)	33.0
N(11)	0.000(12)	-	C(41)	2.072(19)	108.3	C(5)	-0.011(18)	0.6	C(41)	-0.422(19)	22.2
			C(81)	2.017(18)	111.9	C(6)	0.035(18)	1.9	C(81)	-0.511(18)	28.1
			C(31)	0.137(21)	6.5	C(7)	-0.028(16)	1.8	C(31)	-0.805(21)	37.7
C(2)	-0.498(18)	27.4	O(32)	0.473(14)	33.0				O(32)	-1.209(15)	81.1
C(3)	0.256(17)	15.0	O(33)	-0.519(14)	38.6				O(33)	-0.539(14)	38.5
C(4)	1.138(21)	55.0	C(34)	-0.653(23)	28.0	Pd	1.047(00)	-	C(34)	-0.702(24)	29.2
C(5)	0.953(18)	53.0	C(35)	-1.146(24)	47.8	C(2)	-0.371(18)	20.4	C(35)	-0.055(25)	2.2
C(6)	1.421(18)	78.3	C(91)	-0.103(19)	5.5	C(3)	-0.534(18)	30.2	C(91)	-p.983(19)	51.8
C(7)	0.945(15)	62.0	O(92)	-0.919(14)	67.0	C(4)	-0.311(22)	14.4	O(92)	-1.149(15)	78.9
C(8)	1.067(17)	62.0	O(93)	0.707(13)	53.4	C(8)	-0.397(17)	22.9	O(93)	-1.045(13)	78.3
C(9)	0.145(19)	7.7	C(94)	0.527(21)	24.7	C(9)	-0.626(19)	32.4	C(94)	-1.319(22)	60.2
C(10)	-0.521(19)	27.4	C(95)	1.413(24)	58.7	C(10)	-0.387(19)	10.0	C(95)	-1.513(25)	61.6

TABLE 3.34

BEST WEIGHTED LEAST-SQUARES PLANES

Equations of planes of the form

$Ax + By + Cz - D = 0$ (Monoclinic coordinates)

Plane No.	Atoms	A	B	C	D	X^{2*}
1	Pd,N(1),N(11)	0.1647	0.1678	-0.9720	-1.056	0.01
2	N(1),N(11),C(5),C(6),C(7)	0.6336	-0.3424	-0.6938	-4.969	8.26
3	N(1),C(2),C(3),C(4),C(5)	0.7757	-0.1459	-0.6139	-1.545	3.77
4	N911),C(7),C(8),C(9),C(10)	0.4048	-0.5214	-0.7512	-7.623	4.73

TABLE 3.35

DIHEDRAL ANGLES. ($^\circ$)

Plane 1 - Plane 2	43.9
Plane 1 - Plane 3	45.6
Plane 1 - Plane 4	44.8
Plane 2 - Plane 3	14.7
Plane 2 - Plane 4	17.0
Plane 3 - Plane 4	31.7

N(1) - C(5) and N(11) - C(7) bonds.

Best least-squares planes have been computed as follows:

plane 2. N(1), C(5), C(6), C(7), N(11)
plane 3. N(1), C(2), C(3), C(4), C(5)
plane 4. C(7), C(8), C(9), C(10), N(11)

The results are tabulated in Table 3.34. Deviations from planarity for each of these groups of atoms are statistically significant but no atom is more than 2.0 times its esd from a mean plane. It is doubtful if these deviations are significant chemically.

Dihedral angles between these planes, and the PdN_4 plane (designated plane 1) are listed in Table 3.35. Planes 3 and 4 (the pyrrole rings) are inclined to each other at 31.7° and to the chelate ring (plane 2) at angles of 14.7° and 17.0° respectively.

Each half of the ligand is chemically, but not crystallographically equivalent. Apart from the side chains C(31) - C(35) and C(91) - C(95) there is an approximate mirror plane through C(6) and Pd normal to the PdN_4 plane. Most bond distances and angles across this pseudo mirror plane are statistically equivalent[39]. Those which vary by more than 2 esd's are marked with an asterisk in Table 3.31 which groups "equivalent" bonds and angles. All chemically equivalent bond lengths have been averaged and are summarised in Table 3.33 where they are compared with those expected[51] and those obtained by Elder[15] for $Cu(MMPM)_2$. It should be noted that the esd's obtained from Elder's determination are rather higher than those found for this structure due to difficulties in obtaining an accurate data set. Any large deviations can be explained on this basis.

It appears that not all the bonds in the pyrrole rings are equivalent. Both C–C bonds and C–N bonds appear to fall into two distinct categories (types 1 and 2 in Table 3.33). This difference may reflect a decrease in bond order for bonds of type 2 compared with those of type 1. It is possible that deviations from planarity at atoms C(2), C(5), C(7) and C(9) result in a change from sp^2 type of hybridisation towards sp^3 hybridisation on these atoms.

The methyl groups C(11) and C(21) lie 0.16Å and 0.22Å away from the mean planes of the pyrrole rings. The distance between the adjacent groups on opposite ligands is 3.66Å compared with their combined van der Waals radii of 4.0Å. This is very similar to that observed for the psuedo-tetrahedral $Cu(MMPM)_2$ complex. It is of interest to note that some of the intramolecular strain, which is relieved by deviations from planarity in the molecule, is undoubtedly due to contact between the palladium atom and the C(11) and C(21) methyl groups. The combined van der Waals radii of Pd and methyl groups is 4.2Å[40]. In the structure the Pd– C(21) and Pd– C(11) distances are 3.50(2)Å and 3.54(2) Å respectively. The other methyl groups C(81) and C(41) lie within 0.02Å of the mean planes. There is no significant difference in the averaged bond lengths between two types of methyl groups and the pyrrole rings (Types A and B, Chapter 2, Section 2.4).

For maximum π-delocalisation between carboxyl side chain groups and the pyrrole rings it would be expected that these groups would be coplanar with their respective pyrrole rings. From Table 3.34 it can be seen that the groups are not coplanar, since the oxygen atoms lie as much as 0.5Å from the mean planes. This deviation was also observed by Elder and is probably due to intermolecular contacts between adjacent side chains.

The structure obtained for Pd(MMPM)$_2$ is very similar in many respects to that of bis-(bipyridyliminato)palladium(II) obtained by Freeman and Snow[20]. The two structures will be compared in detail in Section 3.4 however it should be noted here that the Pd-N distances obtained for the two structures are very similar (2.024 Å and 2.028Å respectively).

SECTION 3.4

Survey of the Stereochemistries of Some Crowded Chelate Complexes and their Relation to bis-(dipyrromethenato)Palladium(II)

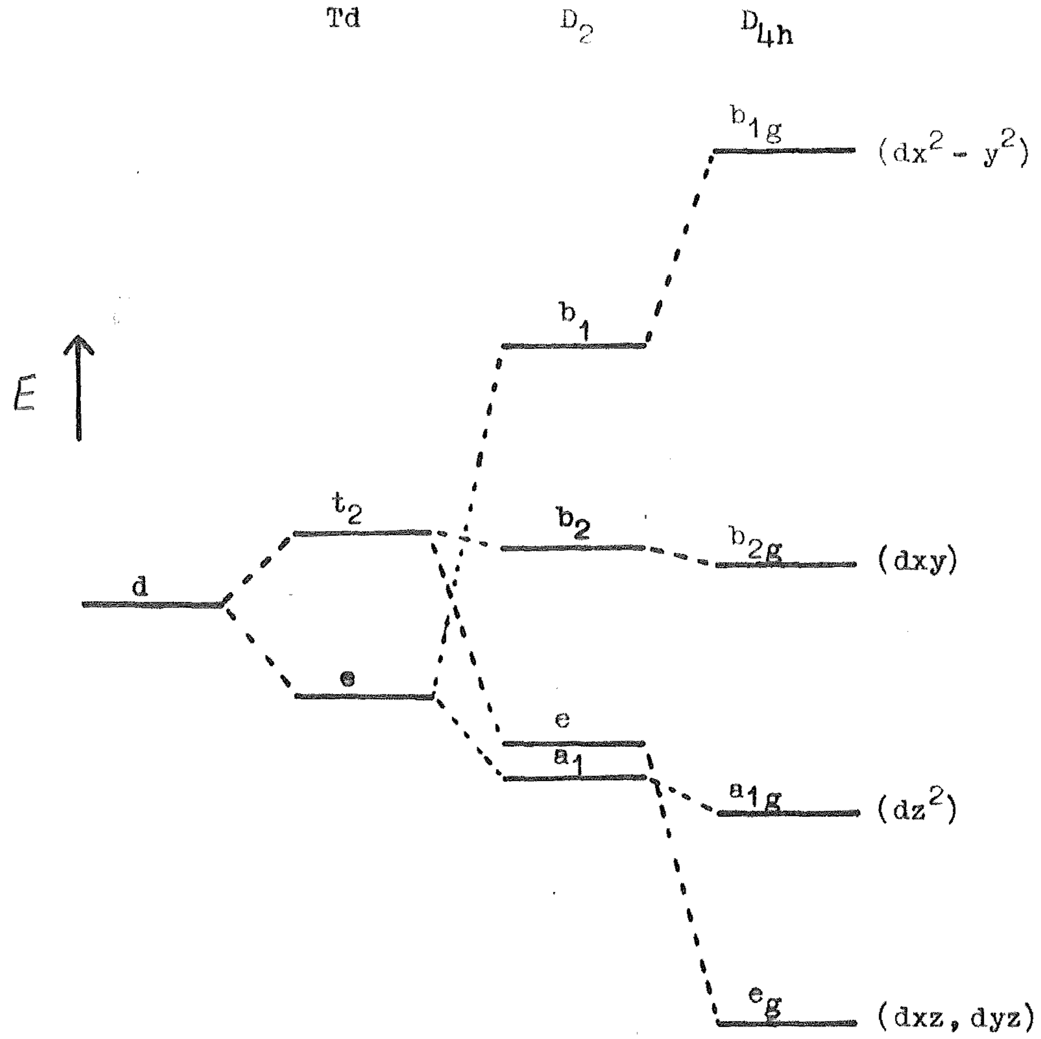
Recently a number of crystal structures have been determined of transition metal complexes of planar bidentate ligands in which intramolecular overcrowding occurs in the region of the metal ion. The complexes considered in this section are those in which the molecular orbital theory and ligand field theory would predict square planar bonding about the metal ion. When overcrowding occurs the complex molecules have been found to deviate from molecular planarity so as to minimize intramolecular interactions. Two types of deviation from molecular planarity have been observed. These are (1) tetrahedral distortion of the coordination plane about the metal, and (2) bending of the bonding at the donor atoms of the ligand so that the plane of the chelate ring is at an angle to that of the square plane about the metal ion.

(1) Tetrahedral distortion:

This is a distortion of the square plane about the metal atom towards a tetrahedral environment as an extreme limit. Such a distortion will alter the splitting pattern of the *d*-orbitals of the central metal ion and should be readily observable in terms of spectral changes. (Figure 3.41).

FIGURE 3.41

EFFECT OF STEREOCHEMISTRY ON METAL D-ORBITAL CONFIGURATION (not to scale)

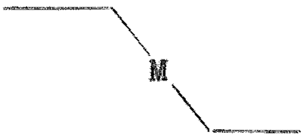


For instance in the case of the $CuBr_4^{2-}$ ion the ligand field spectrum has been interpreted successfully in terms of a distorted tetrahedral stereochemistry[13]. Complexes of this nature can be regarded as being either basically tetrahedral molecules which have undergone tetragonal distortion in order to resolve the degeneracy of the t_2 orbitals (Figure 3.41), such as $CuBr_4^{2-}$, or as being forced away from a basically square planar configuration by intramolecular interaction between substituents on the ligand.

(2) "Stepped" Square Planar Distortion:

Distortion of this nature occurs not at the metal ion, but at the donor atom of the ligand. This type of distortion should result in a decrease in the ligand field resulting from reduced overlap of the donor atom orbitals with those of the metal ion.

Many complexes have now been found where this type of distortion occurs. Such distortion usually allows the chelate rings of opposite ligands to remain parallel, but not coplanar.



Frequently with this type of complex the metal atom resides on a crystallographic center of symmetry. The

TABLE 3.41

DEVIATIONS OF CENTRAL METAL IONS FROM PLANARITY WITH THE CHELATE RINGS OF SOME NITROGEN AND OXYGEN DONOR COMPLEXES.

Compound	Reference	Coordination number	Stereo-Chemistry*	Deviation (Å)
bis-(N-methylsalicylaldiminato)copper(II)	52	4	S.P.	0
bis-(salicylaldoximato)copper(II)	53	6	t-Oh	0.07
bis-(salicylaldiminato)nickel(II)	54	4	S.P.	0
bis-(salicylaldiminato)copper(II)	55	4	S.P.	0.15
bis-(salicylaldehydato)copper(II)	42,56	4	S.P.	0.19
N,N^1-ethylenebis-(acetylacetoneiminato)copper(II)	41	4	S.P.	0.30, 0.06
bis-(dipyrromethenato)copper(II)	15	4	Td	0.31, 0.11
bis-(N-t-butylsalicylaldiminato)copper(II)	46	4	Td	0.63, 0.03
bis-(5-chlorosalicylaldoximato)copper(II)	57	6	t-Oh	0.38
bis-(N-phenylsalicylaldiminato)copper(II)	45	4	S.P.	0.45
bis-(N-methylsalicylaldiminato)copper(II)	58	5	Py	0.47 - 0.55
bis-(3-methyl-1-phenyl-5-p-tolylformazyl)nickel(II)	48	4	S.P.	0.83
bis-(dipyridyliminato)palladium(II)	20	4	S.P.	0.89
bis-(dipyrromethenato)palladium(II)	This work	4	S.P.	1.05

* Abbreviations Used: S.P. square planar; Td distorted tetrahedral
t-Oh tetragonally distorted octahedral; Py square pyramidal.

dihedral angle between the chelate ring and the square plane about the metal ion can be as great as 44°. Table 3.41 lists some complexes where this type of distortion occurs, and the perpendicular distance of the metal ion from the mean planes of the chelate rings is listed for each complex.

It should be noted that this type of deviation is also found with other stereochemistries (including tetrahedrally distorted complexes), and is not restricted to 4 coordinate complexes. Some of these complexes are also listed in Table 3.41.

The "stepped" distortion can occur very readily, as is illustrated by the wide range of compounds for which it has been observed. It is normally attributed to intramolecular non-bonding interactions, but cases have been found where it may result from intermolecular forces. Hall and Waters[41,42] have proposed that a polarisation bond between the copper ion and the conjugated systems of adjacent molecules may account for stepping in the case of N,N'-ethylene bis-(acetylacetoneiminato)copper(II) and bis-(salicylaldehydato)copper(II). In the case of the latter complex the isomorphous nickel(II) compound is planar.

In the tetrahedrally distorted bis(dipyrromethenato)-copper(II) complex[15] the copper ion is found to lie as much as 0.2Å from the mean planes of the ligands. It has been postulated that this deviation can be attributed to interaction between the methyl groups adjacent to the metal and the metal ion itself.

RELATIONSHIP BETWEEN TETRAHEDRAL AND "STEPPED" SQUARE PLANAR DISTORTIONS

Where some form of distortion from molecular planarity is necessary because of steric factors the actual form of the distortion will depend on whether or not the loss in ligand field stabilisation due to the reduced efficiency of overlap between the donor atom and the metal ion bonding orbitals for the "stepped" distortion is greater than the loss in going from a square planar configuration to a distorted tetrahedral one.

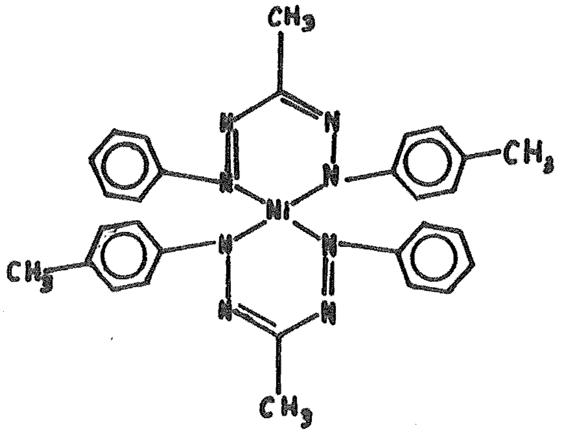
The series of complexes formed with various substituted salicylaldimines and related ligands with nickel(II) copper(II) and palladium(II) provides an extremely good example of how these factors interact. A large number of crystal structure determinations have now been made on complexes of this type. The type of distortion which will occur depends on the nature of the metal ion and on the bulk of the substituents on the ligand. The stereochemical behaviour of nickel(II) is similar to that of copper(II) although regular tetrahedral coordination is known for nickel, but not for copper. A regular tetrahedral configuration has been established for $NiCl_4^{2-}$ [44] and there is good evidence on the basis of ligand field spectra, infrared spectra, and magnetic susceptibility measurements that the dipyrromethene complexes of nickel(II) are regular tetrahedral[12,14]. A stepped square planar configuration is found for bis-(N-phenylsalicylaldimino)-copper(II)[45] which is isomorphous with the nickel complex. On the other hand the isomorphous complexes of N-t-butylsalicylaldimine[46] and of N-isopropylsalicylaldimine[47] with copper and nickel both have distorted tetrahedral stereochemistry.

In the case of palladium(II) tetrahedral complexes have not been isolated, although the preparation in solution of a paramagnetic palladium complex, which may have tetrahedral stereochemistry, has recently been reported[47a]. The stability of the square planar configuration for palladium(II) complexes is large because of the readiness of the d^8 configuration to adopt a low spin conformation. Because of this regular octahedral coordination is rare for palladium(II).

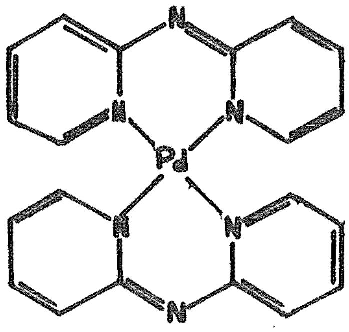
LIGAND DISTORTION OF BIS-(DIPYRROMETHENATO)PALLADIUM(II) AND RELATED COMPOUNDS

It was long thought that some type of distorted tetrahedral configuration would be the most likely stereochemistry for $Pd(MMPM)_2$[5,8]. The aromaticity of the ligands, which would be expected to result from bidentate

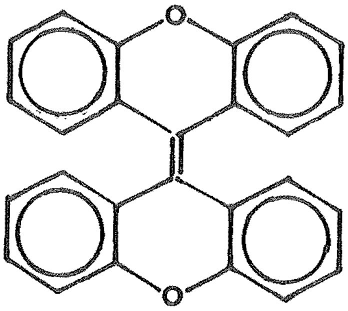
FIGURE 3.42



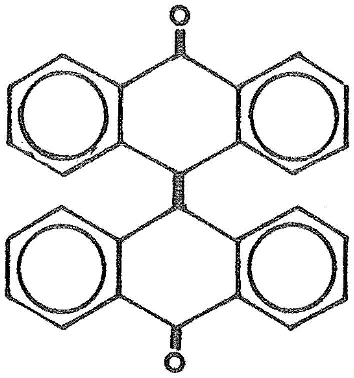
A. bis-(3-methyl-1-phenyl-5-p-tolylformazyl)nickel(II) [48]



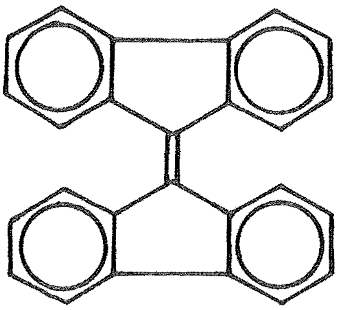
B. bis-(2,2'-dipyridyliminato)palladium(II) [20]



C. 9,9'-bixanthenylene [49]



D. dianthronylidene [50]



E. 9,9'-bifluorenylidene [50a]

coordination to a metal, seemed to require a rigidly planar ligand conformation for maximum stabilisation from π-delocalisation.

Simple molecular framework models indicate that in order to accommodate two ligands in a square planar configuration, with the ligand rigidly planar, the central metal would need to be at least 1.5Å from the plane of the chelate ring. No structures have been determined where a distortion of this magnitude has been observed.

A number of examples are now known where compounds involving extensive π-delocalisation are distorted away from planarity by folding in order to reduce the amount of out of plane bonding at the donor atom. Figure 3.42 illustrates five compounds which distort in a closely analogous fashion to that observed for $Pd(MMPM)_2$.

The structure of $Pd(MMPM)_2$ is very similar to those of A,B,C,D, and E, in that the molecule folds at several positions, rather than at one point only. Usually this folding occurs at the atom bridging the two halves of the molecule resulting in a boat shaped "chelate" ring. The effect is to move the bridging atom out of the plane of the ring by up to 0.2Å. The structure of D has not been determined with sufficient accuracy to provide unambiguous evidence as to whether this occurs in this case as well.

Folding does not occur at the methine bridge in the case of Pd(MMPM)$_2$ where, as in the case of E, all the distortion is accounted for at the ring carbon atoms (in Figure 3.31 these atoms are C(5) and C(7)). Where bending has been established at the bridging group, the "chelate" ring contains heteroatoms which, being more electronegative than carbon, are able to localise electron pairs more readily than the methine group in the case of Pd(MMPM)$_2$.

The effect of the distribution of distortion away from planarity over the whole molecule, in all of these structures, is to divide the π-delocalisation into several regions which will overlap with each other to some degree. In this way loss of π-delocalisation energy at any one point on the molecule will be minimised.

It has been shown that the palladium structure determined here is not unique and it is readily comparable to a number of similar structures. It would seem that aromaticity is not a good criterion for assuming that a molecule will not be readily distorted from planarity since some bending of the molecule, provided it is spread over a number of atoms, seems quite possible without much loss of delocalisation energy. It is difficult to envisage a situation where palladium is likely to be forced to adopt a tetrahedral type of configuration, rather than impose a distortion on the coordinating ligand.

CHAPTER 4

Mixed Ligand Complexes of Palladium

SECTION 4.1

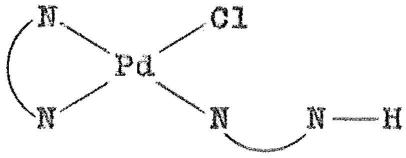
Preparations and Reactions of the Complexes

INTRODUCTION

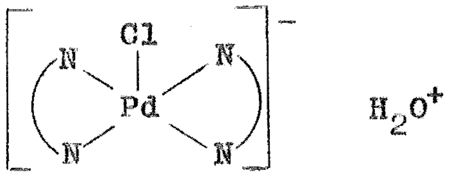
The preparation of the neutral bis-complexes of palladium(II) with 4,4'-dicarboxyethyl-3,3',5,5'-tetramethyldipyrromethene (MMPMH) and 3,4'-dicarboxyethyl-5-chloro-3',4,5'-trimethyldipyrromethene (MClPMH), i.e. $Pd(MMPM)_2$ and $Pd(MClPM)_2$, has been discussed in Chapter 2. In these preparations palladium nitrate was used as a starting material in order to avoid the possibility of the formation of complexes involving strongly coordinating ligands, such as the halogens.

Complexes containing coordinated dipyrromethenes and chloride ions were reported by Porter[5], who used potassium tetrachloropalladite(II) as a source of palladium ions for his preparations. He obtained two complexes of MMPMH in which chloride ions appeared to be acting as ligands. He characterised the compounds by elemental analysis. One of these was postulated as a chloro-bridged complex $Pd_2Cl_2(MMPM)_2$, and the other was thought to be a complex involving the dipyrromethene coordinated as both a monodentate, and a bidentate ligand.

On the basis of Porter's analytical data alone, the second complex could be formulated in a number of different ways. Two of these have been discussed in Chapter 1 (page 8), where it was pointed out that of these two formulations the 4-coordinate square planar stereochemistry seemed the most likely:



However, the complex could also be formulated as a 5-coordinate complex with two bidentate dipyrromethene ligands, such as the one shown below.



In this work an attempt has been made to repeat the preparations of the complexes reported by Porter, and to characterise them more fully using modern physical methods.

Surprisingly it has not been possible to obtain analytically pure samples of the complexes reported by Porter, however evidence from NMR spectra suggests that the compounds have been made, and that any impurities are

TABLE 4.11 MIXED LIGAND COMPLEXES OF PALLADIUM(II) PREPARED IN THIS WORK

$Pd_2Cl_2(MMPM)_2$

* $Pd_2Cl_2(MClPM)_2$

PdCl(MMPM)(MMPMH)

* PdBr(MMPM)(MMPMH)

* PdCl(MClPM)(MClPMH)

* PdBr(MClPM)(MClPMH)

* $[MMPMH^+, K^+][PdBr_4^{2-}]$

---

* Preparation reported for the first time

not organic in nature. The analogous complexes with MClPMH have been prepared analytically pure and have been fully characterised. In addition the bromine analogues of the second type of complex reported by Porter have been prepared and characterised with both dipyrromethene ligands. On the basis of the work presented here it is shown that Porter's formulation of the second type of complex as a 4-coordinate species is correct, and that his complex is in fact PdCl(MMPM)(MMPMH). In addition to the complexes outlined above a complex salt has been prepared, in which a dipyrromethene molecule appears to be acting as a cation. Table 4.11 lists the complexes that have been prepared in this work.

As outlined in Chapter 2, proton NMR spectra were routinely obtained for all products of reaction mixtures and proved extremely useful for the characterisation of all the complexes formed. The NMR spectra are described and discussed in Section 4.3. Ultraviolet-visible spectra were also obtained for all complexes and the results are discussed in Section 4.2.

Infrared spectra were obtained routinely for all preparations of the complexes but as for the neutral bis-dipyrromethene complexes (Chapter 2), the spectra were generally of little use for characterisation of the complexes.

However the absence of absorptions characteristic of water indicated that the complexes were anhydrous. Attempts were made to obtain low frequency infrared spectra (500 cm^{-1} - 40 cm^{-1}) in order to observe the metal-ligand stretching frequencies. It was found that bands in this region were very weak, and because of this were often not reproducible. For this reason it was decided not to continue the investigation.

REACTIONS OF DIPYRROMETHENES WITH TETRAHALOPALLADITE(II) ANIONS

A series of complexes K_2PdX_4 where X = Cl^-, Br^-, I^-, SCN^- and CN^-, in aqueous solution were mixed with ethanolic solutions of MMPMH and MClPMH. Reaction occurred with the tetrachloro- and tetrabromopalladite ions only. Reaction of potassium tetrachloropalladite(II), K_2PdCl_4, with MMPMH and MClPMH gave three products of general formulae PdL_2, $Pd_2Cl_2L_2$ and PdCl(L)(LH). All three products could be identified in admixture by their proton NMR spectra (Section 4.3).

Reactions of the ligands with potassium tetrabromopalladite(II), K_2PdBr_4, gave only two identifiable products PdL_2 and PdBr(L)(LH). No evidence was found for the formation of a bromo-bridged complex.

Refinment of the preparative methods enabled each of the products to be isolated independently. The presence of other compounds in admixture, or organic impurities could be readily detected from the NMR spectra of the reaction products.

The PdX(L)(LH) Complexes, X = Cl,Br, L = MMPM, MClPM

The complex of MMPMH reported by Porter[5] as having one monodentate, and one bidentate dipyrromethene has been shown to be PdCl(MMPM)(MMPMH), mainly on the basis of comparisons of the NMR spectra of the four complexes with MMPMH and MClPMH as ligands. (Section 4.3). The alternative, 5-coordinate, formulation H_3O^+ $PdCl(MMPM)_2^-$, which would have two bidentate dipyrromethene ligands is eliminated on the basis of the following considerations:

(1) Infrared spectra of these complexes show a band at 3200 cm^{-1}. Ferguson and West[19] reported the presence of a band in this region for the complexes $MX_2(LH)_2$, (page 9) and assigned it to the N-H stretching mode. Although the agreement with the observations of Ferguson and West is good, the possibility of this band being due to the H_3O^+ cation cannot be ignored.

(2) The conductivities of these complexes in nitromethane are low, indicating that they are non-electrolytes.

(3) The complex nature of the NMR spectra for these complexes, in contrast to the very simple spectra found for the neutral bis-dipyrromethene complexes, and for the

bridged complexes indicates that there are four pyrrole rings present in different chemical environments (Section 4.3, page 103). This would not be the case if the complex was 5-coordinate containing both dipyrromethenes acting as bidentates.

(4) The ultraviolet-visible spectra are in agreement with the presence of two dipyrromethenes coordinated in different ways for these complexes (Section 4.2).

The complexes were readily obtained on the addition of an ethanolic solution of dipyrromethene ligand to a large excess of K_2PdCl_4 or K_2PdBr_4 in aqueous solution.

The bromo- complexes could also be readily prepared from their chloro- analogues if the latter were dissolved in chloroform and shaken with a concentrated aqueous solution of potassium bromide for several hours

$$PdCl(L)(LH) \ + \ Br^- \longrightarrow PdBr(L)(LH) \ + Cl^-.$$

The reverse reaction did not occur.

When the chloro- or bromo- complexes were shaken with aqueous solutions of hydrobromic or hydrochloric acid respectively, complex salts were obtained. These are thought to be of the type $[LH_2^+]_2[PdX_4]$ where X = Cl^-, Br^-. The compounds PdL_2 and decomposition products of the ligands were also obtained. Hence it was not possible to prepare pure samples of the salts by this method. The complex salts and their properties are more fully described on page 88.

Attempts were made, unsuccessfully, to replace the chloride and bromide ligands by iodide, thiocyanate and cyanide by shaking chloroform solutions of the chloro- and bromo- complexes with concentrated aqueous solutions of the potassium salts of these anions. The products included unchanged starting materials, free dipyrromethene ligand, decomposition products of the ligands and (presumably) salts of PdX_4^{2-} anions.

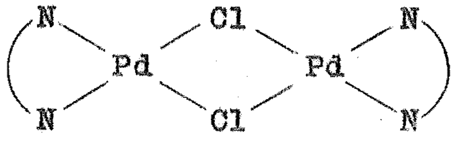
The stabilities of the complexes with respect to reaction with potassium salts of halogen and halogen-like anions varied according to the order

$$Cl < Br < (I, SCN, CN)$$

which is the order expected from studies of the trans effect[60]. It was found that the MMPMH complexes were more liable to decompose in solution than the MClPMH complexes.

The Bridged Complexes, $Pd_2Cl_2L_2$, $L = MMPM^-$, $MClPM^-$

Porter[5] reported the complex $Pd_2Cl_2(MMPM)_2$, which he postulated contained bridging chloride groups



In this work the complex $Pd_2Cl_2(MClPM)_2$ has been prepared and fully characterised. The MMPM complex reported by Porter has been prepared and characterised by NMR, however elemental analyses are in poor agreement with the calculated values. No evidence has been obtained for the formation of a dimeric bromine-bridged complex. Evidence obtained from NMR spectra of the MClPM complex suggests that <u>cis</u>- <u>trans</u> isomerisation occurs in this complex (See Figure 4.32). The evidence is described in detail in Section 4.3.

Porter[5] observed that the complex $PdCl_2(MMPM)_2$ reacted with excess ligand in hot ethanol to give $Pd(MMPM)_2$. In view of the ready conversion of PdCl(L)(LH) to PdL_2 in hot ethanol (page 9) the following reaction sequence seems reasonable.

$$Pd_2Cl_2L_2 \xrightarrow[LH]{} 2PdClL(LH) \longrightarrow 2PdL_2$$

However the intermediate compound could not be isolated from this system.

Attempts were made to prepare complexes of the type PdCl(L)(py) and $PdCl(L)(py)_2$ by heating pyridine solutions of $Pd_2Cl_2L_2$. Examination of solutions of residues from the reaction mixtures gave no evidence for the formation of a pyridine adduct. The chloroform soluble residues appeared to contain mainly ligand decomposition products.

<u>The Ionic Complexes</u>

A complex salt, thought to be $\left[MMPMH_2{}^{+}, K^{+}\right]\left[PdBr_4{}^{2-}\right]$

has been prepared as described on page 93. It has a conductivity in dimethylformamide corresponding to a 1:1 electrolyte, but is insoluble in chloroform. It is thought that the dipyrromethenilium cation ($MMPMH_2^+$) forms an ion pair with the $PdBr_4^{2-}$ ion and this may explain the low conductivity found. The ultraviolet-visible spectrum of the salt in dimethylformamide is similar to that observed for $MMPMH_2Cl$ in the same solvent.

Some reactions described for the PdX(L)(LH) complexes on page 85 gave chloroform soluble products which had similar NMR spectra to the protonated ligands. It is thought that these salts are very similar to the complex salt $\left[MMPMH_2^+, K^+\right]\left[PdBr_4^{2-}\right]$, the difference in solubilities being due to the relative ability of the salts to associate in solution. Unfortunately the second type of complex salt, which is thought to be $\left[LH_2^+\right]_2\left[PdX_4^{2-}\right]$ could not be prepared chemically pure.

EXPERIMENTAL

As in Chapter 2 the following abbreviations are used for the dipyrromethene ligands in order to avoid tedious repetition:

MMPMH	5,5'-dimethyldipyrromethene
MClPMH	5-chloro-5'-methyldipyrromethene

(i) Potassium palladite(II) Salts, K_2PdX_4; $X = Cl^-, Br^-, SCN^-, CN^-, I^-$.

A small excess of the potassium salt (KX) in minimum water was added to a concentrated aqueous solution of palladium nitrate (prepared as on page 26). The tetrachloro- and tetrabromo palladites were obtained as crystalline solids, and were used in reactions without further investigation. The tetraiodo-, tetrathiocyanato- and tetracyanopalladites were not isolated from solution. Any precipitate which formed on the addition of the potassium salt (KX) was redissolved and the solutions of the K_2PdX_4 salts were mixed with ethanolic solutions of the ligands without further investigation.

A red microcrystalline solid thought, on the basis of its infrared spectrum, to be $[H_3O^+, K^+][PdBr_4^{2-}]$ or $[H_3O^+]_2[PdBr_4^{2-}]$ was precipitated from an aqueous solution of palladium nitrate in the presence of hydrobromic acid when potassium bromide was added. On reaction with an ethanolic solution of the ligand this salt gave different products to those found with K_2PdBr_4 (see page 87).

(ii) Chloro-(5,5'-dimethyldipyrromethenato)-(5,5'-dimethyldipyrromethene)palladium(II), PdCl(MMPM)(MMPMH)[5].

The ligand (0.2gm) was dissolved in minimum ethanol with a little sodium acetate and was slowly added with stirring to a concentrated aqueous solution of potassium tetrachloropalladite (0.5gm). After several hours a microcrystalline precipitate separated. The solution was filtered and the residue was washed thoroughly with water, and dried in vacuo.

Attempts at recrystallisation from acetone and chloroform resulted in decomposition of the complex.
Analysis: Calculated for $C_{38}H_{47}ClN_4O_8Pd$: C, 55.0; H, 5.6; N, 6.8%. Found: C, 36.4; H, 4.0; N, 4.4%.

(iii) Bromo-(5,5'-dimethyldipyrromethenato)-(5,5'-dimethyldipyrromethene)palladium(II), PdBr(MMPM)(MMPMH).

The method of preparation was the same as outlined in (ii) above, using potassium tetrabromopalladite as a starting material, except that the complex could be recrystallised successfully from chloroform and then acetone.
Analysis: Calculated for $C_{38}H_{47}BrN_4O_8Pd$: C, 52.2; H, 5.3; N, 6.4%. Found: C, 51.7; H, 5.4; N, 6.3%.
Conductivity (nitromethane), Λ_m (20°C) = 0.008 ohms^{-1} moles^{-1} cm^2.

(iv) Chloro-(5-chloro-5'-methyldipyrromethenato)-(5-chloro-5'-dipyrromethene)palladium(II), PdCl(MClPM)(MClPMH).

The ligand, MClPMH, (0.2gm) was dissolved in minimum ethanol and was slowly added to a concentrated solution of potassium tetrachloropalladite (0.5gm) in water with vigorous stirring. As with the MMPM compound a precipitate slowly formed over a period of several hours, which was filtered and dried in vacuo. The complex was recrystallised from chloroform and then acetone.

Analysis: Calculated for $C_{36}H_{41}Cl_3N_4O_8Pd$: C, 49.7; H, 4.4; N, 6.4%. Found: C, 50.5; H, 4.9; N, 6.3%.

Conductivity: (nitromethane), Λ_m (20°C) = 0.1 ohms^{-1} moles^{-1} cm^2.

Crystallographic Preliminary Study: The crystal symmetry is monoclinic with systematic absences hkl for h+k = 2n and hol for l = 2n, indicating space group Cc (non-centrosymmetric) or C2/c (centrosymmetric). The centrosymmetric space group would impose crystallographic mirror symmetry on the molecule. Approximate cell constants are a = 17.50, b = 20.88, c = 10.19Å, β = 95.62° at 20°C (room temperature), giving a cell volume of 3751 Å^3. The calculated density for four molecules to the unit cell is 1.54 g/cm^3. The experimental density (floatation in bromobenzene/carbon tetrachloride solution) is 1.52g/cm^3.

Molecular Weight: Calculated, 870. Found (crystallographic method), 859± 10.

(v) Bromo-(5'-chloro-5'-methyldipyrromethenato)-(5-chloro-5'-methyldipyrromethene)palladium(II), PdBr(MClPM)(MClPMH).

The complex was prepared using potassium tetrabromo palladite as outlined in (iv) above.

Analysis: Calculated for $C_{36}H_{41}BrCl_2N_4O_8Pd$: C, 47.2; H, 4.2; N, 6.1%. Found: C, 47.3; H, 4.6; N, 6.3%.
Conductivity: (nitromethane), Λ_m (20°C) = 0.008 ohms^{-1} moles^{-1}cm^2.

(vi) Di-μ-chlorobis-(5,5'-dimethyldipyrromethenato)-dipalladium(II), $Pd_2Cl_2(MMPM)_2$.

The filtrate from (ii) above was evaporated under a stream of compressed air until a microcrystalline precipitate formed. The solution was filtered and the residue was thoroughly washed with water.

Recrystallisation from chloroform or acetone decomposed the complex.

Analysis: Calculated for $C_{38}H_{46}Cl_2N_4O_8Pd_2$: C, 52.8; H, 5.3%. Found: C, 40.1; H, 4.5%.

(vii) di-μ-chlorobis-(5-chloro-5'-methyldipyrromethenato) dipalladium(II), $Pd_2Cl_2(MClPM)_2$.

The filtrate obtained from (iv) above was evaporated under stream of compressed air until a microcrystalline precipitate formed. The solution was filtered, and the residue was dried in vacuo. It was recrystallised from chloroform and then acetone.

Analysis: Calculated for $C_{36}H_{40}Cl_4N_4O_8Pd_2$: C, 42.7; H, 4.0; N, 5.5%. Found: C, 44.7; H, 4.4; N, 5.5%.

(viii) Potassium, (5,5'-dimethyldipyrromethenilium) tetrabromopalladite(II), $\left[(\mathrm{MMPMH_2}^{+}),\mathrm{K}^{+}\right]\left[\mathrm{PdBr_4}^{2-}\right]$

The red salt prepared as outlined in (i) above was reacted with a solution of MMPMH in ethanol. A red finely divided precipitate separated out of the solution. The product was filtered and dried in vacuo. It was insoluble in chloroform but dissolved readily in dimethylformamide.

Analysis: Found: C, 31.6; H, 4.5; N, 4.1%. Calculated for $C_{19}H_{24}Br_2KN_2O_4Pd$, $((\mathrm{MMPMH_2},\mathrm{K})\mathrm{PdBr_4})$, C, 28.2; H, 3.0; N, 3.5%. Calculated for $C_{38}H_{48}Br_4N_4O_8Pd$, $((\mathrm{MMPMH_2})_2\mathrm{PdBr_4})$, C, 41.3; H, 4.5; N, 5.1%. Conductivity (dimethylformamide): Λ_m (20°C) = 61.7 ohms^{-1} moles^{-1} cm^2.

SECTION 4.2

Ultraviolet-Visible Spectra

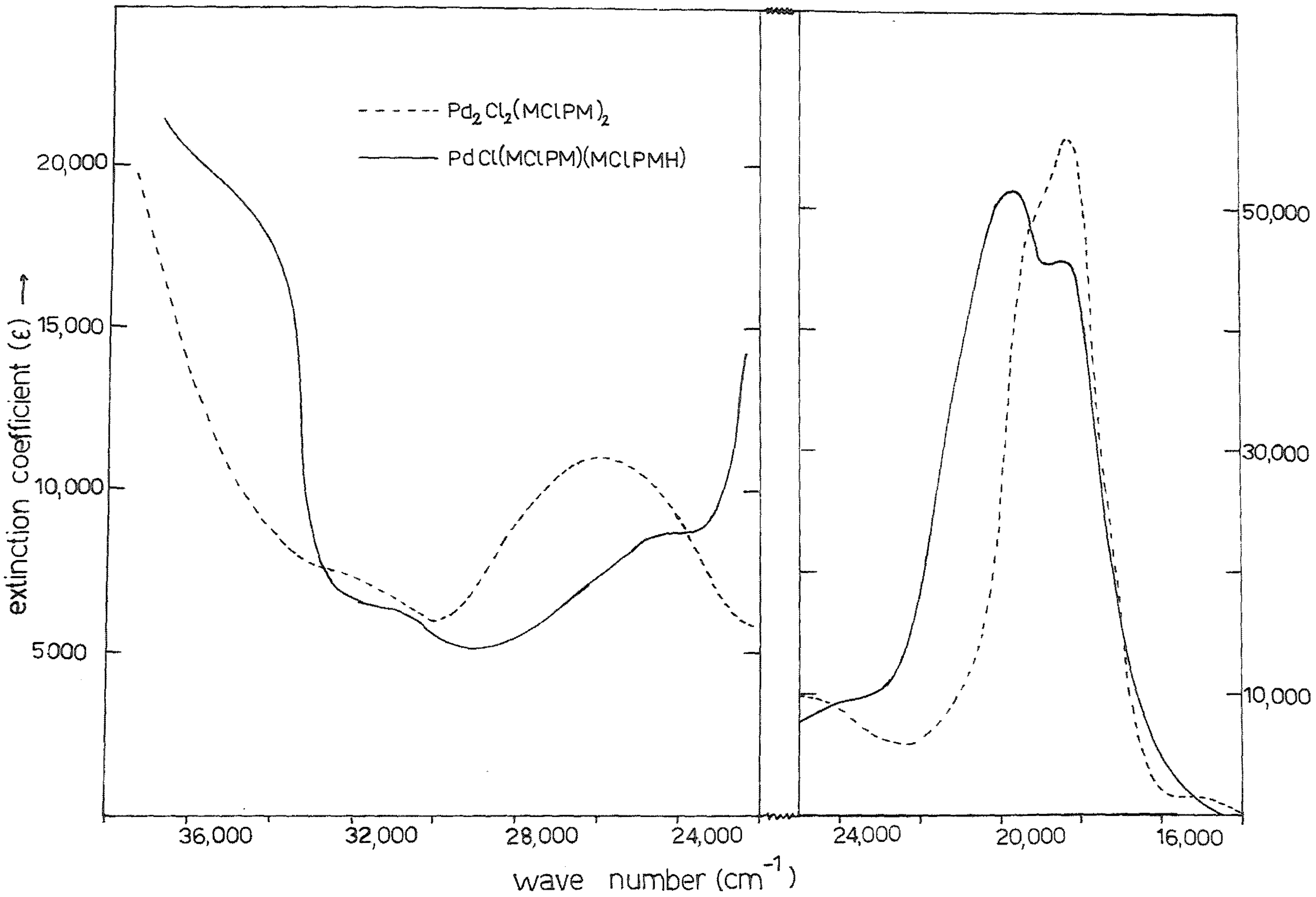
INTRODUCTION

The ultraviolet-visible spectra of the ligands, the protonated ligands, and the neutral bis-complexes of the dipyrromethene ligands, have been reported and discussed in Section 2.3. The spectra of the present complexes, as with those in Section 2.3, can be divided into three regions corresponding to: (1) a low energy intraligand $\pi \rightarrow \pi^*$ transition, (2) a metal ⟶ ligand charge transfer transition and (3) high energy intraligand $\pi \rightarrow \pi^*$ transitions. No ligand field bands have been observed in solution, or in the solid state, for these complexes, presumably because the least energetic ligand field band is masked by the low energy $\pi \rightarrow \pi^*$ transition.

The reasons for the assignments for the bands have been discussed in Section 2.3. The spectra obtained for the palladium mixed ligand complexes are very similar in many respects to those of the ML_2 complexes however interesting differences are found.

All spectra discussed here have been measured in chloroform solution and the data for them are listed in Table 4.21. The spectra of $Pd_2Cl_2(MClPM)_2$ and PdCl(MClPM)MClPMH) are typical of those found and are shown in Figure 4.21.

FIGURE 4.21



$Pd_2Cl_2(MClPM)_2$
PdCl(MClPM)(MClPMH)
20,000
15,000
10,000
5000
50,000
30,000
10,000
extinction coefficient (ε) →
36,000
32,000
28,000
24,000
24,000
20,000
16,000
wave number (cm^{-1})

The Bridged Complex, $Pd_2Cl_2(MClPM)_2$

(i) Low energy $\pi \rightarrow \pi^*$ intraligand transition

As with most of the monomeric bis complexes (ML_2), the low energy $\pi \rightarrow \pi^*$ transition for the bridged complex has one dominant band with a shoulder to higher energy. The intensity of the main band is comparable with that of the neutral ligand, unlike the intensities found for the band for the ML_2 complexes which are usually much greater (Table 2.3).

The band is found at lower energy for the bridged complex than for $Pd(MClPM)_2$. This may reflect a greater degree of metal - ligand π-bonding for the bridged complex, which is not subject to the same steric strain as is the $Pd(MClPM)_2$ compound and is therefore expected to be planar. (cf. Section 3.4).

(ii) Metal → Ligand Charge Transfer Band

This is observed for the bridged complex in a similar position to that found for $Pd(MClPM)_2$ and is of approximately the same intensity.

(iii) High energy $\pi \rightarrow \pi^*$ Transitions

As with the ML_2 complexes bands in the high energy region of the spectrum are poorly resolved and little useful information can be obtained from them.

The PdX(L)(LH) Complexes:

(i) Low Energy $\pi \rightarrow \pi^*$ Transitions

The spectra of the complexes which have both monodentate and bidentate dipyrromethene ligands show two bands in the region of the low energy $\pi \rightarrow \pi^*$ transition. The band at lowest energy is usually poorly resolved and is observed as a prominent shoulder on the side of the main band. The composite spectrum found is no doubt due to the presence of the two dipyrromethenes which have two different modes of coordination.

The band at higher energy may be due to the monodentate ligand, and that at lower energy to the bidentate ligand, since the relative positions of the two bonds are similar to those of the protonated ligands and the bridged complexes respectively.

The intensities of the bands are comparable with the intensities of the bands found for the free ligands, as would be expected.

(ii) Charge Transfer Transitions

For each complex a band is observed at about 25,000 cm^{-1} which, by comparison with the spectra of the bridged complexes, and the PdL_2 complexes, can be assigned to metal → ligand charge transfer. Unfortunately the band is not always well resolved, and hence the comparative positions and intensities are not known. For this reason little further information can be obtained.

(iii) High Energy Intraligand $\pi \rightarrow \pi^*$ Transitions:

As with the other complexes studied here, and in Section 2.3, little useful information can be derived from the region of the spectrum above 30,000 cm^{-1}, since the bands are poorly resolved.

SECTION 4.3

Nuclear Magnetic Resonance Spectroscopy

INTRODUCTION

The proton NMR spectra of the ligands MClPMH and MMPMH, the protonated ligands (LH_2^+) and the bis-complexes of zinc, cadmium, mercury and palladium(ML_2), have been discussed in Chapter 2. Resonances of the methyl groups labelled (A), (B) and (C) (Figure 2.41) have been assigned for all these compounds.

The spectra discussed in this section were recorded under similar conditions to those discussed in Section 2.4, i.e. at a concentration of approximately 50 mgs of complex in 0.25mls of deutero chloroform and with a probe temperature of 35°C.

The resonances of the dipyrromethene complexes of palladium containing halo-ligands are listed in Table 4.31, and their positions in relation to those of the ligands and the PdL_2 complexes are shown in Figure 4.31. Table 4.32 lists the different types of methyl groups found for the PdX(L)(LH) complexes together with their predicted and observed chemical shifts.

THE BRIDGED COMPLEXES: $Pd_2Cl_2L_2$

The NMR spectra of these complexes are comparatively simple and resonance assignments can be readily made.

The spectra are similar to those obtained for the monomeric complexes (PdL_2). Since the spectra are uncomplicated, they indicate that the complexes are symmetric, with both pyrrole rings of the ligands equivalently coordinated to the metal ion.

In the spectrum of $Pd_2Cl_2(MMPM)_2$ the peaks were not as well resolved as for the other spectra discussed in this section. It is thought that this was due to the presence of impurities in the sample, and explains the poor agreement of the elemental analyses found for this complex compared with the calculated values. There can be no doubt however that the NMR spectral results are meaningful, and that the compound was in fact prepared, if not purified.

The Ethyl Ester Side Chains:

These groups give rise to two sets of resonances with chemical shifts of approximately 1.3ppm and 4.3ppm. The resonances of these groups have been assigned as outlined in Section 2.4, and are found to be similar in all respects to those of the ML_2 series. For this reason they will not be discussed further.

The Ring-substituted Methyl Groups:

These are designated as methyl groups (A) and (B) for $Pd_2Cl_2(MMPM)_2$ and (A), (B) and (C) for Pd_2Cl_2 $(MClPM)_2$. These labels are the same as those used in Section 2.4. The integral ratios of the resonances, with respect to that of the methine proton which is taken as 1 (see below), are 6:6 for the MMPM$^-$ complex and 3:3:3 for the MClPM$^-$ complex.

Group A: The resonance due to this group is moved downfield on coordination to the $PdCl_2Pd$ group, to about 2.6ppm. The deshielding is small and is to be expected in terms of a decrease in electron density in the region of the nitrogen atom on coordination. In direct contrast the ML_2 complexes studied in Section 2.4 generally show a considerable shielding of the (A) group on coordination, particularly in the case of PdL_2. This effect has been accounted for in terms of interaction of the (A) methyl protons with the shielding cone of an adjacent pyrrole ring (page 57). This interaction will not occur in the case of the bridged complexes.

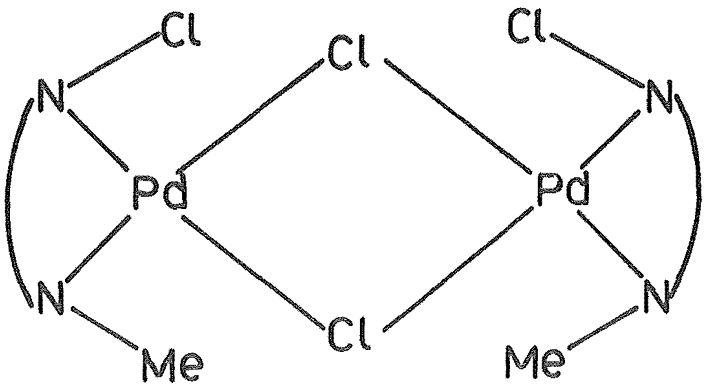
The assignment of the resonance at about 2.6ppm to the (A) group is justified on the following grounds:

(1) As outlined in Section 2.4 for the $M(MClPM)_2$ complexes, the relative chemical shifts of groups (B) and (C) remain virtually constant irrespective of the coordinated metal ion. For this reason the resonances at 2.52ppm and 2.22ppm are assigned to these two groups respectively for $Pd_2Cl_2(MClPM)_2$, leaving the resonance at 2.63ppm to be assigned to group (A).

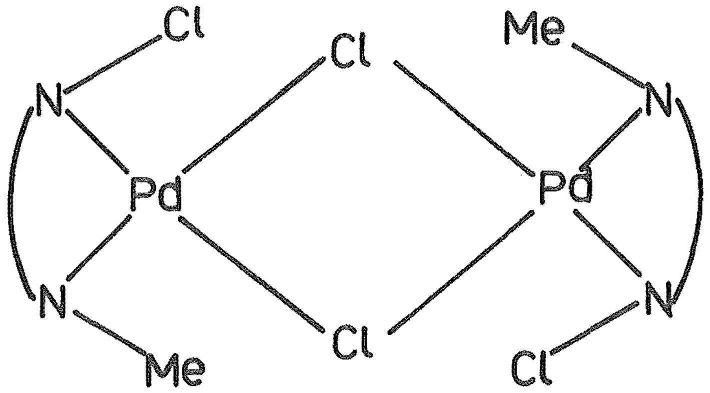
(2) For both $Pd(MClPM)_2$ and $Pd_2Cl_2(MClPM)_2$ where the

FIGURE 4.32

CIS AND TRANS ISOMERS OF $PdCl_2(MClPM)_2$



I *cis*-dichloro-μ-bis-(5-chloro-5'-methyldipyrromethenato)dipalladium(II).

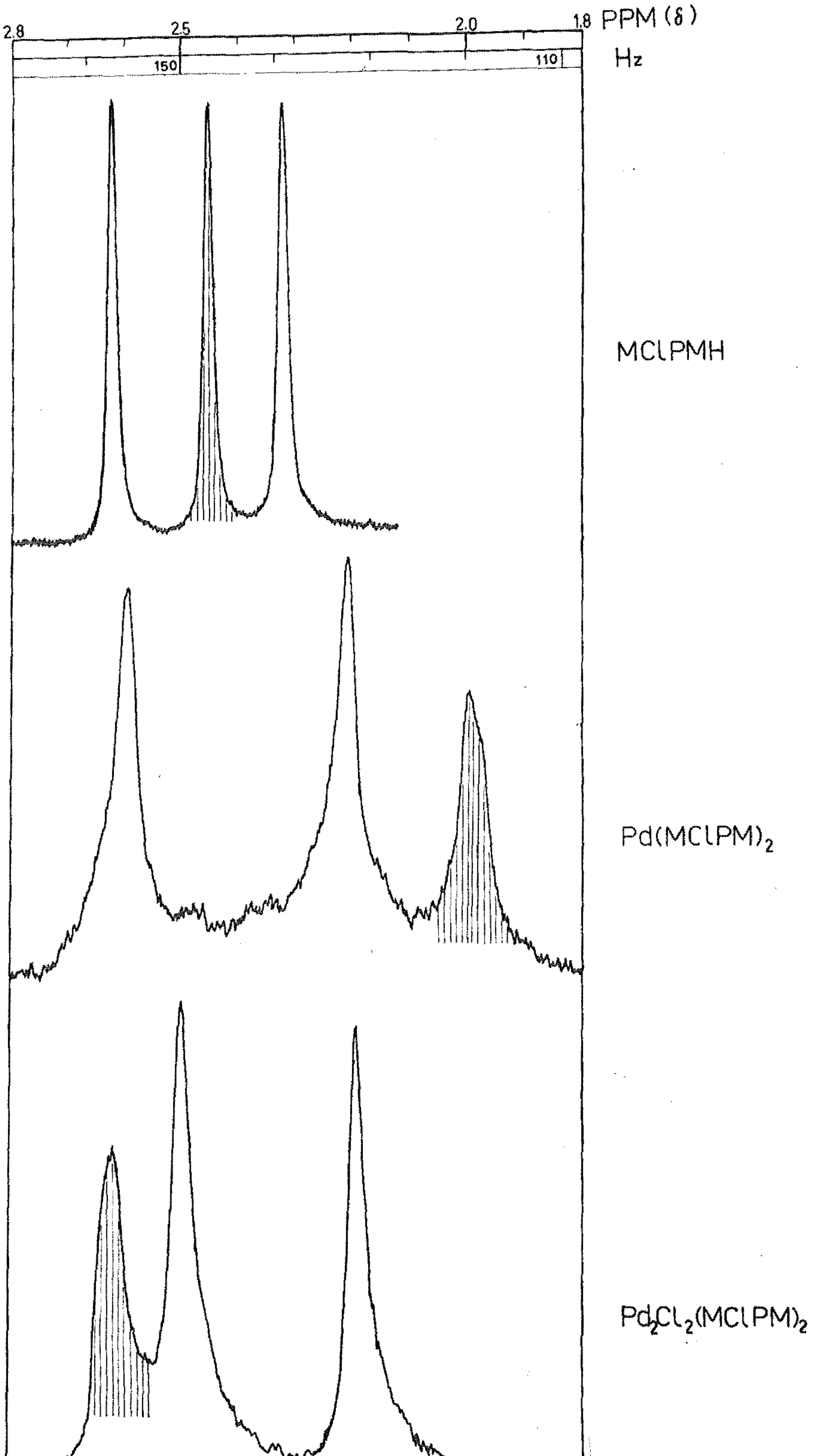


II *trans*-dichloro-μ-bis-(5-chloro-5'-methyldipyrromethenato)dipalladium(II).

FIGURE 4.33

NMR EVIDENCE FOR CIS & TRANS ISOMERS

(methyl(A) resonance shaded)



ligand is unsymmetrically substituted, two isomers are possible with the chlorine atoms of the ligand cis- and trans- with respect to each other (Figure 4.32). Evidence for the existence of cis- and trans- isomers in admixture has been found from studies of the thin layer chromatography of the $Pd(MClPM)_2$ complex (page 27). For each of the two isomers I and II in Figure 4.32 the chemical shifts of (B) and (C) are identical, but that of (A) is slightly different for isomer(I) with respect to that of isomer(II). This difference is found to be very small (less than 0.005ppm) and is only detected as a broadening of the resonance peak, with a consequent loss in height relative to the resonance peaks of (B) and (C), (Figure 4.33). This effect is also apparent in the spectrum of $Pd(MClPM)_2$.

Groups (B) and (C): Group (B) of $Pd_2Cl_2(MMPM)_2$ and groups (B) and (C) of $Pd_2Cl_2(MClPM)_2$ are shielded on coordination. In terms of ring current effects as discussed in Section 2.4, this may reflect a decrease in pyrrole ring current on coordination.

The Methine Proton

The methine proton of both ligands is deshielded considerably on coordination, although not to the same extent as for the corresponding proton in PdL_2 (Figure

4.31). The smaller deshielding in the case of the $Pd_2Cl_2L_2$ complexes is surprising since in these cases the chelate ring should be planar. This would be expected to result in larger ring current effects than in the bent chelate ring of the PdL_2 complexes.

MIXED MONODENTATE AND BIDENTATE DIPYRROMETHENE COMPLEXES

PdX(L)(LH)

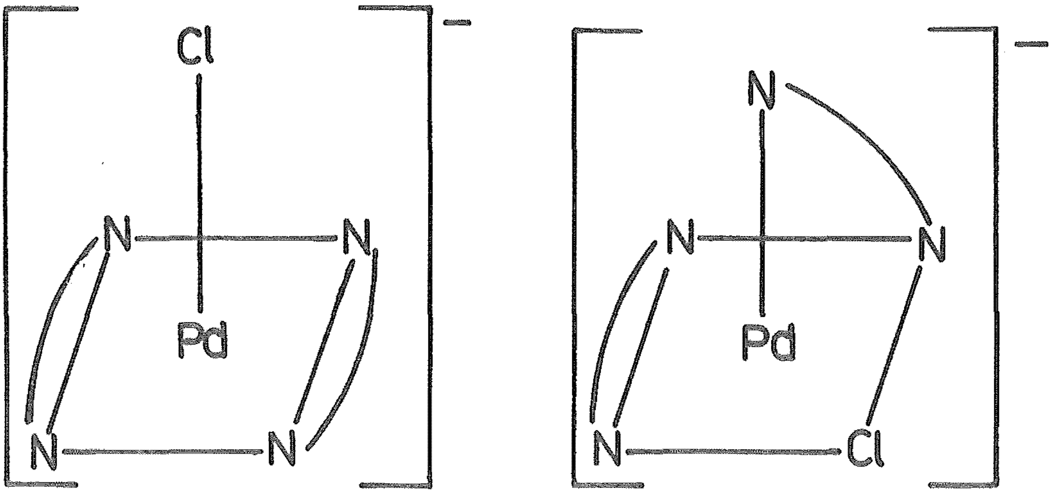
The spectra of the mixed monodentate and bidentate dipyrromethene complexes are much more complicated than those discussed previously in this section, and in Section 2.4. The presence of two methine proton resonances, and the complexity of the resonances due to the ring substituted methyl groups confirms that there are two chemically distinguishable dipyrromethene molecules in the complexes. A detailed study of the spectra indicates that one of the ligands is coordinated as a monodentate.

The Ethyl Ester Side Chains:

The resonances due to the methylene and methyl protons form complicated overlapping patterns indicating that at least three, and possibly all four, of the side chains are in chemically different environments for complexes fo both MClPMH and MMPMH. Because these regions are extremely complicated no useful data can be extracted.

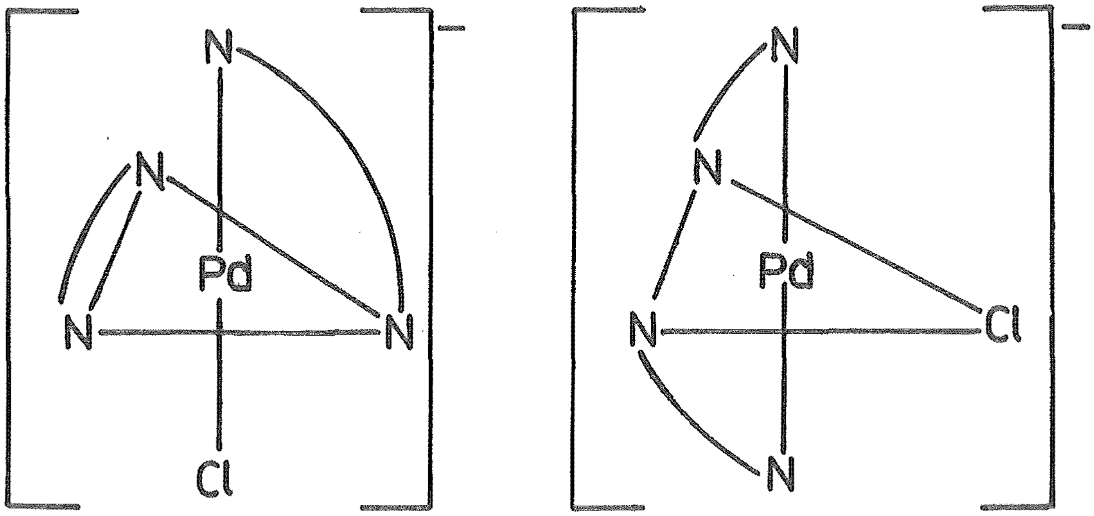
FIGURE 4.34

POSSIBLE FIVE-COORDINATE FORMULATIONS FOR THE PdX(L)(LH) COMPLEXES



4 equivalent pyrrole rings

2 equivalent pyrrole rings



2 equivalent pyrrole rings

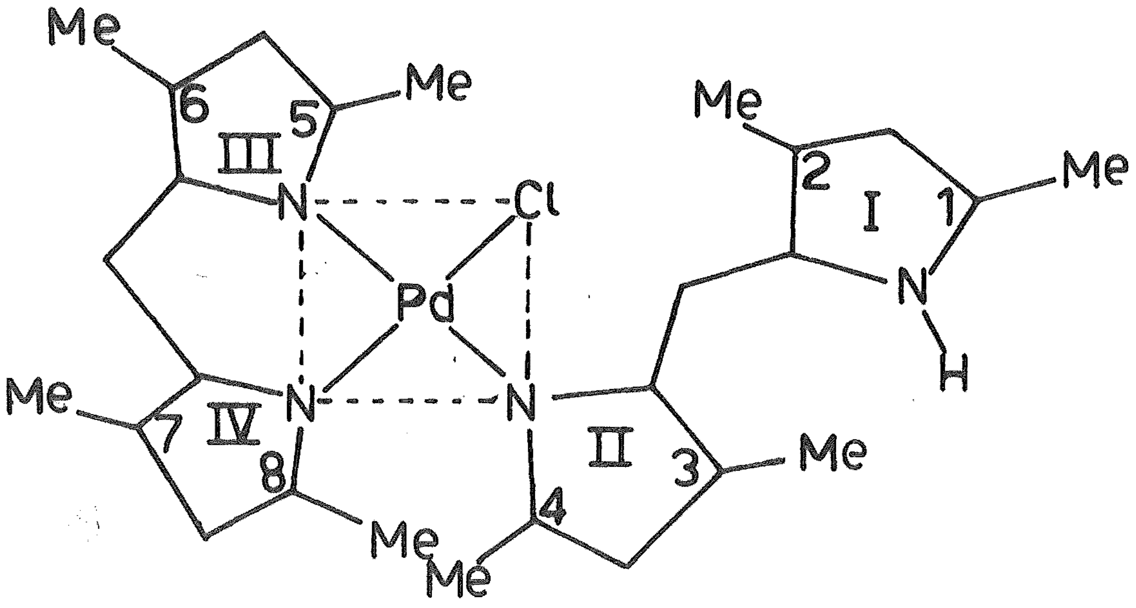
2 x 2 equivalent pyrrole rings

The Ring-substituted Methyl Groups

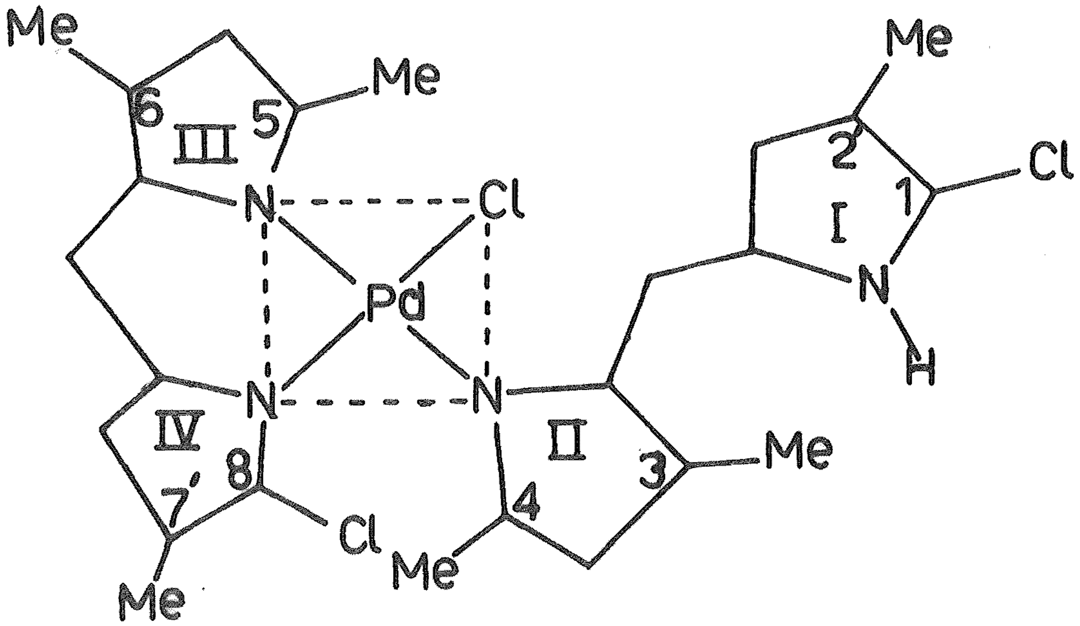
For PdCl(MMPM)(MMPMH) six resonance peaks are observed between 3.6ppm and 1.6ppm with integral ratios of 3:3:6:6:3:3 with respect to each of the methine resonance integrals taken as 1. These resonances correspond to eight methyl groups, four from each ligand, with two of the groups having resonances which overlap with two others, giving rise to two "double" resonance peaks. For the analogous bromo- complex one of the "double" peaks is split, presumably because one of the methyl groups contributing to the resonance is more affected by the halo-ligand than the other. Seven resonances are therefore observed with integral ratios of 3:3:6:3:3:3:3. The PdX(MClPM)(MClPMH) complexes have five resonances, with integral ratios 3:3:6:3:3, and six resonances with integral ratios 3:3:3:3:3:3, for the chloro- and bromo- complexes respectively.

For the bromo- complexes of both dipyrromethene ligands the observed splitting pattern is only possible if there are four pyrrole rings in different chemical environments in each of the complexes. No 5-coordinate formulation will give more than three chemically distinguishable pyrrole rings (Figure 4.34) and hence the NMR data conclusively show that the four coordinate formulation is correct, in agreement with evidence from conductivity

FIGURE 4.35



(a) PdCl(MMPM)(MMPMH)



(b) PdCl(MClPM)(MClPMH)

measurements and ultraviolet-visible and infrared spectra.

It is possible to arrive at a reasonable assignment of the methyl resonances for the complexes PdX(L)(LH) on the basis of the molecular models shown in Figure 4.35(a) and (b). Simple framework molecular models (Prentice-Hall, Inc.) indicate that these conformations are the ones most likely to be found assuming square planar 4-coordination about the metal ion, with one of the dipyrromethenes coordinated as a monodentate.

In the following discussion methyl groups will be referred to by the number assigned to each position on the skeleton as illustrated in Figure 4.35, (a) and (b), since the labels (A), (B) and (C) previously used do not adequately describe the differences between each methyl group. It should be noted, however, that in Figure 4.35(a) methyl groups of type (A) are found at positions 1,4,5 and 8 and those of type (B) are found at positions 2,3,6 and 7; while in Figure 4.35(b), (A) type methyls are found at positions 4 and 5, (B) type methyls at positions 3 and 6, and (C) type methyls at positions 2' and 7'.

Only one isomer is possible for the complexes of the symmetrically substituted MMPMH ligand (Figure 4.35(a)). However, four isomers are theoretically possible for the complexes of MClPMH since this ligand is not symmetrically substituted. The positions of the ligand chlorine atoms in Figure 4.35(b) are based on what would be expected chemically if it is postulated that only one of the four isomers possible is in fact found. This restriction is reasonable since:

(1) The pyrrole ring which is not coordinated to the metal for the monodentate ligand (ring I) is similar to the pyrrole rings of the protonated ligand (LH_2^+) and will carry some positive charge. The presence of a chlorine atom will assist in the dispersal of the charge.

(2) Framework models indicate that there will be considerable interaction between a substituent at position 5 and ring II. Since ring II is coordinated to the metal ion it would be expected to carry some positive charge, although this will probably be less than that carried by ring I. If a chlorine atom is substituted at position 8 there will be an attractive dipole-dipole interaction between the chlorine atom and ring II. For this reason the substituent at position 8 is more likely to be a chlorine atom than a methyl group.

Table 4.32 summarises the direction of shifts of the resonances expected for the various methyl groups on the basis of the model proposed (Figure 4.35). The chemical shifts actually found for the PdCl(L)(LH) complexes are listed, along with the changes in chemical shift observed

Table 4.32a MMPM Complexes

Position on Skeleton	Type	Expected shift in resonances shift with respect to neutral ligand	Reason	Expected effect of changing halogen ligand	Observed chemical shift (ppm)		
					wrt TMS	wrt MMPMH	On subst of Br for Cl
1	A	Strongly deshielded	partial +ve charge on ring I; proximity to N atom	negligible	3.55	1.10	0.00
2	B	Deshielded, but not to the same extent as 1	partial +ve charge on ring I, distant from N atom	negligible	2.88	0.30	0.00
3	B	Fairly small, direction not predictable	dipole intramolecular interactions	small	2.30	-0.28	-0.03
4	A	Fairly small, probably shielded	may be affected by shielding cone of ring IV	small, in the same direction as 3.	2.35	-0.10	-0.03
5	A	Should be deshielded, however environment is similar to that of 4	deshielding predicted in comparison with bridged complexes	comparatively large	2.35	-0.10	0.07
6 + 7	B	Shielded slightly	should behave similarly to (B) groups of the bridged complex	negligible	2.48	-0.10	0.00
8	A	Strong shielded	Interaction with shielding cone of ring II	negligible	1.67	-0.78	0.00

Table 4.32b MClPM Complexes

Position on Skeleton	Type	Expected resonance shift w.r.t the neutral ligand.	Reason	Expected effect of changing the halogen ligand.	wrt TMS	wrt MClPMH	On subst. of Br for Cl	wrt MMPM Comple
2'	C	Deshielded	+ve charge on ring I	negligible	2.92	0.59	0.00	-
3	B	as for MMPMH Complexes		small	2.27	-0.35	0.00	-0.03
4	A	"		small	2.38	-0.08	0.00	0.03
5	A	"		comparatively large	2.38	-0.08	0.07	0.03
6	B	"		negligible	2.52	-0.10	0.01	+0.04
7'	C	Shielded slightly similarly to 7 for MMPMH complexes		negligible	2.08	-0.25	0.00	-

when the chloro- ligand is replaced by a bromo- ligand.

A comparison of the spectra of the PdXL(LH) complexes in Figure 4.31 reveals two resonances found for the MMPM complexes only, at 3.55ppm and 1.67ppm. These would be expected to be due to methyl groups which are substituted in positions occupied by chlorine atom substituents in the MClPM complexes, i.e. the methyl groups at positions 1 and 8 in Figure 4.35(a). The strongly deshielded group with a resonance at 3.55ppm is likely to be methyl(1), since ring I is expected to carry a partial positive charge compared with ring II of the same ligand, and with rings III and IV of the bidentate ligand. This methyl group is also close to the nitrogen atom of ring I, which may result in further deshielding.

The strongly shielded group with a resonance at 1.67 ppm is likely to be methyl(8) since framework models indicate that the protons of this group will be approximately 2.5 - 3.0 Å above the center of ring II and, as a result, will be well within the shielding cone of this ring. (cf. Figure 2.43). In view of this, the observed shielding of the group by about 1ppm would appear to be quite reasonable by comparison with the chemical shifts found for the (A) methyls of the PdL_2 complexes (page 57).

The spectra of the MClPMH complexes have one resonance at 2.08ppm which is not present in the spectra of the MMPMH complexes. It is to be expected that this resonance would be due to a (C) methyl group since such a group would not be found for the MMPMH complexes. The resonance at this position has been assigned to methyl (7').

The remainder of the resonance peaks are in very similar positions for all the complexes and must be assigned to methyl groups which should be found in the same, or in very similar, chemical environments for complexes of both the dipyrromethene ligands. The resonance at about 2.9ppm is assigned to methyl (2) for the MMPMH complexes and to methyl (2') for the MClPMH complexes, since these groups are substituted on ring I which, as has already been pointed out, must carry some positive charge, and will consequently produce a shielding effect on the methyl groups substituted to it.

The "double" resonance at 2.48ppm for the MMPMH complexes is assigned to methyls (6) and (7), and the resonance at 2.42ppm is assigned to group (6) for the MClPMH complexes since these groups are all (B) methyls and will be in virtually the same chemical environments. Furthermore, they should not be greatly affected by changing the halo- ligand. The "double" resonance found at 2.35ppm for PdCl(MMPM)(MMPMH) and at 2.38ppm for PdCl(MClPM)(MClPMH) is assigned to groups (4) and (5), since these are the groups likely to be those most affected by changing the halo-ligand. In the bromo- complexes these resonances are both split to give two "single" resonance peaks. The resonance moved furtherest from its position in the equivalent chloro- complex is assigned to methyl (5) since this group is nearest to the halo- ligand. The position of the (5) methyl group resonance seems anomalous since the (A) methyls of the bridged complexes, which are in very similar chemical environments, are deshielded with respect to the neutral ligand. Group (5), also on (A) type methyl group, is shielded by about 0.1ppm in the PdCl(L)(LH) complexes compared with its position in the neutral ligands.

The remaining resonance at about 2.3ppm for both the MClPMH and MMPMH complexes is assigned to methyl group (3). The position of the resonance is not affected by changing the halo- ligand, as would be expected.

The Methine Protons

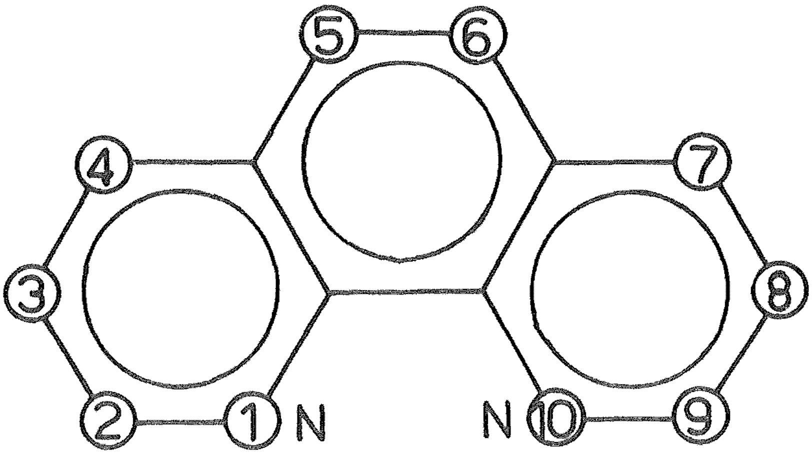
Two resonances, with equal integrals, which can be attributed to the methine protons, are observed for these complexes. The two resonances correspond to the methine protons of each ligand, and occur because of the different modes of coordination of the two ligands in these complexes. In the MMPMH complexes both methine protons are shielded with respect to that of the neutral ligand, and in the MClPMH complexes one is shielded, and the other deshielded, with respect to the methine proton of the free ligand.

In view of the fact that methine protons are strongly deshielded in all the other dipyrromethene complexes studied (pages 54 and 101) and in the protonated ligands (page 52) assignment of the resonances to particular protons is not possible. Although the behaviour of the methine protons in these complexes is different from that observed in other dipyrromethene complexes, they behave similarly to such protons in similar environments in acetylacetone and porphyrin complexes. (Table 2.44). It is not clear at this stage why the ring current arguments, found to be useful for explaining the changes in chemical shift of methine protons in other dipyrromethene complexes, do not apply to the PdX(L)(LH) complexes.

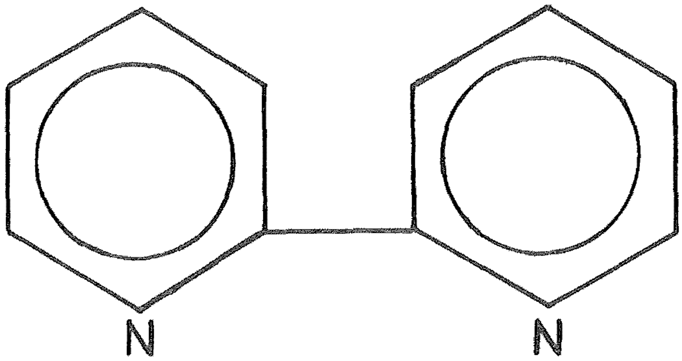
PART II

A STUDY OF ASPECTS OF THE CHEMISTRY OF o-PHENANTHROLINE COMPLEXES

FIGURE 5.11



(a) o-PHENANTHROLINE SKELETON AND NUMBERING SYSTEM



(b) BIPYRIDYL SKELETON

CHAPTER 5

Preparations of Some Substituted o-phenanthroline Complexes of Iron(II) and Ruthenium(II)

SECTION 5.1

A Review of Selected Aspects of the Chemistry of bis and tris-(o-phenanthroline) Complexes of Iron(II) and Ruthenium(II)

INTRODUCTION

The nitrogen heterocyclic compound 1,10-phenanthroline, or o-phenanthroline (o-phen), Figure 5.11a, is one of a large number of conjugated nitrogen donor ligands. Its coordination chemistry is closely related to that of 2,2'-bipyridyl (bipy), Figure 5.11b, and is similar in many respects to that of pyridine (py). It coordinates as a bidentate ligand to a wide range of metal ions, often forming stable complexes with the same metal in several oxidation states.

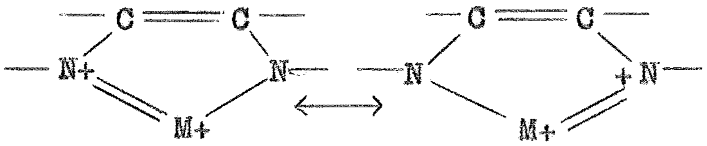
The existence of the tris-(o-phenanthroline)iron(II) cation (ferroin) was first reported by Blau in 1898[61]. Werner[62] resolved the cation into its optical isomers showing that the complex had octahedral stereochemistry. In the past 40 years much of the extensive research that has been carried out on complexes of o-phenanthroline and bipyridyl, especially those of iron(II), has been as a result of their importance as analytical reagents, and as oxidation-reduction indicators. Extensive reviews have been published on the coordination chemistry[63], and the use of the tris- complexes of various substituted phenanthrolines as analytical reagents[64,65].

The preparation of the tris-(o-phenanthroline) ruthenium(II) cation and its resolution into optical isomers was reported by Dwyer et al[66,67] in 1947 and 1949.

STABILITY AND BONDING IN THE IRON(II) COMPLEXES

The solution chemistry of the o-phenanthroline-iron(II) system is unusual in that the Irving-Williams order of stabilities[68] is not followed. The observed order, $K_3 \gg K_2 > K_1$[69], is explained in terms of a change from a high spin d-electron configuration of the mono- and bis-compounds to a low spin configuration on the formation of the tris species from the bis, with a consequent decrease in electronic repulsion energy.

Bonding between the phenanthroline ligand and the metal ion is usually described in terms of σ-donation of electrons from non-bonding orbitals of the nitrogen atoms into the empty d-orbitals of the metal, together with π-back donation of d-electrons of the metal into empty π^*-orbitals of the ligand. Burstall and Nyholm[70] and Sone[71] (1952) proposed that π- bonding in these complexes would involve delocalisation of π-electrons in the five membered chelate rings of the tris- complexes.



It has recently been suggested that π-bonding of this kind is important only for the spin-paired complexes with a $^1A_1$ ground state. This has been deduced from comparisons of the infrared spectra for highspin and low spin complexes[72].

THE bis-(o-PHENANTHROLINE)IRON(II) COMPLEXES

The chemistry of the bis-(o-phenanthroline)iron(II) complexes has recently been reviewed[73]. The preparation of the six-coordinate high spin complex Fe(o-phen)$_2$Cl$_2$ was first reported by Basolo and Dwyer (1954)[74]. A large number of complexes of general formula Fe(o-phen)$_2$X$_2$ have now been prepared where the range of anionic ligands (X) is such as to include virtually the full range of the spectrochemical series[73]. The complexes may be divided into three main types: (1) high spin complexes, (2) low spin complexes and (3) complexes whose magnetic susceptibilities show anomalous temperature dependence. These will be discussed separately.

(1) High Spin Complexes

A series of six-coordinate pseudo octahedral complexes Fe(o-phen)$_2$X$_2$, X = Cl$^-$, Br$^-$, I$^-$, N$_3^-$, SeCN$^-$, SCN$^-$ and CN$^-$ were prepared by Baker and Bobonich (1962, 1964)[75,76], who measured their magnetic susceptibilities. All these complexes, except the dicyano- complex are paramagnetic with magnetic moments of approximately 5.2 B.M. at room temperature, indicating a high spin electronic configuration ($^5T_2$ ground state).

The dicyano-complex has a magnetic moment of 0.7B.M. at room temperature and the tris-(o-phenanthroline) complex has a magnetic moment of about 1 B.M. Both of these are considered to be low spin with $^1A_1$ ground states. The bisthiocyanato- and bisselenocyanato- complexes show anomalous temperature dependence of their magnetic moments which drop to approximately 1.7B.M. over a temperature range of 3 °K at approximately 170°K. These two types of complex will be discussed later.

High spin complexes are also formed with cyanato- (coordinated through the nitrogen) and aceto- ligands. The oxalato- and malonato- complexes have magnetic moments of about 3.9B.M. and are considered to have $^3T_1$ ground states[73] (intermediate between the high spin $^5T_2$ and low spin $^1A_1$ ground states).

Generally the high spin complexes cannot be obtained from aqueous solutions since they readily disproportionate in the presence of water to give the tris-complex:

$$3Fe(\underline{o}\text{-phen})_2X_2 \longrightarrow 2Fe(\underline{o}\text{-phen})_3X_2 + FeX_2(aq)$$

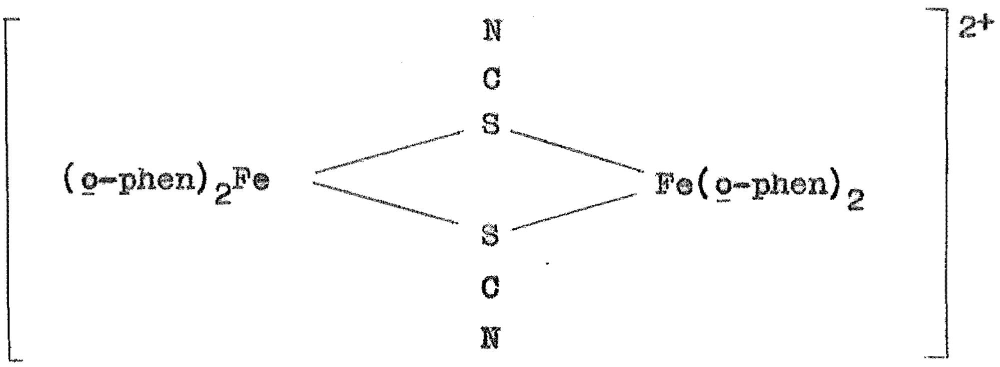
(2) Low Spin Complexes

These complexes usually involve good π- acceptor ligands such as cyanide, nitrite and cyanate (coordinated through the oxygen atom). All the low spin complexes including the tris-(o-phenanthroline) complex exhibit temperature independent paramagnetism[73].

In general these complexes are more stable with respect to disproportionation than the high spin complexes. For instance the dicyano- complex can be prepared from aqueous solution[77,78]. However it has been found to disproportionate to give the tris- complex over a period of time[79].

(3) The bis-thiocyanato- and bis-selenocyanato- Complexes

The unusual temperature dependence of the magnetic moments of these complexes was first reported by Baker and Bobonich[75,76], who proposed that the complexes were bridged



In a series of papers, Konig and Madeja, e.g.[79,80] have shown on the basis of infrared studies that the anionic ligands coordinate through the nitrogen atoms and from studies of the temperature dependent changes of Mössbauer, infrared and ultraviolet-visible spectra, that the complexes are monomeric and have a *cis* configuration. They have proposed that the temperature dependence of the magnetic moments is a result of a cross over between $^5T_2$ and $^1A_1$ ground states. The residual paramagnetism observed at low temperatures is thought to be due to "the presence of some molecules in the $^5T_2$ high spin state"[81]. The observation that different preparations of the same complex (for both *o*-phenanthroline and 2,2' bipyridyl complexes) give different residual magnetic moments at low temperatures is thought to be in accord with this hypothesis.

It has been reported that a crystallographic phase change occurs at the same temperature as the observed change in magnetic moment[82]. Independent studies of the Mössbauer spectra and NMR spectra of these complexes at different temperatures[83] has given support to the theory that a reversible interchange occurs between ground state terms.

i) Stereochemistry

A *cis* stereochemistry has been proposed for

$Fe(\underline{o}\text{-phen})_2(CN)_2$ because the C≡N stretching mode in the infrared spectrum of this compound is split[77]. The NMR spectrum in anhydrous hydrogen fluoride of the diprotonated complex $Fe(\underline{o}\text{-phen})_2(CNH)_2^{2+}$ has been analysed on the basis of a cis configuration[84]. Baker and Bobonich[75] proposed that the complexes $Fe(\underline{o}\text{-phen})_2X_2$, X = Cl^-, Br^-, I^- and CN^-, are all cis isomers because of the similarity of their X-ray powder patterns. Duncan and Mok[85] reported that the Mössbauer spectra of several of the $Fe(\underline{o}\text{-phen})_2X_2$ complexes indicated cis rather than trans stereochemistry.

At different times preparations of trans isomers of $Fe(\underline{o}\text{-phen})_2(SCN)_2$ [86], its bipyridyl analogue[87], and $Fe(\underline{o}\text{-phen})_2(CN)_2$ [88,89] have been reported. However in each of these cases later evidence has suggested that the complexes are cis rather than trans[90,91].

RUTHENIUM(II) COMPLEXES

The preparation of the tris(o-phenanthroline)ruthenium (II) cation was reported by Dwyer et al (1947)[66] who also measured the redox potentials of the $Ru(\underline{o}\text{-phen})_3^{2+}$/ $Ru(\underline{o}\text{-phen})_3^{3+}$ couple for a number of salts of the complex cation. The preparation of a series of neutral bis-(o-phenanthroline)ruthenium(II) complexes $Ru(\underline{o}\text{-phen})_2X_2$, X = Cl^-,Br^- and I^-, was reported by Dwyer, Goodwin and Gyarfas (1963)[92]. Bosnick and Dwyer[93] reported the preparation of the series of complex ions $Ru(\underline{o}\text{-phen})_2Xpy^{n+}$, where, for n = 1, X = Cl^-, Br^-, I^-, N_3^-, NCS^-, NO_2^- and CN^-, and for n = 2, X = NH_3, CH_3CN and py. The complex cation $Ru(\underline{o}\text{-phen})_2(py)_2^{2+}$ was resolved into its optical isomers, and it was found that the mono-substituted complexes prepared from the optically active bis-pyridine complex were also optically active, indicating that all the complexes were cis isomers. The neutral complex $Ru(\underline{o}\text{-phen})_2(CN)_2$ has also been reported to have a cis configuration[94]. All the ruthenium complexes prepared so far are diamagnetic as expected.

SECTION 5.2

Scope of the Present Work in Part II

A number of iron(II) and ruthenium(II) o-phenanthroline and substituted o-phenanthroline complexes prepared in this work are listed in Table 5.21. Those prepared for the first time in this work are marked with an asterisk. The series of complexes cis-M(phen)$_2$X$_2$ has been prepared for M = Fe(II), Ru(II); X = Cl^-, Br^-, I^-, SCN^- and CN^-; and phen = o-phenanthroline (o-phen), 5-methyl-o-phenanthroline (5MePh) and 5-nitro-o-phenanthroline(5NO$_2$Ph) for iron, and o-phenanthroline, 5-methyl-o-phenanthroline and 5-chloro-o-phenanthroline (5ClPh) for ruthenium.

Some of the complexes containing the substituted o-phenanthrolines have been prepared for the first time, although the o-phenanthroline complexes of both iron(II) and ruthenium(II) are well known[73,92].

A comparative study of the ultraviolet-visible spectra of these complexes has been attempted and is described in Chapter 6. It was necessary to measure the spectra of the iron complexes in the solid state (potassium bromide discs and nujol mulls). Difficulty was experienced in trying to obtain good solid state spectra. The techniques used are described in Section 6.3. In general the spectra obtained are not of a sufficient quality for useful comparisons.

Table 5.21 COMPLEXES PREPARED IN THE PRESENT WORK IN PART II

Compound	Elemental Analysis								Conductivity Λ_m (20°) (ohms^{-1} moles^{-1} cm^2) nitrobenzene
	Found (%)				Calculated (%)				
	C	H	N	X	C	H	N	X	
$Fe(\underline{o}\text{-phen})_3Cl_2 \cdot 6H_2O$	55.6	4.9	-	10.9	55.7	4.7	-	9.2	
$Fe(\underline{o}\text{-phen})_3Br_2 \cdot 3H_2O$	53.8	4.0	-	19.0	53.4	3.7	-	19.7	
$Fe(\underline{o}\text{-phen})_3I_2 \cdot 4H_2O$	47.5	3.3	-	28.0	46.9	3.5	-	27.6	
$Fe(\underline{o}\text{-phen})_2Cl_2$	58.2	3.9	-	14.0	59.2	3.3	-	14.6	
$Fe(\underline{o}\text{-phen})_2I_2$	42.5	2.4	-	36.9	43.5	2.4	-	37.9	
$Fe(\underline{o}\text{-phen})_2Br_2$	49.9	2.9	-	27.6	50.0	2.9	-	27.8	
$Fe(\underline{o}\text{-phen})_2(SCN)_2 \cdot H_2O$	56.2	3.3	15.2	-	56.7	3.3	15.3	-	
$Fe(\underline{o}\text{-phen})_2(CN)_2 \cdot H_2O$	64.0	4.0	16.8	-	64.2	3.7	17.3	-	
$Fe(5NO_2Ph)_3Cl_2 \cdot 4H_2O$	49.1	4.0	-	8.2	49.4	3.3	-	8.1	
* $Fe(5NO_2Ph)_2Cl_2$	50.1	2.7	14.6	-	49.9	2.4	14.6	-	
* $Fe(5NO_2Ph)_2Br_2 \cdot H_2O$	42.1	2.6	13.0	-	42.1	2.3	12.3	-	
* $Fe(5NO_2Ph)_2I_2 \cdot 5H_2O$	33.9	2.1	9.5	-	33.9	2.8	9.9	-	
* $Fe(5NO_2Ph)(SCN)_2$	50.2	2.5	17.8	-	50.2	2.3	18.0	-	
$Fe(5NO_2Ph)(CN)_2 \cdot 3H_2O$	50.3	3.2	18.8	-	50.9	3.3	18.3	-	
* $Fe(5MePh)_2Cl_2 \cdot H_2O$	59.9	4.0	-	13.5	59.0	4.2	-	13.9	
* $Fe(5MePh)_2Br_2$	51.3	3.5	-	26.5	51.7	3.3	-	26.5	
* $Fe(5MePh)_2I_2 \cdot 4H_2O$	38.0	3.6	-	-	40.5	2.7	-	-	
$Fe(5MePh)_3Cl_2 \cdot 2H_2O$	63.6	4.9	-	9.3	62.8	4.6	-	9.5	
* $Fe(5MePh)_2(SCN)_2$	59.7	3.8	15.0	-	60.0	3.6	15.0	-	
$Fe(5MePh)_2(CN)_2 \cdot 4H_2O$	59.3	4.4	14.5	-	59.2	4.9	14.8	-	
$Ru(\underline{o}\text{-phen})_3I_2 \cdot H_2O$	47.2	2.9	-	26.2	47.3	2.9	-	27.8	
$Ru(\underline{o}\text{-phen})_3Cl_2 \cdot 4H_2O$	55.2	3.9	-	9.2	55.0	4.1	-	9.1	
$Ru(\underline{o}\text{-phen})_2Cl_2 \cdot H_2O$	52.3	3.2	-	12.8	52.4	3.3	-	12.9	0.3
$Ru(\underline{o}\text{-phen})_2Br_2 \cdot H_2O$	45.2	2.6	-	23.7	45.1	2.8	-	25.1	0.6
$Ru(\underline{o}\text{-phen})_2I_2$	40.2	2.3	7.7	-	40.3	2.2	7.8	-	3.0
$Ru(\underline{o}\text{-phen})_2(SCN)_2$	53.3	3.1	14.0	-	54.0	2.8	14.6	-	5.5
$Ru(\underline{o}\text{-phen})_2(CN)_2 \cdot 2H_2O$	56.4	3.5	15.3	-	56.8	3.6	15.3	-	2.1
* $Ru(5MePh)_2Cl_2 \cdot 4H_2O$	49.9	4.1	8.9	11.4	49.4	4.4	8.9	11.2	
* $Ru(5MePh)_2Br_2 \cdot H_2O$	46.7	3.8	7.9	22.9	46.8	3.3	8.4	24.0	
* $Ru(5MePh)_2I_2 \cdot 3H_2O$	39.4	3.0	6.9	-	39.2	3.3	7.0	-	
* $Ru(5MePh)_2(SCN)_2 \cdot 2H_2O$	52.2	3.8	11.9	-	52.4	3.7	13.1	-	
* $Ru(5MePh)_2(CN)_2 \cdot 3H_2O$	55.8	4.5	12.7	-	56.5	4.4	14.1	-	
* $Ru(5ClPh)_2Cl_2 \cdot 3H_2O$	44.5	2.9	8.1	20.9	43.9	3.1	8.5	21.6	
* $Ru(5ClPh)_2Br_2 \cdot 3H_2O$	38.6	2.5	7.5	-	38.7	2.7	7.5	-	
* $Ru(5ClPh)_2I_2 \cdot 2H_2O$	34.8	2.0	6.9	-	35.1	2.2	6.8	-	
* $Ru(5ClPh)_2(SCN)_2 \cdot 4H_2O$	43.3	2.3	12.8	-	43.5	3.1	11.7	-	
* $Ru(5ClPh)_2 \cdot 4H_2O$	46.8	3.3	12.8	-	47.7	3.4	12.8	-	

* Complexes reported for the first time

The spectra of the ruthenium complexes have been measured in dichloromethene solutions (Section 6.2). The assignments of absorption bands are discussed and changes in these bands are compared with those obtained from a series of similar complexes of 2,2'-bipyridyl[96]. Changes in the positions of bands for the intraligand and charge transfer transitions of the ruthenium complexes are discussed in detail and an attempt is made to correlate trends with the types of ligands coordinated to the metal ion.

SECTION 5.3

Experimental

The ferrous complexes were prepared by the methods of Basolo and Dwyer[74], Baker and Bobonich[75,76], Madeja and Konig[79] and Shilt[78]. These methods have been reviewed by Konig[73]. The ruthenium complexes were prepared by the methods of Dwyer et al[66,92]. Infrared spectra (4000 - 1400 cm^{-1}) were recorded for all preparations and were useful for checking the purity of subsequent preparations of the same complex. The infrared spectra indicated the presence of water of crystallisation in many of the complexes, and confirmed the elemental analysis in this respect.

IRON(II) COMPLEXES

(i) tris-(o-phenanthroline)iron(II)dichloride hexahydrate, $Fe(\underline{o}\text{-phen})_3Cl_2.6H_2O$

Ferrous chloride (1 millimole) was dissolved in the minimum amount of water or ethanol and added to a solution of o-phenanthroline hydrate ($\underline{o}\text{-phen}.H_2O$) (3millimoles) in the minimum amount of ethanol. The resultant red coloured solution was evaporated to a small volume and left to crystallise. The product was recrystallised from ethanol and dried in vacuo.

(ii) tris-(o-phenanthroline)iron(II)dibromidetrihydrate, $Fe(\underline{o}\text{-phen})_3Br_2.3H_2O$.

The complex was prepared as for (i) above. Use of ferrous bromide required a carbon dioxide atmosphere.

(iii) tris-(o-phenanthroline)iron(II)di-iodide tetrahydrate, $Fe(\underline{o}\text{-phen})_3I_2.4H_2O$

The complex salt was prepared by precipitation from a concentrated aqueous solution of $Fe(\underline{o}\text{-phen})_3Cl_2$ by the addition of a large excess of potassium iodide. It was washed with a little cold water, recrystallised from ethanol and dried in vacuo.

(iv) dichlorobis-(o-phenanthroline)iron(II), $Fe(\underline{o}\text{-phen})_2Cl_2$

Finely divided $Fe(\underline{o}\text{-phen})_3Cl_2.6H_2$ was refluxed in benzene (10 hrs). The blue product was filtered, dried and then heated to constant weight at 100°C in vacuo for several hours and was cooled in a desiccator.

(v) dibromobis-(o-phenanthroline)iron(II), Fe(o-phen)$_2$Br$_2$ [75]

Finely divided Fe(o-phen)$_3$Br$_2$.3H$_2$O was refluxed in methylcyclohexane for four days. The purple compound obtained was filtered and dried in vacuo.

(vi) di-iodobis-(o-phenanthroline)iron(II), Fe(o-phen)$_2$I$_2$ [75]

Finely divided Fe(o-phen)$_3$I$_2$.4H$_2$O was heated in vacuo at 180°C until no further loss of o-phenanthroline was observed visually.

(vii) bisthiocyanatobis-(o-phenanthroline)iron(II) monohydrate, Fe(o-phen)$_2$(SCN)$_2$.H$_2$O [75]

Ferrous chloride hydrate (0.5gm) and potassium thiocyanate (35gm) were dissolved in water (100mls) and pyridine (1.5ml) was added. A yellow precipitate of Fe(pyridine)$_4$(SCN)$_2$ immediately formed. It was filtered and dried in vacuo over calcium chloride.

The freshly prepared pyridine complex (1gm) was dissolved in chloroform (about 20 mls) and o-phenanthroline hydrate (1gm) was added. The purple product which crystallised out was filtered and dried in vacuo.

(viii) dicyanobis-(o-phenanthroline)iron(II)monohydrate, Fe(o-phen)$_2$(CN)$_2$.2H$_2$O [78]

The ligand o-phenanthroline hydrate (1.5gm) and ferrous sulphate heptahydrate (0.7gm) were dissolved in water (100mls). The dark red solution was heated to just below boiling and a freshly prepared solution of potassium cyanide (2.5gm in 2.5mls of water) was added with stirring to the hot solution, which was left to cool. A blue product separated after several hours which was filtered and dried in vacuo.

(ix) tris-(5-nitro-o-phenanthroline)iron(II)dichloride tetrahydrate, $Fe(5NO_2PH)_3Cl_2.4H_2O$

This was prepared as described for $Fe(o\text{-}phen)_3Cl_2.6H_2O$ ((i) above).

(x) dichlorobis-(5-nitro-o-phenanthroline)iron(II), $Fe(5NO_2ph)_2Cl_2$

Pyridine was added to an ethanolic solution of ferrous chloride in the ratio of 4 moles of pyridine to 1 mole of Fe. The purple solution was evaporated to dryness to obtain $Fe(py)_4Cl_2$.

A solution of $Fe(py)_4Cl_2$ (1gm) in dry pyridine (10mls) was heated to boiling under a nitrogen atmosphere and filtered through a sintered glass disc into a hot solution of dry (resublimed) 5-nitro-o-phenanthroline (0.7gm) in dry pyridine (2ml). Violet crystals of $Fe(5NO_2ph)_2Cl_2$ were obtained. These were filtered, washed with dry pyridine followed by ether and dried in vacuo.

(xi) dibromobis-(5-nitro-o-phenanthroline)iron(II) hydrate, $Fe(5NO_2Ph)_2Br_2.H_2O$.

Ferrous bromide (1 millimole) and 5-nitro-o-phenthroline (2 millimoles) were dissolved in ethanol. The red solution was evaporated to a small volume. The purple product was filtered, washed with water, and dried in vacuo.

(xii) di-iodobis-(5-nitro-o-phenanthroline)iron(II)pentahydrate, $Fe(5NO_2Ph)_2I_2.5H_2O$

$Fe(5NO_2Ph)_3Cl_2.3H_2O$ prepared as in (ix) above, was dissolved in ethanol, and excess potassium iodide was added to the hot solution. The resulting precipitate was filtered, washed with water and dried in vacuo.

(xiii) bis-thiocyanatebis-(5-nitro-o-phenanthroline)iron(II), $Fe(5NO_2Ph)_2(SCN)_2$

The complex was prepared as described for Fe(ophen)$_2$-$(SCN)_2.H_2O$ ((vii) above).

(xiv) dicyanbis-(5-nitro-o-phenanthroline)iron(II)trihydrate, $Fe(5NO_2Ph)_2(CN)_2.3H_2O$

The complex was prepared as described for Fe(o-phen)$_2$-$(CN)_2.H_2$) ((viii) above).

(xv) tris-(5-methyl-o-phenanthroline)iron(II)dichloride dihydrate, $Fe(5MePh)_3Cl_2.2H_2O$

The complex was prepared as described for Fe(o-phen)$_3$-$Cl_2.6H_2O$ ((i) above).

(xvi) dichlorobis-(5-methyl-o-phenanthroline)iron(II) hydrate, $Fe(5MePh)_2Cl_2.H_2O$

Finely divided $Fe(5MePh)_3Cl_2.2H_2O$ was heated in vacuo at 180°C to constant weight (approx. 20hrs).

(xvii) dibromobis-(5-methyl-o-phenanthroline)iron(II), $Fe(5MePh)_2Br_2$

The complex $Fe(5MePh)_3Br_2$, prepared as described in (ii) above for $Fe(o\text{-}phen)_3Br_2.3H_2O$, was finely divided and heated in vacuo at 180 - 190°C for about 100 hours until evolution of 5-methyl-o-phenanthroline ceased.

(xviii) di-iodo-bis-(5-methyl-o-phenanthroline)iron(II) tetrahydrate, $Fe(5MePh)_2I_2.4H_2O$

Finely divided $Fe(5MePh)_3I_2$, prepared as described for $Fe(o\text{-}phen)_3I_2.4H_2O$ in (iii) above, was heated for several days at 150 - 180°C until evolution of 5-methyl-o-phenanthroline ceased.

(xix) bis-thiocyanatebis-(5-methyl-o-phenanthroline)iron(II), $Fe(5MePh)_2(SCN)_2$

The complex was prepared from $Fe(py)_4(SCN)_2$ as described for $Fe(o\text{-}phen)_2(SCN)_2$ ((vii) above).

(xx) dicyanobis-(5-methyl-o-phenanthroline)iron(II) tetrahydrate, $Fe(5MePh)_2(CN)_2\ 4H_2O$

The complex was prepared as described for $Fe(o\text{-}phen)_2(CN)_2.H_2O$ ((viii) above).

RUTHENIUM(II) COMPLEXES

(i) o-phenanthrolinium tetrachloro-(o-phenanthroline)-ruthenate(III) monohydrate, $[o\text{-phenH}^+][RuCl_4(o\text{-phen})^-]\cdot H_2O$ [66]

Potassium pentachloroaquoruthenate ($K_2RuCl_5H_2O$) (1 millimole) (page 28) was dissolved in the minimum amount of 1N HCl in a stoppered flask. The ligand o-phenanthroline hydrate (1 millimole) was added to the solution at 30°C and the mixture was shaken vigorously to dissolve the base. It was left to stand overnight on a cooling waterbath. Light brown needles of the complex were collected, washed with cold water, and dried in vacuo. The complex was used for further preparations without further investigation.

(ii) tris-(o-phenanthroline)ruthenium(II) di-iodide monohydrate, $Ru(o\text{-phen})_3I_2\cdot H_2O$

Potassium pentachlorohydroxyruthenate (K_2RuCl_5OH) (1gm), (page 28) was dissolved in hot water (25ml) containing 1 drop of 5NHCl. The ligand o-phen.H_2O (0.8g) was added with shaking, and after boiling for a few minutes a deep green-brown solution was obtained. Hypophosphorous acid (30%, 1ml), neutralised with a few drops of 2N sodium hydroxide was added to the solution and the mixture was refluxed for 10-15 minutes. The colour changed to a deep red. The solution was filtered and saturated aqueous potassium iodide was added slowly until crystallisation started. The mixture was shaken vigorously for several hours and the crystalline solid which separated was filtered, washed with a little cold water, and dried in vacuo.

(iii) tris-(o-phenanthroline)ruthenium(II) dichloride tetrahydrate, $Ru(\underline{o}\text{-phen})_3Cl_2.4H_2O$

Ruthenium trichloride hydrate ($RuCl_3.3H_2O$) (0.3gm) and o-phenanthroline (1.0gm) were refluxed in ethanol (400ml) for several hours until a green solution was obtained. Sodium dithionite (0.1gm) was added to the hot solution and gave a vigorous reaction. The solution changed colour to orange-red and was distilled down to a small volume and finally evaporated to dryness on a water bath. The residue was redissolved in a small volume of water. The solution was filtered and a large excess of A.R. potassium chloride was added to precipitate the complex. The product was filtered, washed with a few drops of cold water, and dried in vacuo.

(iv) dichlorobis-(o-phenanthroline)ruthenium(II) monohydrate, $Ru(\underline{o}\text{-phen})_2Cl_2.H_2O$ [92]

The compound $[\underline{o}\text{-phenH}^+][RuCl_4(\underline{o}\text{-phen})^-]$ (1gm) was suspended in redistilled dimethylformamide (20ml) and refluxed for 2 hours. The brown solution changed to a deep purple colour. The solution was reduced in volume to 5 ml by distillation under reduced pressure over a period of an hour. The remaining solution was cooled and the complex was precipitated by the addition of acetone (20ml). The product was filtered and was suspended in a 50% ethanol/water mixture which was refluxed, filtered, and left on a water bath until the ethanol had evaporated. Freshly recrystallised lithium chloride (10gm) was added and after 4 hours at room temperature the complex was filtered, washed with water, methanol, and finally acetone, before drying in vacuo.

(v) dibromobis-(o-phenanthroline)ruthenium(II) monohydrate, $Ru(\underline{o}\text{-phen})_2Br_2.H_2O$ [92]

The compound $Ru(\underline{o}\text{-phen})_2Cl_2.H_2O$ was suspended in a 50% ethanol/water mixture and the solution was refluxed until all the solid had dissolved. The violet solution was filtered and a large excess of A.R. potassium bromide was added. The solution was evaporated to a small volume on a waterbath and the complex was left to crystallise. The product was filtered, washed with water and dried in vacuo.

(vi) di-iodobis-(o-phenanthroline)ruthenium(II), $Ru(\underline{o}\text{-phen})_2I_2$ [92]

The complex was prepared from $Ru(\underline{o}\text{-phen})_2Cl_2.H_2O$ as for (v) above using A.R. potassium iodide.

(vii) bisthiocyanatebis-(o-phenanthroline)ruthenium(II) $Ru(o\text{-}phen)_2(SCN)_2$ [92]

The complex was prepared from $Ru(o\text{-}phen)_2Cl_2.H_2O$ as outlined in (v) above using AR potassium thiocyanate.

(viii) dicyanobis-(o-phenanthroline)ruthenium(II) dihydrate, $Ru(o\text{-}phen)_2(CN)_2.2H_2O$ [92]

The complex was prepared as outlined in (v) above, using AR potassium cyanide.

(ix) 5-methyl-o-phenanthrolinium tetrachloro-(5-methyl-o-phenanthroline)ruthenate(III), $[5MePhH^+][RuCl_4(5MePh)^-]$

The complex was prepared from potassium pentachloroaquoruthenate as outlined in (i) above using 5-methyl-o-phenanthroline. It was used for further preparations without further investigation.

(x) dichlorobis-(5-methyl-o-phenanthroline)ruthenium(II) tetrahydrate, $Ru(5MePh)_2Cl_2.4H_2O$

The compound $[5MePhH^+][RuCl_4(5MePh)^-]$ (1.0gm) was suspended in ethanol (100ml). Zinc powder (0.5gm) and 5N HCl (10ml) were added and the mixture was refluxed until the colour changed from brown to deep purple. The heating was continued until effervescence ceased. The solution was filtered and evaporated to dryness. The residue was extracted in a soxhlet using a 10% water/ethanol mixture. An excess of lithium chloride was added to the extract which was left to cool. The complex crystallised slowly and was filtered, washed with water and dried in vacuo.

The following complexes (numbers (xi) to (xiv)) were prepared from $Ru(5MePh)_2Cl_4.4H_2O$ by the methods outlined in (v), (vi), (vii) and (viii) above:

(xi) dibromobis-(5-methyl-o-phenanthroline)ruthenium(II) monohydrate, $Ru(5MePh)_2Br_2.H_2O$

(xii) di-iodobis-(5-methyl-o-phenanthroline)ruthenium(II) trihydrate, $Ru(5MePh)_2I_2.3H_2O$

(xiii) bisthiocyanatobis-(5-methyl-o-phenanthroline) ruthenium(II)dihydrate, $Ru(5MePh)_2(SCN)_2.2H_2O$

(xiv) dicyanobis-(5-methyl-o-phenanthroline)ruthenium(II) trihydrate, $Ru(5MePh)_2(CN)_2.3H_2O$

(xv) 5-chloro-o-phenanthroliniumtetrachloro-(5-chloro-o-phenanthroline)ruthenate(III), $[5ClPhH^+][Ru(5ClPh)Cl_4^-]$

The compound was prepared by the method outlined for 5MePhH $Ru(5MePh)Cl_4$ in (ix) above. It was used for further reactions without further investigation.

(xvi) dichlorobis-(5-chloro-o-phenanthroline)ruthenium(II) trihydrate, $Ru(5ClPh)_2Cl_2.3H_2O$.

The complex was prepared by zinc/hydrochloric acid reduction of $[5ClPhH^+][Ru(5ClPh)Cl_4^-]$ as outlined in (x) above.

The following complexes (numbers (xvii) to (xx)) were prepared from $Ru(5ClPh)_2Cl_2.3H_2O$ as outlined in (v), (vi), (vii) and (viii) above.

(xvii) dibromobis-(5-chloro-o-phenanthroline)rutheni
hydrate, $Ru(5ClPh)_2Br_2.2H_2O$

(xviii) di-iodobis-(5-chloro-o-phenanthroline)ruthenium(II)
dihydrate, $Ru(5ClPh)_2I_2.2H_2O$.

(xix) bisthiocyanatobis-(5-chloro-o-phenanthroline)
ruthenium(II)tetrahydrate, $Ru(5ClPh)_2(SCN)_2.4H_2O$

(xx) dicyanobis-(5-chloro-o-phenanthroline)ruthenium(II)
tetrahydrate, $Ru(5ClPh)_2(CN)_2.4H_2O$

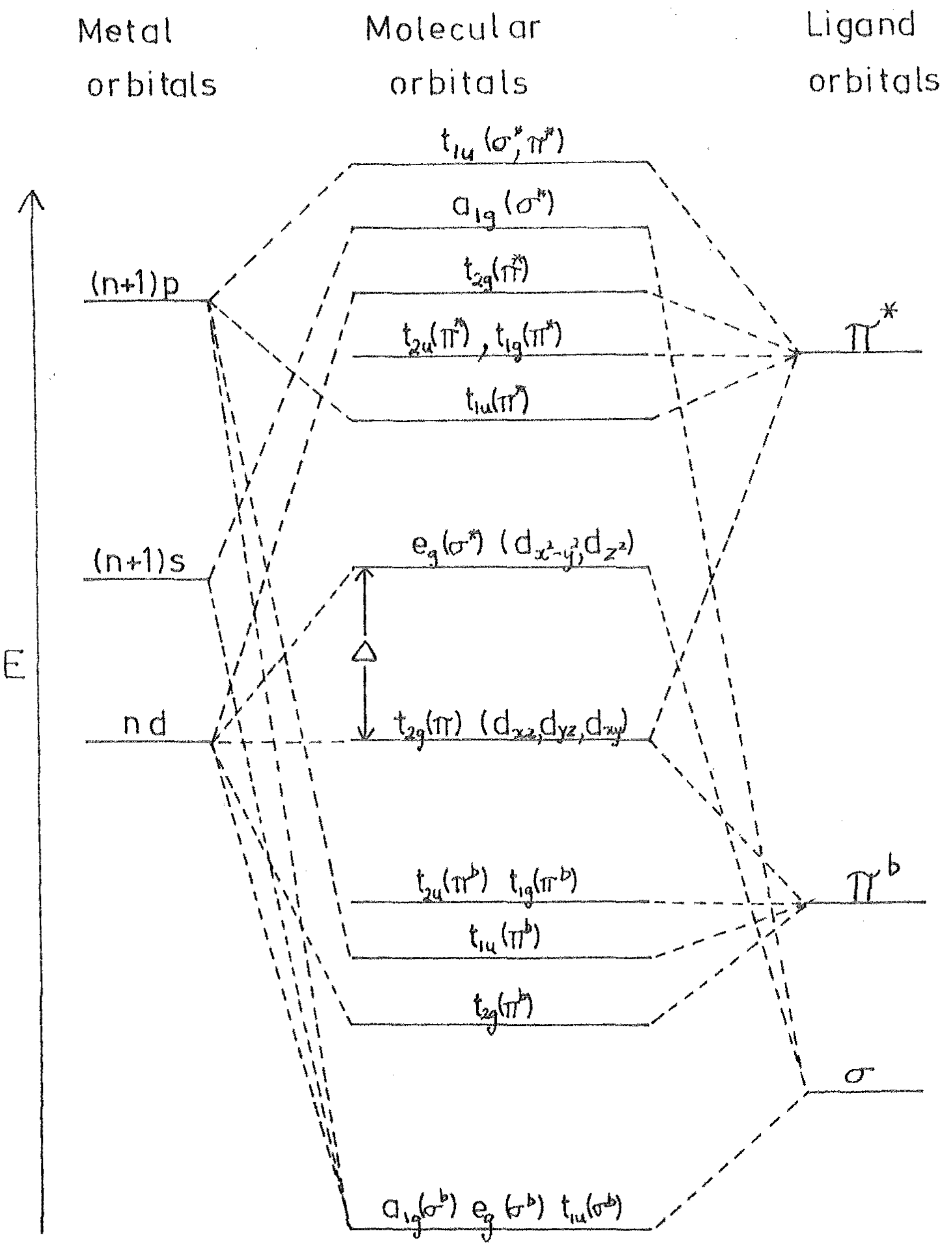
(xxi) 5-nitro-o-phenanthrolinium tetrachloro(5-nitro-o-phenanthroline)ruthenium(III), $[5NO_2PhH^+][RuCl_4(5NO_2Ph)^-]$

The compound 5-nitro-o-phenanthroline (0.5gm) was added to a solution of potassium pentachloroaquoruthenate (0.7gm) in 1N HCl (10ml) at 80°C (on a waterbath). The mixture was shaken vigorously as an orange precipitate formed. The mixture was left on the water bath for 1 to 1½ hours. A brown precipitate was obtained which was filtered, washed with water and dried in vacuo.

A number of attempts were made to prepare bis-(5-nitro-o-phenanthroline)ruthenium(II) complexes using the above compound as a starting material. Reduction in dimethylformamide resulted in a complex which was suspected to contain coordinated carbonyl groups. This was deduced from the presence of bands in the infrared spectra of the reaction product in the region 2100 - 1950 cm^{-1}. Zinc/hydrochloric acid reduction gave mixtures of compounds which could not be purified. These were suspected to contain 5-amino-o-phenanthroline since N-H stretching bands could be detected in the infrared spectra of the complexes.

Because of the difficulty experienced in purifying the compounds formed they were not further investigated.

FIGURE 6.11



Molecular orbital diagram for an octahedral complex containing π-bonding ligands.
(Gray and Beach[97])

CHAPTER 6

Ultraviolet-Visible Spectra

SECTION 6.1

General Introduction

Three main types of electronic transitions are expected for the bis- and tris- o-phenanthroline complexes of ruthenium(II) and iron(II): (1) ligand field transitions, (2) charge transfer transitions and (3) intraligand $\pi \rightarrow \pi^*$ transitions. The following discussion will be based on the molecular orbital scheme shown in Figure 6.11. This molecular orbital model was derived by Gray and Beach[97] for hexacyano- and hexacarbonyl- complexes. Use of this model for the o-phenanthroline complexes can only be qualitative because:

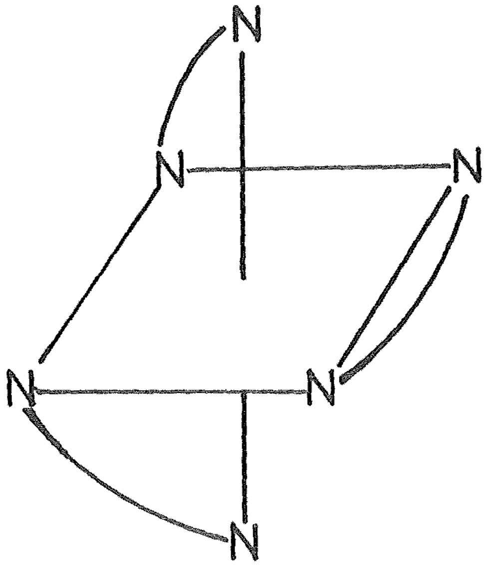
(1) the hexacyano and hexacarbonyl complexes have regular octahedral symmetry whereas the tris- and bis- octahedral complexes of o-phenanthroline have D_3 and C_2 symmetry respectively (assuming the latter to have the cis configuration), as in Figure 6.12.

(2) The role played by π- bonding in the o-phenanthroline complexes is not well known. It is usually considered to be an important feature of the bonding, however direct evidence is lacking.

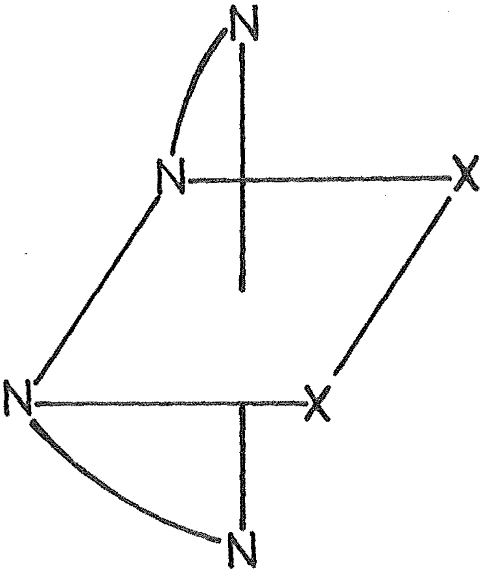
(3) The cyano- and carbonyl ligands have only one set of

FIGURE 6.12

SYMMETRY OF THE bis- and tris-
(o-PHENANTHROLINE) COMPLEXES



Tris (D_3)



Bis (C_2)

non-degenerate π- orbitals, whereas o-phenanthroline has several.

(4) The presence of two different types of ligands in the complexes will complicate the relatively simple molecular orbital scheme derived using six identical ligands. The effect on the overall molecular orbital scheme cannot be readily predicted.

Metal orbitals will be grouped as t_2 and e although these groups will be split by the low symmetry.

INTRALIGAND $\pi \rightarrow \pi^*$ TRANSITIONS

Three intraligand $\pi \rightarrow \pi^*$ transitions for o-phenanthroline give absorbtion bands in the accessible region of the ultraviolet spectrum below 50,000 cm^{-1}. These bands occur at 31,000 cm^{-1} ($\varepsilon \sim 300$), 38,000 cm^{-1} ($\varepsilon \sim 30,000$) and 43,500 cm^{-1} ($\varepsilon \sim 38,000$) and have recently been assigned (in terms of the four lowest excited singlet states of phenanthene: α, p, β, β' to the α, β' and β bands respectively, with the p band contained within the envelope of the β' band [103]. This disagrees with a previous assignment of the o-phenanthroline spectrum[103a]. No $n \rightarrow \pi^*$ transitions are observed for o-phenanthroline[98].

The approach used in the present work is an empirical one and the spectra will be discussed in terms of a high energy $\pi \rightarrow \pi^*$ (2) transition (the β band) and a low energy $\pi \rightarrow \pi^*(1)$ transition (p and β' bands). The α band is weak and is frequently not resolved in the spectra of the complexes.

The Low Energy Intraligand Transition ($\pi \rightarrow \pi^*(1)$)

The low energy $\pi \rightarrow \pi^*$ band has considerable structure both in the spectra of the free ligands (Figure 6.21) and in the complexes. This structure may be due to vibrational effects e.g.[103], and is also due to the presence of two transitions within the band envelope (the p and β' transitions). The band generally shifts to lower energy on coordination of the ligand to a metal ion. This has been attributed to the influence of positive charge on the energy levels of the ligand[99,100,101]. The effect is observed for the protonated ligands[102,103] and is often found to be greater for complexes of trivalent metal ions than for those of divalent metals[96].

High Energy Intraligand Transition ($\pi \rightarrow \pi^*(2)$)

The high energy $\pi \rightarrow \pi^*$ transition has not been observed in most spectral studies of o-phenanthroline complexes. Consequently it has not been discussed. In a study of the closely related bis- and tris- (2,2'-bipyridyl)iron(II) and ruthenium(II) complexes it was found that shifts in the position of the $\pi \rightarrow \pi^*(2)$ band were less regular than those of the low energy ($\pi \rightarrow \pi^*(1)$) band[96].

CHARGE TRANSFER TRANSITIONS

Two types of charge transfer are possible for these complexes: (1) ligand → metal charge transfer and (2) metal → ligand charge transfer. These will be discussed separately.

(1) Ligand → Metal Charge Transfer

Ligand → metal charge transfer involves the promotion of an electron from orbitals localised mainly on the ligands to orbitals localised mainly on the metal ions. The acceptor orbitals of the metal will be the e (σ^*) orbitals in the case of the low spin complexes and may be either the t_2 or e orbitals of the high spin complexes. No bands have been assigned to ligand → metal transitions in the present work, nor have they been observed for the closely related bipyridyl complexes[96].

(2) Metal → Ligand Charge Transfer

Metal → ligand charge transfer corresponds to the transfer of an electron from molecular orbitals localised mainly on the metal (t_2) to orbitals localised mainly on the ligand (π^*). Many α- di-imine complexes with iron group metals, including those of o-phenanthroline and 2,2'-bipyridyl[104a,b] have an intense band near 20,000cm^{-1} ($\varepsilon \sim 10^4$). This band has been assigned as a metal → ligand charge transfer band, both empirically e.g.[104,105], and on the basis of theoretical calculations e.g.[99,100]. The band is observed to move to higher energy as the strength of the average ligand field about the metal ion is increased[79,96,105]. This corresponds to an increasing stabilisation of the t_2-orbitals with respect to the ligand π^*-antibonding orbitals (see page 143).

The band has considerable structure with one or more shoulders on the high energy side of the main band. This has been assigned to vibrational structure[100,103,105]. A recent theoretical study has shown that two overlapping charge transfer transitions occur within the band envelope[117]. For some complexes shoulders have also been observed on the low energy side of the band.

A second band at about 28,000 cm^{-1} has been observed for some complexes of 2,2'-bipyridyl. This band has been assigned to a high energy metal ⟶ ligand charge transfer transition[96,106]. The energy of this band, like the $\pi \rightarrow \pi^*(1)$ band, increases as the average ligand field strength about the metal ion increases. For the bipyridyl complexes the energy difference between the two intraligand $\pi \rightarrow \pi^*$ transitions is of the same order as that between the two charge transfer transitions (approximately 7,000 cm^{-1})[96] suggesting that the same two π^*-acceptor orbitals may be involved in each case.

LIGAND FIELD TRANSITIONS

Generally the ligand field bands are masked by the intense charge transfer band in the visible region. Attempts have been made to observe the ligand field spectra of the $Fe(\underline{o}\text{-phen})_2X_2$ complexes[79], and of the tris-(o-phenanthroline)ruthenium(II) cation[95].

Iron Complexes

Reflectance spectra have been measured for the high spin compounds $Fe(\underline{o}\text{-phen})_2X_2$, X = Cl^-, Br^-, SCN^-, N_3^-, OCN^-, $HCOO^-$, and for the low spin compound $Fe(\underline{o}\text{-phen})_2(CN)_2$.[79] For the high spin complexes two bands were observed near 10,000 cm^{-1}. The average energy of the two bands was observed to increase as the anionic ligand was changed in the above order from chloride to formate. These bands were assigned to the $^5T_2 \longrightarrow {}^5E$ transition, the observed splitting being due to the low symmetry of the cis- compounds. For the low spin complexes $Fe(\underline{o}\text{-phen})_2(CN)_2$, $Fe(\underline{o}\text{-phen})_3Cl_2$ and $Fe(bipy)_3Cl_2$ a low intensity band has been observed at about 12,000 cm^{-1} [73,79]. For the dicyano- complex the band was originally assigned to the $^1A_1 \longrightarrow {}^1T_1$ transition, however it has been recently assigned to the spin forbidden $^1A_1 \longrightarrow {}^3T_1$ transition[73,106].

Ruthenium Complexes

All the ruthenium(II) complexes prepared so far are low spin with $^1A_1$ ground states. An attempt has been made to determine the ligand field bands of $Ru(\underline{o}\text{-phen})_3^{2+}$ from the emission spectrum of the complex. A band observed at 17,700 cm^{-1} was initially assigned to the $^1T_1 \longrightarrow {}^1A_1$ ligand field transition[95], but has recently been assigned as a $\pi^* \longrightarrow t_{2g}$ charge transfer emission band[95a].

Ligand field bands have not been observed in the present work and will not be discussed further.

EFFECT OF LIGAND SUBSTITUENTS

A number of studies have been made of the stability constants and reduction-oxidation potentials of the ferroin and ferroin-ferriin systems involving substituted phenanthroline ligands e.g.[107,108,109]. Similar studies have also been carried out on the ruthenium system[110]. The stability of the complexes to acid decomposition generally follows the order of pKa's of the substituted ligands e.g. 5MePh > o-phen > 5PhenylPh > 5ClPh > $5NO_2Ph$[108].

The ligand field band energies of the bis-(o-phenanthroline)copper(II) complexes also follow this order[111]. The observed order may be attributed to substituent indicative effects on the σ-system of the phenanthroline ligands.

The positions of the $t_2 \longrightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands will depend on the effect of the substituents on the π-system of the ligand. This will not necessarily be the same as the influence of the substituents on the σ- bonding system.

Day and Saunders[100] have investigated the position of the $t_2 \longrightarrow \pi^*(1)$ transition for a number of methyl-substituted ferroin complexes. They found that when more than

TABLE 6.11 - ABSORPTION MAXIMA OF THE LOW ENERGY $t_2 \longrightarrow \pi^*(1)$ BAND

(Solvent : water)

(a) Iron(II) Complexes [108]

Complex	ν_{max} (cm^{-1})
$Fe(5MePh)_3^{2+}$	19,400
$Fe(\underline{O}\text{-}phen)_3^{2+}$	19,600
$Fe(5\ Phenyl\ Ph)_3^{2+}$	19,400
$Fe(5ClPh)_3^{2+}$	19,550
$Fe(5NO_2Ph)_3^{2+}$	19,600

(b) Ruthemium(II) Complexes [110]

Complex	ν_{max} (cm^{-1})
$Ru(\underline{o}\text{-}phen)_3^{2+}$	22,400
$Ru(5MePh)_3^{2+}$	22,300
$Ru(5ClPh)_3^{2+}$	22,250

one substituent was present the overall influence of the substituents was additive.

Table 6.11(a) lists the energy in cm^{-1} for the $t_2 \longrightarrow \pi^*(1)$ transition of several ferroin complexes of 5-substituted o-phenanthrolines[108]. Similar data is listed in Table 6.11(b) for some tris-(5-substituted-o-phenanthroline) ruthenium complexes[110]. The order of energies found is:

$$M(\text{o-phen})_3^{2+} = M(5NO_2Ph)_3^{2+} >$$
$$M(5MePh)_3^{2+} > M(5ClPh)_3^{2+}$$

It can be seen that inductive substituents, both electron donating and electron withdrawing, have a greater effect on the position of the band than does the mesomeric nitro-substituent. The position of the $\pi \rightarrow \pi^*(1)$ band for the 5-substituted-o-phenanthrolines used in the present work follows a similar order (Table 6.21).

TABLE 6.21

ULTRA VIOLET - VISIBLE SPECTRA OF THE O-PHENANTHROLINE LIGANDS [a]

Compound	Solventor Solid state Matrix	b	$\pi \rightarrow \pi^*$(1) Band	$\pi \rightarrow \pi^*$(2) Band
o-phen	H_2O	ν	37,450; (29,400; 30,900; 32,300; 34,900; 36,900)	44,400; (43,500)
		ε	2.4×10^4	5.8×10^4
	CH_2Cl_2	ν	37,750; (29,600; 30,300; 30,900; 32,300; 34,700, 36,200)	
		ε	2.6×10^4	
	KBrdisc	ν	37,200; (33,900)	44,400
5McPh	CH_2Cl_2	ν	37,200; (29,800; 30,300; 33,200; 34,500)	
		ε	3.0×10^4	
	KBrdisc	ν	36,700; (34,000)	43,900
5ClPh	CH_2Cl_2	ν	36,100; (28,000; 29,500; 33,000; 37,000)	
		ε	3.03×10^4	
$5NO_2Ph$	CH_2Cl_2	ν	36,430; (28,800; 30,300; 31,500)	(41,300)
		ε	2.25×10^4	

a Shoulders associated with the main band are in parentheses   b wave number (ν) in cm^{-1}.

SECTION 6.2

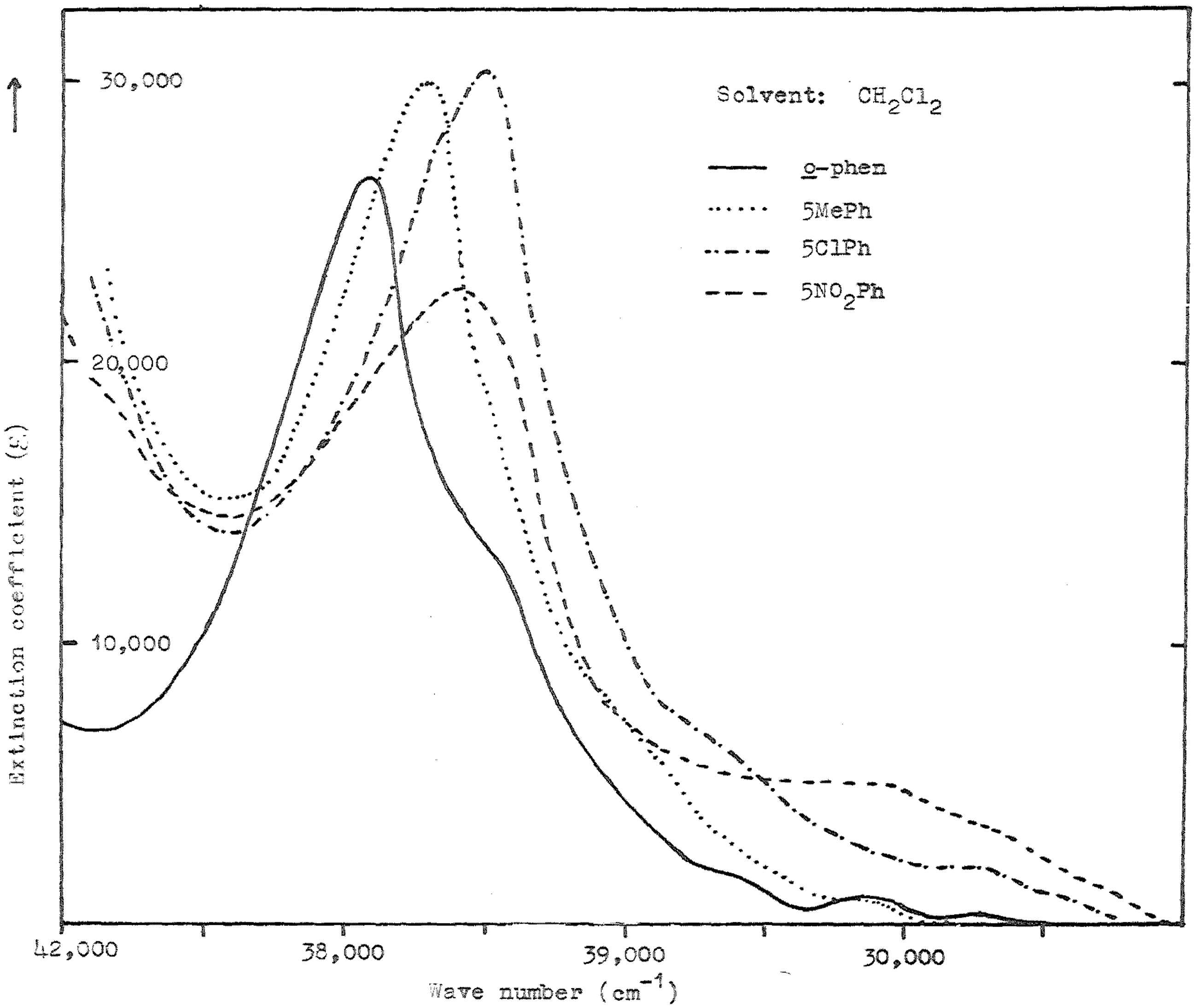
Discussion of the Electronic Spectra of some o-phenanthroline Complexes of Ruthenium(II)

INTRODUCTION

The ultraviolet-visible spectra of the complexes $Ru(phen)_2X_2$ have been measured where phen = o-phenanthroline, 5-chloro-o-phenanthroline and 5-methyl-o-phenanthroline, and X = Cl^-, Br^-, I^-, SCN^- and CN^-. Only one tris- complex, $Ru(o\text{-}phen)_3Cl_2$, has been studied. Solvents used were nitrobenzene and dichloromethene rather than strongly coordinating solvents such as water and ethanol[112]. Some spectra were also measured in dimethylformamide solutions. Numerical data for the free ligands whose complexes are studied in this section and in Section 6.3 are listed in Table 6.21. Numerical data for all the ruthenium complexes are listed in Table 6.22, and the spectral curves for some of the o-phenanthroline complexes, which are typical of those obtained, are illustrated in Figure 6.22.

All the complexes gave spectra with a band near 20,000 cm^{-1} ($\varepsilon \sim 10^4$) with one or more shoulders to higher energy and, for some of the complexes, a shoulder to lower energy. The spectra of some complexes showed a band at $\sim$ 28,000 cm^{-1} ($\varepsilon \sim 500$). These bands are both assigned

FIGURE 6.21


30,000
20,000
10,000
Extinction coefficient (ε)
Solvent: CH_2Cl_2
o-phen
5MePh
5ClPh
$5NO_2Ph$
42,000
38,000
39,000
30,000
Wave number (cm^{-1})

to metal ⟶ ligand charge transfer transitions.

All the compounds have a band at ~ 38,000 cm^{-1} ($\varepsilon \sim 10^5$) which is assigned to an intraligand transition. This band has a large number of shoulders to lower energy which are attributable to vibrational structure and to the presence of two overlapping transitions within the band envelope (page 134).

DISCUSSION

Charge Transfer Transitions

(1) The Low Energy Charge Transfer Band ($t_2 \rightarrow \pi^*(1)$)

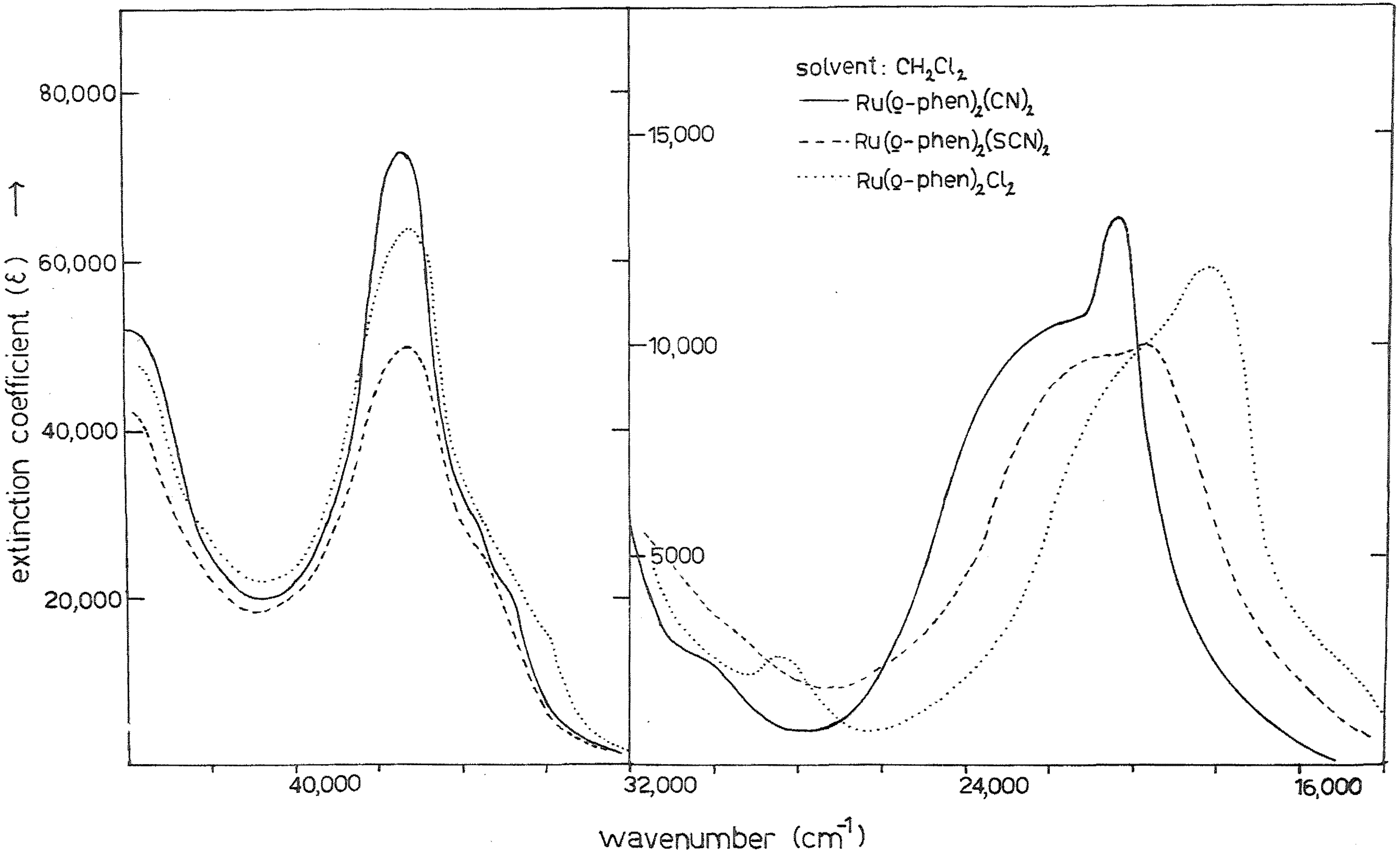
The band near 20,000 cm^{-1} has been assigned by previous workers (page 136) to a metal ⟶ ligand charge transfer transition[99,100,104,105]. For bipyridyl complexes the intensity of the band has been shown to increase as one, two and three bipyridyl ligands are coordinated to the metal[96] indicating that the transition involves the bipyridyl ligand. This has also been generally observed in the present work for the bis- and tris-(o-phenanthroline) complexes.

The energy of the band varies greatly with increasing average ligand field strength about the metal ion as follows:

$$(\underline{o}\text{-phen}) > CN^- > SCN^- > I^- \sim Br^- > Cl^-$$

The order is essentially the same for the complexes of

FIGURE 6.22



solvent: CH_2Cl_2
$Ru(\underline{o}\text{-phen})_2(CN)_2$
$Ru(\underline{o}\text{-phen})_2(SCN)_2$
$Ru(\underline{o}\text{-phen})_2Cl_2$
extinction coefficient (ε) ↑
80,000
60,000
40,000
20,000
15,000
10,000
5000
40,000
32,000
24,000
16,000
wavenumber (cm^{-1})

all the substituted phenanthroline ligands (Figure 6.22) although the relative energy of the bands for the di-iodo- and dibromo- complexes differ.

As the average ligand field strength about the metal ion is increased the metal t_2-orbitals will be increasingly stabilised with respect to the ligand π^*- orbitals. This effect is, as expected, more pronounced when good π-acceptor ligands such as thiocyanate, cyanide and o-phenanthroline are coordinated to the metal ion (Figure 6.23). The energy of this band can be regarded as reflecting the increasing importance of π-bonding in the series.

$$Cl^- \sim Br^- \sim I^- < SCN^- < CN^- < \underline{o}\text{-phen.}$$

The order of band energies for the different phenanthroline ligands is

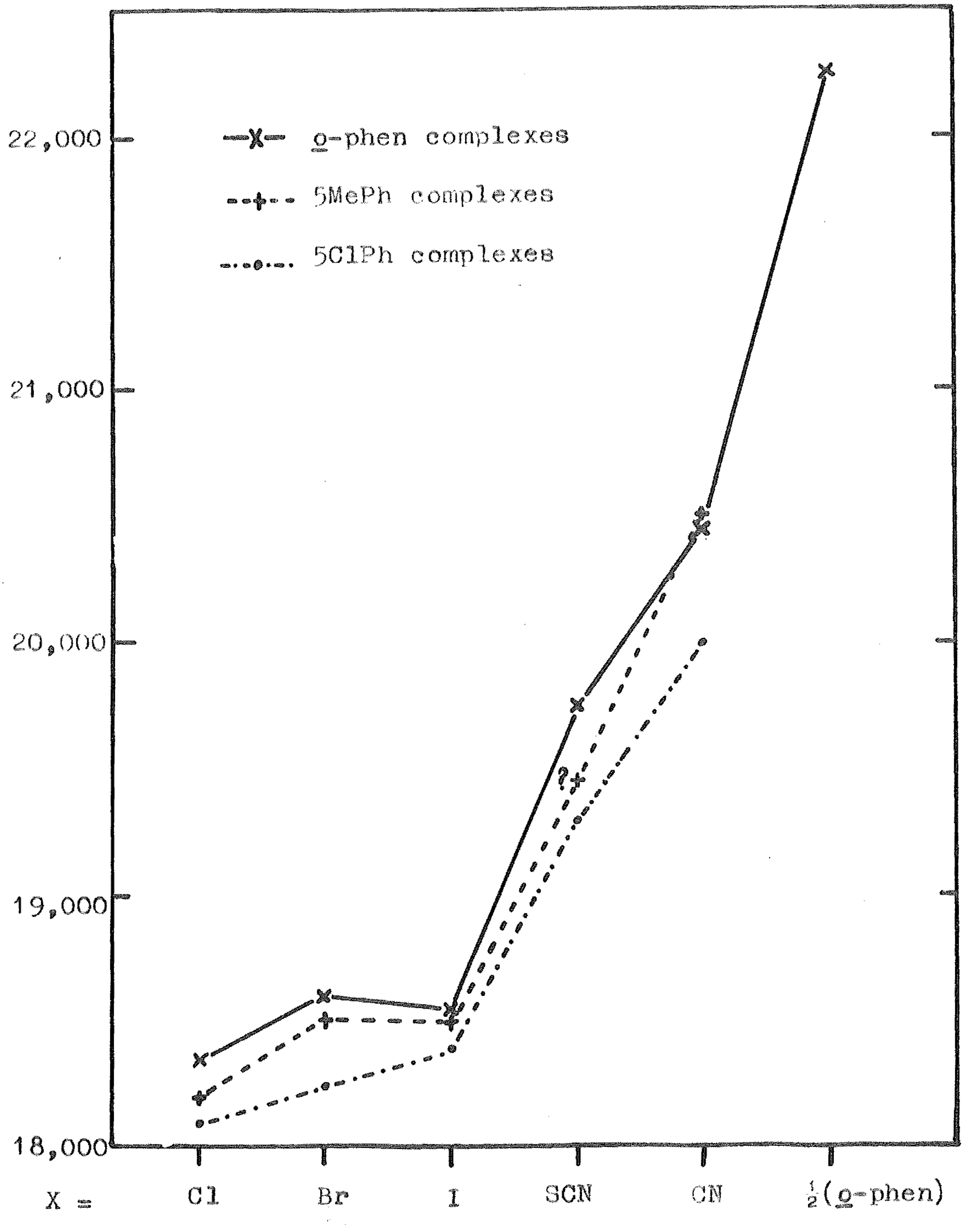
$$\underline{o}\text{-phen} \gtrsim \text{5MePh} > \text{5ClPh}$$

which is similar to that found for the tris- complexes of iron(II) [108] and ruthenium(II) [110].

For the complexes $Ru(phen)_2X_2$ the energy of the band varies more when X changes than when the substitutent or the phenanthroline ligand is changed (Figure 6.23). Therefore any differences in the metal-ligand bonding which result from the introduction of substituents on to the phenanthroline skeleton do not seem to be reflected in the energy of the low energy metal → ligand charge

FIGURE 6.23

ENERGY OF THE $t_2 \longrightarrow \pi^*(1)$ BAND FOR THE $Ru(phen)_2X_2$ COMPLEXES (Solvent: CH_2Cl_2)



transfer band to any great extent.

The position of the band is markedly dependant on the solvent in which the spectra are measured. For Ru(o-phen)$_2$(CN)$_2$ the order of band energy for different solvents is

$$\mathrm{EtOH} > \mathrm{CH_2Cl_2} > \mathrm{DMF} > \phi\mathrm{NO_2}$$

For the complexes of the weak field ligands chloride and bromide the order is

$$\mathrm{DMF} > \mathrm{CH_2Cl_2} > \phi\mathrm{NO_2}$$

The solvent induced shifts in the band energy cannot be attributed to differences in the dielectric constants of the solvents which are in the following order[113,115]:

$$\mathrm{DMF}(36.7) > \phi\mathrm{NO_2}(34.8) > \mathrm{EtOH}(24.3) > \mathrm{CH_2Cl_2}(9.08)$$

In this work comparisons of the positions of bands are made for spectra measured in the same solvent.

(2) The High Energy Charge Transfer Transition ($t_2 \rightarrow \pi^*(2)$)

An absorption band is observed for some of the complexes near 28,000 cm^{-1} with an extinction coefficient of ~ 500. The band is clearly resolved only for the o-phenanthroline complexes with weak field ligands. Some of the complexes of the substituted phenanthrolines have bands near 28,000 cm^{-1}, but usually an unresolved shoulder is observed.

The spectra of the bipyridyl complexes, $Ru(bipy)_2X_2$, where X is a weak field ligand, have a band in this region with an intensity close to that of the low energy charge transfer band[96]. For these complexes the band energy changes in a similar way to that of the low energy band as the average ligand field strength about the metal ion changes. It is assigned to the $t_2 \longrightarrow \pi^*(2)$ transition [96,99]. In the phenanthroline complexes the band shifts in a similar way only for the $Ru(\underline{o}\text{-phen})_2X_2$ complexes. For the complexes of the substituted phenanthrolines the shifts are less regular.

Resolution of the band is poor and changes in the positions of shoulders on the low energy side of the intense $\pi \rightarrow \pi^*$ band and on the high energy side of the low energy charge transfer band will have a large effect on the position of the band. Because of this a definite assignment of the band position is not possible. The intensity of the band would seem to exclude assignment to a ligand field transition.

On the basis of comparison with the spectra of the bipyridyl complexes[96], the band is tentatively assigned to a high energy metal ⟶ ligand charge transfer transition.

Intraligand $\pi \longrightarrow \pi^*$ Transitions

Only the band corresponding to the low energy $\pi \longrightarrow \pi^*$ transition ($\pi \longrightarrow \pi^*(1)$) has been resolved for all the complexes in the present study. The high energy band ($\pi \longrightarrow \pi^*(2)$) is sometimes observed as a shoulder but will not be discussed since its position is not known with sufficient accuracy for meaningful trends to emerge.

For o-phenanthroline and 5-methyl-o-phenanthroline the band generally shifts to lower energy on coordination. This shift has been attributed to the influence of charge on the ligand π-orbital system (page 135), but this cannot be the only important factor.

In contrast a shift to higher energy is observed for 5-chloro-o-phenanthroline. Interaction between the t_2-orbitals of the metal and the π^*-orbitals of the ligands will increase the energy of the π^*-orbitals of the ligand and decrease that of the t_2-orbitals. It might be concluded from the direction of the shift in energy of the $\pi \longrightarrow \pi^*$ band for the 5-chloro-o-phenanthroline complexes that a greater degree of π-interaction occurs for the complexes of this ligand than for those of the other phenanthrolines. The $t_2 \longrightarrow \pi^*(1)$ charge transfer transition is observed at slightly lower energy for the 5-chloro-o-phenanthroline complexes than for the other complexes (Figure 6.23). This may imply that the relative energies of the metal ion t_2-orbitals and the free ligand π^*-orbitals are closer together than is the case for the other free phenanthroline ligands.

For all the complexes of all the phenanthroline ligands the $\pi \rightarrow \pi^*(1)$ band moves to higher energy in the order

$$Cl^- \sim Br^- < I^- \sim SCN^- < CN^- < \underline{o}\text{-phen}$$

which is similar to the order observed for the energy of the $t_2 \longrightarrow \pi^*(1)$ transition, although the effect is less marked for the intraligand transition. The order found is consistent with the shifts that would be predicted in terms of increasing π-overlap of the metal t_2-orbitals with the π-orbitals of the phenanthroline ligands.

For $Ru(\underline{o}\text{-phen})_3Cl_2$, the only tris- complex studied in this work, the band is found at higher energy than for free <u>o</u>-phenanthroline, as for the 5-chloro-<u>o</u>-phenanthroline complexes. In terms of the π-interaction interpretation used above this suggests a greater degree of metal-ligand π-interaction for the tris-complexes than for any of the bis-complexes. This is in agreement with the observations of the relative energies of the $t_2 \longrightarrow \pi^*(1)$ charge transfer band.

The cyano- and thiocyanato- ligands might be expected to give rise to their own $\pi \rightarrow \pi^*$ transition. In the case of the dicyano- complex the band would be expected at about 45,000 cm^{-1} [97]. The spectra for the complexes of these ligands show no additional shoulders which could be assigned to this transition.

SECTION 6.3

Discussion of the Electronic Spectra of some bis- and tris-(o-phenanthroline) Complexes of Iron(II)

INTRODUCTION

The ultraviolet-visible spectra of a number of high spin and low spin iron(II) phenanthroline complexes have been measured in solutions and in the solid state.

Numerical data for spectra of the low spin complexes $Fe(phen)_3^{2+}$ and $Fe(phen)_2(CN)_2$, where phen = o-phenanthroline, 5-methyl-o-phenanthroline and 5-nitro-o-phenanthroline, are listed in Table 6.31.

Considerable experimental difficulties were experienced in the measurement of the spectra of the high spin complexes $Fe(phen)_2X_2$ where "phen" is as above, and X = Cl^-, Br^-, I and SCN^-. The spectra of some of these complexes have been measured in dry dichloromethane, however many complexes were either insoluble in the solvent or immediately disproportionated in solution. Because of this measurement of the spectra was attempted in the solid state. Some of the difficulties experienced in this work are described below. Numerical data obtained from the spectra of the high spin complexes are listed in Table 6.32.

The three basic types of spectral bands found for these complexes (both high spin and low spin) are the same as those found for the low spin ruthenium(II) complexes, i.e., $t_2 \longrightarrow \pi^*(1)$ and $t_2 \longrightarrow \pi^*(2)$ charge transfer, and intraligand $\pi \rightarrow \pi^*(1)$ transitions.

MEASUREMENT OF SOLID STATE SPECTRA

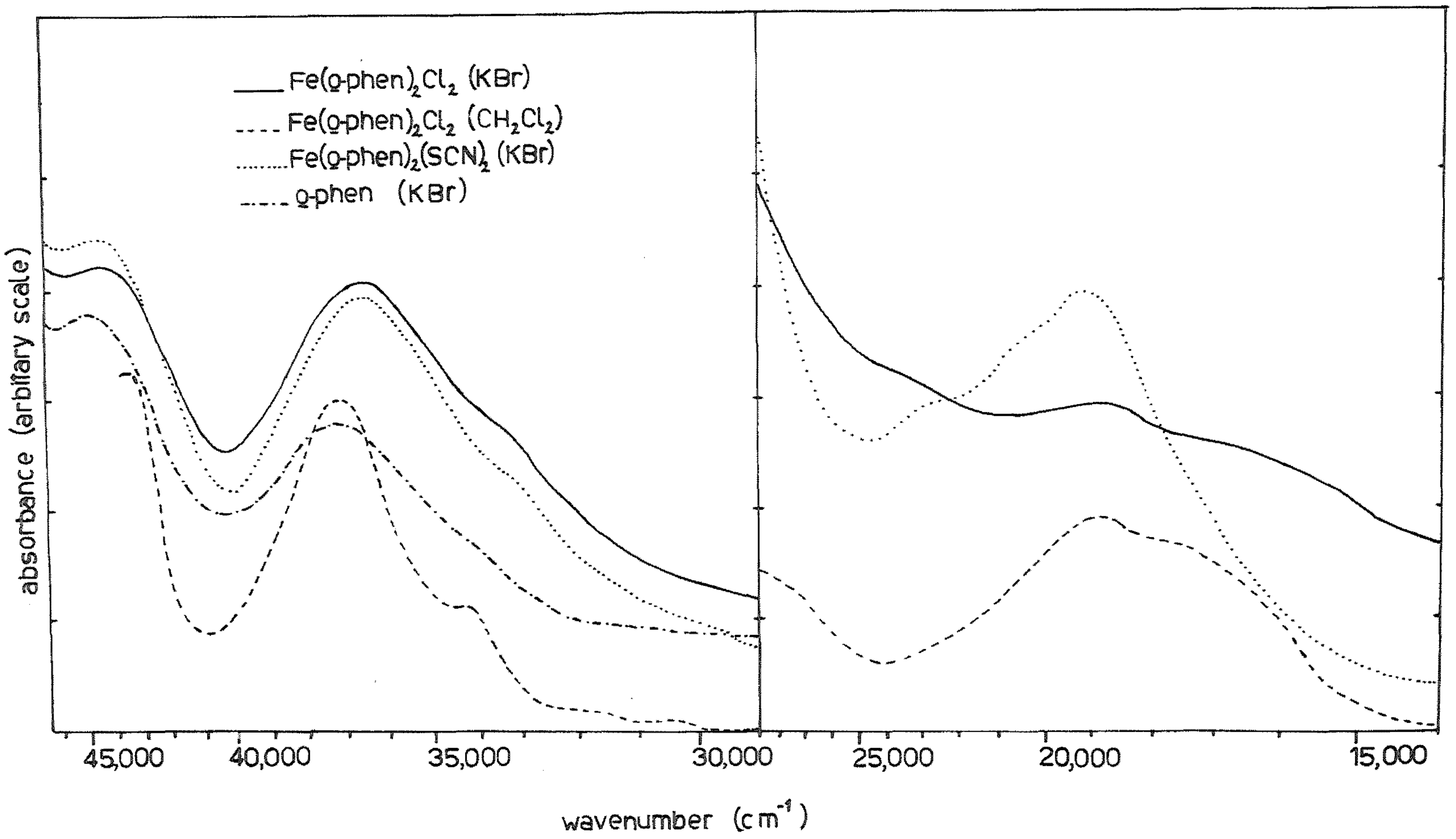
The methods used were: (1) diffuse reflectance, (2) potassium bromide disc absorption and (3) nujol mull absorption. These will be discussed separately.

(1) Diffuse Reflectance Spectra

The method used was to powder the complex and to dilute it by intimately mixing the finely ground sample with magnesium oxide. The mixture was put into a holder and covered with a silica glass window, or spread on a white filter paper.

Konig and Madeja have reported the reflectance spectra of a number of bis-(o-phenanthroline)iron(II) complexes[79]. In the present work spectra of the standard reported by these workers could not be obtained. The charge transfer and intraligand transitions generally gave broad featureless plateau regions extending on both sides of the expected band positions. In addition the positions of the bands could not be reproduced when the complexes were further diluted with magnesium oxide. This is probably due to

FIGURE 6.31


Fe(o-phen)$_2$Cl$_2$ (KBr)
Fe(o-phen)$_2$Cl$_2$ (CH$_2$Cl$_2$)
Fe(o-phen)$_2$(SCN)$_2$ (KBr)
o-phen (KBr)
absorbance (arbitary scale)
45,000
40,000
35,000
30,000
25,000
20,000
15,000
wavenumber (cm^{-1})

different components of the bands being accentuated at different dilutions[116].

(2) Potassium Bromide Disc Absorption Spectra

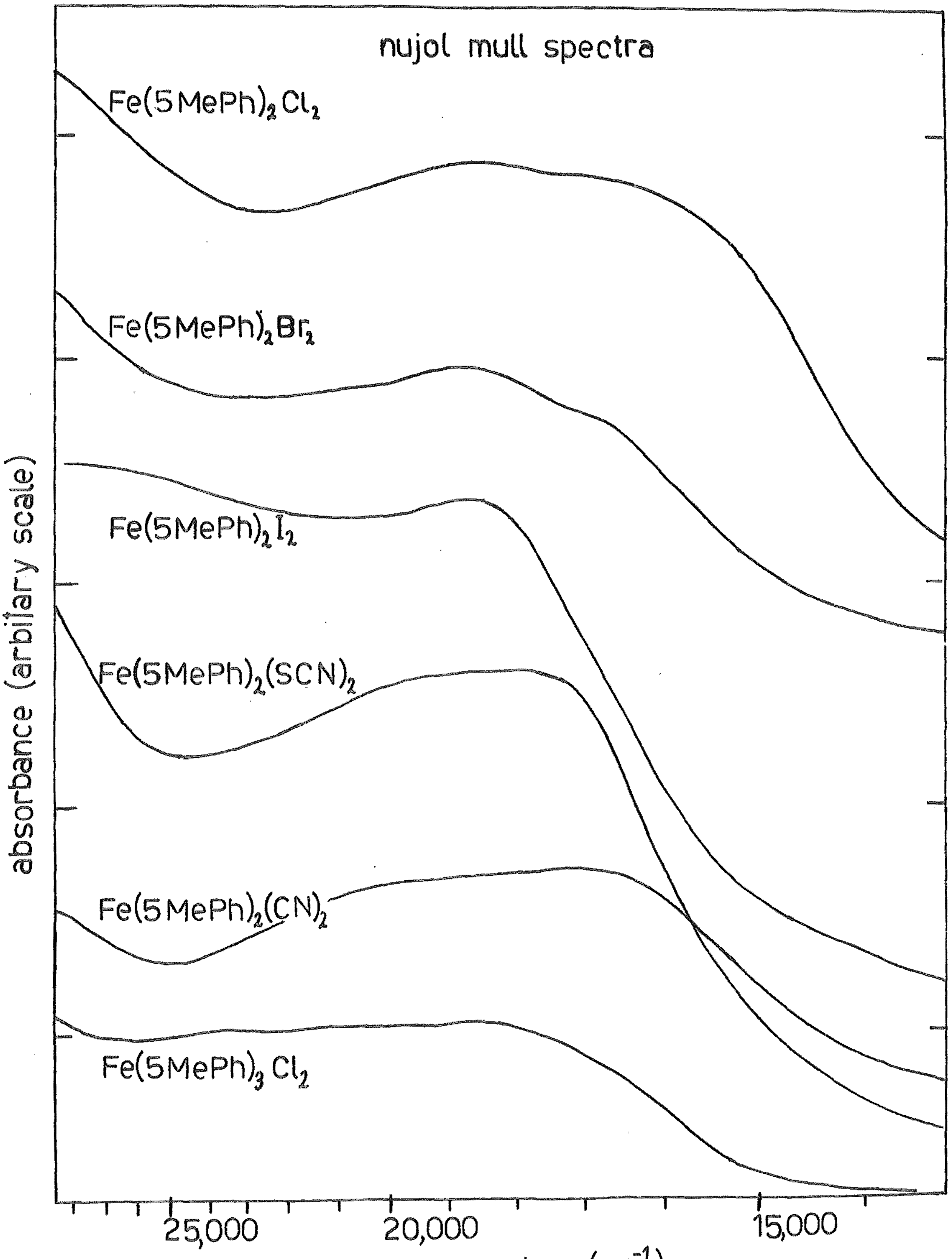
Typical absorption curves obtained for some complexes in potassium bromide discs are shown in Figure 6.31, where a solution spectrum is also reproduced for comparison.

The discs were prepared by intimately grinding 0.5 - 2.0 mg of the complex with about 150mg of very dry potassium bromide in a mortar and pestle, and finally in a ball mill. The finely powdered mixture was placed in a disc and subjected to a high pressure under vacuum for 5 minutes. The resulting discs were stored over calcium chloride and were handled with care in order to avoid fogging the surfaces.

Resolution obtained for the intense charge transfer and intraligand bands was often comparable with solution spectra, and reproducibility on dilution of the complex was good. However under the conditions used in making the discs there is the possibility of ligands such as chloride, iodide, thiocyanate and cyanide being replaced by bromide ions. It is difficult to ensure that such replacement has not occurred, and for this reason the spectra obtained must be regarded with caution.

An attempt was made to produce discs with potassium chloride and potassium iodide in order to remeasure the

FIGURE 6.32


nujol mull spectra
Fe(5MePh)$_2$Cl$_2$
Fe(5MePh)$_2$Br$_2$
Fe(5MePh)$_2$I$_2$
Fe(5MePh)$_2$(SCN)$_2$
Fe(5MePh)$_2$(CN)$_2$
Fe(5MePh)$_3$Cl$_2$
absorbance (arbilary scale)
25,000
20,000
15,000
wavenumber (cm^{-1})

spectra of Fe(o-phen)$_2$Cl$_2$ and Fe(o-phen)$_2$I$_2$. The surfaces of the discs clouded very rapidly even in a dry atmosphere. For this reason they were unsuitable for ultraviolet-visible work.

(3) Nujol Mull Absorption Spectra

Typical absorption curves obtained from nujol mulls of some complexes are shown in Figure 6.32. The method used was to grind the complexes with a little nujol between ground glass plates until a smooth mull was obtained. The mulls were then spread between optically flat silica glass plates.

Resolution of the charge transfer band at ~ 20,000 cm^{-1} was usually poor, but better than that obtained from the reflectance spectra. Intraligand bands could not be resolved by this method. Reproducibility of the resolved bands on dilution was usually good.

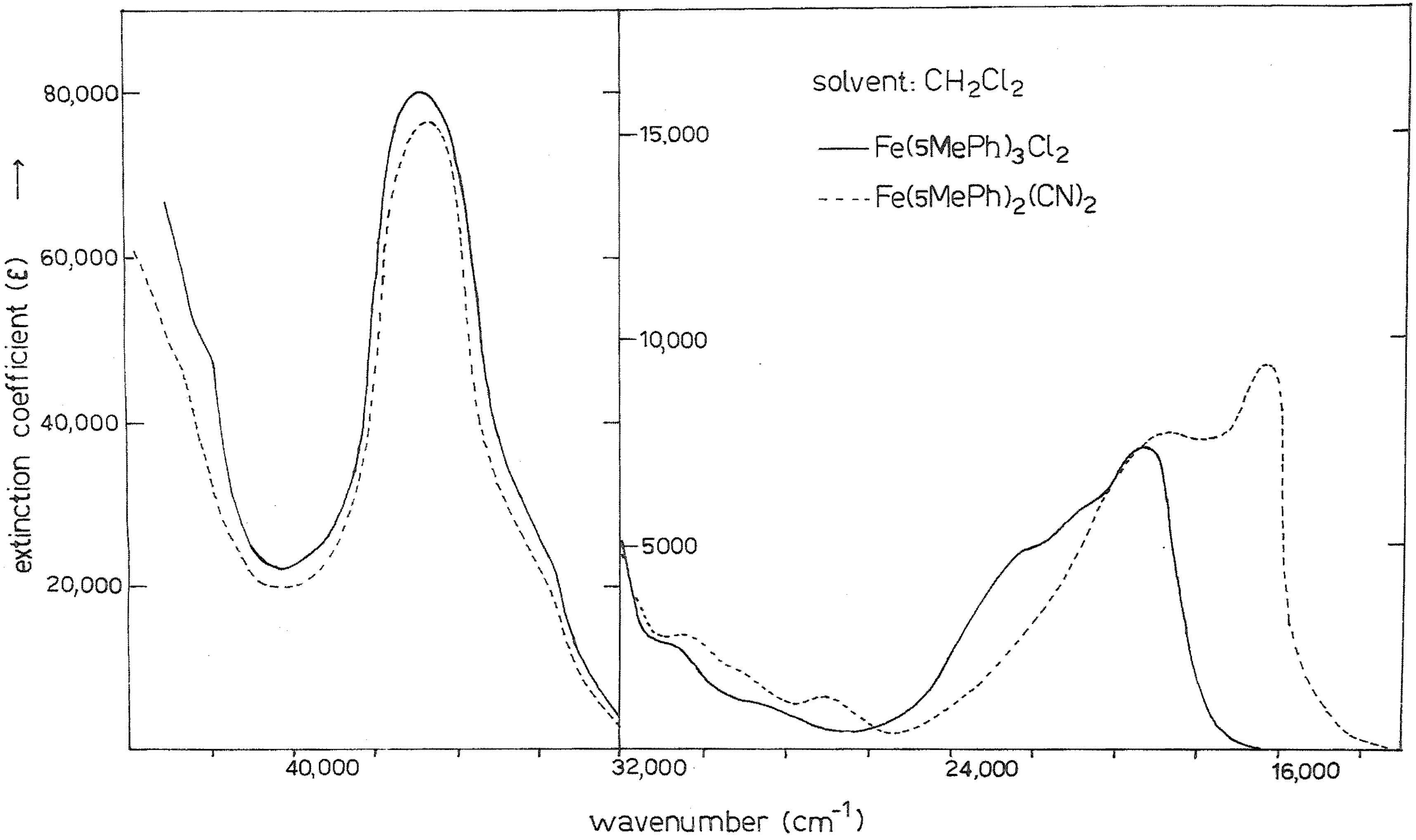
LOW SPIN COMPLEXES

The numerical data for the spectra of the low spin complexes is listed in Table 6.31. The spectra curves for Fe(5MePh)$_2$(CN)$_2$ and Fe(5MePh)$_3$Cl$_2$ in dichloromethane, which are typical of those obtained, are illustrated in Figure 6.33.

Low Energy Charge Transfer Transition ($t_2 \longrightarrow \pi^*(1)$)

The changes in energy of the low energy charge transfer transition ($t_2 \longrightarrow \pi^*(1)$) for different ligand substituents

FIGURE 6.33



solvent: CH_2Cl_2
$Fe(5MePh)_3Cl_2$
$Fe(5MePh)_2(CN)_2$
extinction coefficient (ε) →
80,000
60,000
40,000
20,000
15,000
10,000
5000
40,000
32,000
24,000
16,000
wavenumber (cm^{-1})

have been discussed (page 139). As for the ruthenium complexes (Section 6.2) the band is at higher energy for the tris-complexes than for the bis-complexes. The band due to this transition is at lower energy for the iron(II) complexes than for the analogous ruthenium(II) complexes, indicating that the metal t_2-orbitals of ruthenium are at lower energy than those of iron. This has also been found for complexes of these metals with bipyridyl[96] and has been attributed to a greater degree of metal — ligand π-bonding with ruthenium than with iron[97].

High Energy Charge Transfer Transition ($t_2 \longrightarrow \pi^*(2)$)

A band is found near 28,000 cm^{-1} with an extinction coefficient of about 500 for the dicyano-complexes of o-phenanthroline and 5-methyl-o-phenanthroline. For the 5-nitro-o-phenanthroline complex the bond is probably masked by the prominant shoulders on the low energy $\pi \rightarrow \pi^*$ bands in this region (Figure 6.21). The band is not observed in the spectra of tris-complexes. It appears to be similar to the band found in this region for some of the ruthenium complexes and is tentatively assigned as a metal ⟶ ligand charge transfer band.

Low Energy Intraligand Transition ($\pi \longrightarrow \pi^*(1)$)

The $\pi \rightarrow \pi^*(1)$ band is at higher energy for the iron tris-complexes than for the bis-complexes, as found for the ruthenium complexes. For some complexes the band is at higher energy than for the free ligands. These changes in position are similar to those observed for the ruthenium system and can be explained in terms of the effect of metal-ligand π- interaction.

HIGH SPIN COMPLEXES

Discussion of the spectra of the high spin complexes is limited by the poor quality of the spectra. Differences in the positions of the bands from one complex to another are smaller than the differences found between spectra measured by different methods. However the following general observations can be made.

(1) Differences in the positions of the bands from one complex to another are smaller than those found for the low spin complexes.

(2) A band corresponding to the high energy charge transfer band ($t_2 \longrightarrow \pi^*(2)$) is not generally observed. This may be because of the poor quality of the spectra.

(3) Generally the following trend in energy is observed for both the low energy charge transfer band ($t_2 \longrightarrow \pi^*(1)$) and the low energy intraligand band ($\pi \rightarrow \pi^*(1)$):

$$\mathrm{SCN} > \mathrm{I} > \mathrm{Br} > \mathrm{Cl}$$

This trend is not as marked as that found for the low spin complexes.

The low energy charge transfer band has been assigned to the $t_2 \longrightarrow \pi^*(1)$ transition as for the low spin complexes[73,79]. On the basis of the effects of differences in the t_2-orbital stabilisation by π- interaction the band would be expected at lower energy for the high spin complexes. In fact, for all the high spin complexes, the band is found between the band energies of the low spin bis- and tris- o-phenanthroline complexes. This observation cannot be explained in terms of our present knowledge, but suggests that it is not reasonable to compare high spin and low spin complexes.

SUMMARY

It is apparent that the energy of the t_2 metal orbitals and hence their position relative to the π and π^*-orbitals of the o-phenanthroline ligands is important in deciding trends in the electronic transitions for the o-phenanthroline complexes of iron(II) and ruthenium(II). This applies particularly to the charge transfer bands of the low spin complexes and, to a lesser extent, to the high spin complexes. The low energy $\pi \rightarrow \pi^*(1)$ transition is also affected but to only a small degree. The energy of the $\pi \rightarrow \pi^*(1)$ band can be interpreted in terms of π-interaction between the metal and the ligand in these complexes. Changing the substituents on the o-phenanthroline ligand has a small effect on the energy of the $t_2 — \pi^*(1)$ transition relative to the effect of changing the average ligand field strength about the metal ion.

CHAPTER 7

Ligand Substituents and their Value in the Study of the Chemistry of Complexes

Studies of the physico-chemical behaviour of a series of complexes which differ only in the nature of the ligand substituents are potentially a valuable method of obtaining information about metal-ligand bonding in such complexes. In each part of this work a comparison has been made of the influence of different ligand substituents on aspects of the chemistry of the complexes. It is clear that studies of the effects of ligand substituents on metal-ligand bonding and metal stereochemistry in complexes require use of a wide range of techniques for worthwhile results to be obtained. In Part I a detailed study has been made while in Part II only the electronic spectra have been used as a probe into the complexes. The overall findings are briefly summarised in this chapter.

In the case of the four-coordinate dipyrromethene complexes discussed in Part I the metal ions are forced to adopt a tetrahedral or severely distorted square planar configuration in order to overcome intramolecular interactions between the ligands. Structural modification of the ligand occurs when the stereochemical requirements of the metal dominate. One would expect that changes of stereochemistry and ligand configuration would be easily observed by the usual physico-chemical methods. Changes in bonding are more subtle and are probably best investigated by consideration of an extensive series of related compounds with slight variations within the series.

PROTON MAGNETIC RESONANCE SPECTROSCOPY

NMR spectroscopy is a valuable method of studying the environment of atoms in a molecule and the stereochemistry of compounds. The method is also potentially capable of giving information on the nature of the metal-ligand bonding in the complexes. The results in Part I indicate that whereas the presence of different substituents is valuable for the assignment of resonance peaks, the changes in peak position are difficult to interpret in terms of substituent effects on bonding. However shifts resulting from a stereochemical change are significant and can be used to assign structures. The significance of certain shifts in the PdL_2 complexes was only apparent when the X-ray crystal structure of $Pd(MMPM)_2$ was solved, but with this as background the interpretation of the NMR of the PdX(L)(LH) complexes could be used as a method of structural investigation.

ELECTRONIC SPECTRA

Electronic spectral studies have been made of the complexes in both parts of the present work. In these complexes, and in particular the o-phenanthroline complexes, metal-ligand orbital interactions will affect the relative energies of the metal t_2 and ligand π and π^*-orbitals. The relative energy of these orbitals is estimated from a study of the charge transfer spectra ($t_2 \longrightarrow \pi^*$ transitions) and of the intraligand spectra ($\pi \longrightarrow \pi^*$ transitions).

It was found that substituents on the ligands have little effect on the energy of the charge transfer transitions, however considerable differences have been found in the way the intraligand $\pi \longrightarrow \pi^*$ bands shift on coordination, particularly in the case of the dipyrromethene complexes.

On the other hand, other ligands (e.g. X in M(o-phen)$_2$X$_2$) have a large influence on the energy of the metal t_2- orbitals and hence on the position of the charge transfer bands. The observed trends can be correlated with metal-ligand π-interactions.

X-RAY SINGLE CRYSTAL ANALYSIS

The X-ray single crystal study of Pd(MMPM)$_2$ was of considerable importance in the study of the dipyrromethene complexes and, as indicated earlier, helped in the interpretation of NMR spectra. Whereas this technique is very powerful, especially for stereochemical studies, it is quite possible that the small differences observed in the electronic spectra of the complexes would not be predicted from the

X-ray study of such a series of compounds.

CONCLUSION

The present study has not revealed any major differences in metal-ligand bonding which result from ligand substituents alone. On the other hand factors such as the nature of the metal ion, the position of the ligand substituent relative to the metal ion and neighbouring ligands, and the presence of other ligands in the complexes have led to significant changes in the electronic and molecular structure of the complexes.

APPENDIX A

Experimental Methods

Ultraviolet-Visible Spectra

Ultraviolet-visible spectra were recorded over the range from 45,000 cm^{-1} to 7,000cm^{-1} on a Shimadzu Multipurpose Spectrophotometer or on a Beckman DK-2A Spectrophotometer. All solution spectra were recorded using silica glass 1cm cells. Solid state absorption spectra were recorded as described on pages 149 to 151. Solid state reflectance spectra were recorded using either the Shimadzu or Beckman reflectance attachments.

Molar extinction coefficients ($\mathcal{E}$) were determined from the solution spectra according to the expression

$$\mathcal{E} = D/c$$

where D is the optical density and

c is the concentration in moles/litre.

The solution spectra were reproducible to within 100 cm^{-1} for different runs with the same complex. The instruments were calibrated at 3-monthly intervals using a mercury lamp.

Infrared Spectra

Spectra in the region 4000 cm^{-1} - 400cm^{-1} were recorded for samples in nujol mulls or potassium bromide discs using either a Shimadzu IR-27G spectrophotometer or a Perkin-Elmer 337 spectrophotometer, calibrated with polystyrene.

Spectra in the region 400 - 40cm^{-1} were recorded for samples in nujol mulls on polyethylene discs using a R.I.I.C. F.S.-720 Fourier Spectrophotometer.

Nuclear Magnetic Resonance Spectra

NMR spectra were recorded on a Varian A-60 spectrometer over the range 16ppm to -8 ppm with respect to T.M.S. in deuterochloroform solutions. T.M.S. and chloroform were used as internal standards. Reproducibility was within ± 0.05cps ($\sim$ 0.01ppm).

Conductivities

Molar conductivities were measured at 20°C using a Philips P.R. 9550/01 conductance bridge and a cell with removable platinum electrodes. The cell was calibrated with a standard potassium chloride solution[118]. The molar conductivity (Λ_m) is given by the expression

$$\Lambda_m = \text{cell constant} \times 10^3/cR$$

where C is the concentration in moles/litre (usually 10^{-3}) and R is the resistance of the solution in ohms.

Representative values of Λ_m (ohms^{-1}moles^{-1} cm) for the solvents used in this work are:

Ion type	nitrobenzene	nitromethane	dimethylformamide
1:1	20 - 30	70 - 90	60 - 80
1:2	45 - 55	150 - 170	110 - 130
1:3	70 - 80	230 - 250	160 - 180

Magnetic Susceptibilities

(1) Gouy Method: The compound tris-(ethylenediamine) nickel(II) thiosulphate[119] was used as a calibrant. Gram magnetic susceptibilities (χ_g) were calculated from the formula

$$10^6 \chi_g = (\alpha - \beta F)/W$$

where W is the weight of the sample and α and β are tube constants. F is the difference in weight of the sample in the presence or absence of a magnetic field.

(2) NMR Method[120]: This method was used to determine whether some compounds were diamagnetic. Magnetic susceptibilities may be calculated using the equation

$$\chi_g = 3\Delta f/2\pi f_m + \chi_o + \chi_o(d_o - d_s)/m$$

where f is the frequency separation between two peaks (c.p.s.), f is the frequency of proton resonances in cps (60×10^6), m is the mass of substance in 1ml of solution, χ_o is the mass susceptibility of the solvent and d_o and d_s are the densities of the solvent and solution respectively.

Provided dilute solutions ($\sim 10^{-3}$m) are used and the compound molecular weight is about 1000,

$$\chi_o = -\chi_o(d_o - d_s)/m$$

If no peak separation could be achieved the sample was assumed to be diamagnetic.

Analyses

Carbon, hydrogen and nitrogen analyses were determined at the Microanalytical Laboratory, University of Otago, Dunedin. Halides were determined gravimetrically as their silver salts.

Molecular Weights:

Unless otherwise stated molecular weights were determined by osmometry using a Hewlett-Packard 301A Vapour Pressure Osmometer. Chloroform solutions of concentrations between 10^{-2} and 10^{-3} moles/litre were used, and the instrument was calibrated over this range of concentrations using chloroform solutions of azobenzene.

Purification of Solvents

Dichloromethane: The solvent was dried over magnesium sulphate for about 48 hours and then fractionally distilled (B.P. 39 - 40°C). It was stored over molecular sieves.

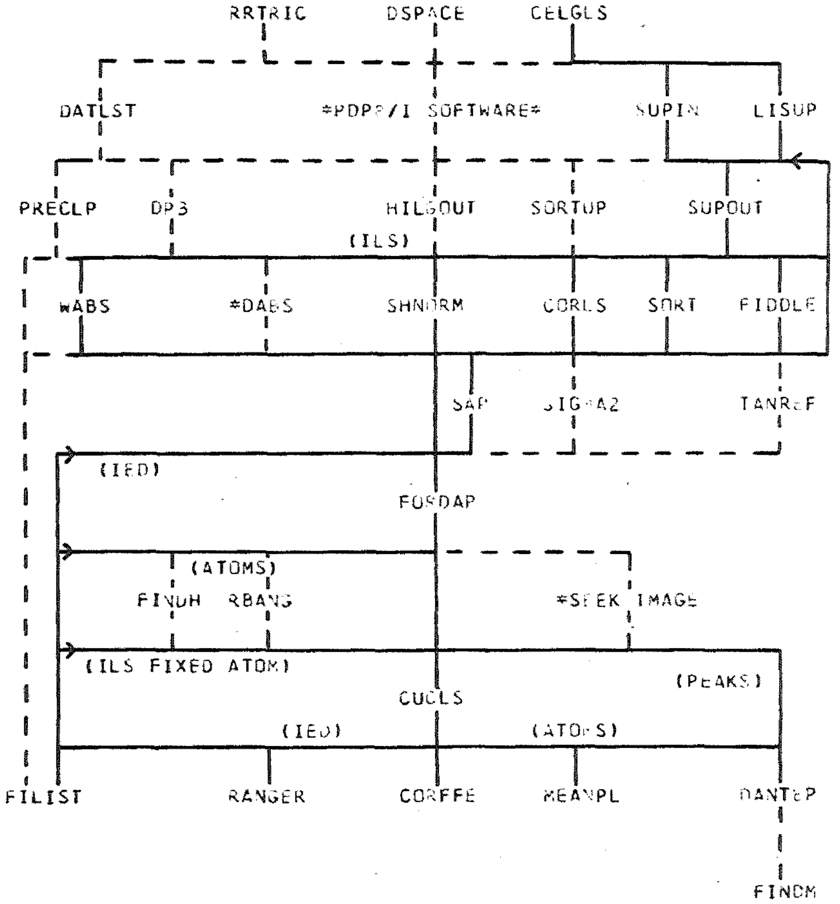
Nitromethane and nitrobenzene: The solvents (A.R. grade) were stored over molecular sieves.

Dimethylformamide: The solvent was mixed with 10% by volume of benzene and the benzene-water azeotrope was distilled at 80°C. The dimethylformamide was fractionally distilled under reduced pressure, the first and last 10% of the fractionated solvent being discarded. It was stored over molecular sieves.

TABLE B1

UNIVERSITY OF CANTERBURY CRYSTALLOGRAPHY GROUP
(NOVEMBER 1969)

PROGRAM CONFIGURATION



PRELIMINARY INVESTIGATIONS OF CELL CONSTANTS

PREPARATION OF INPUT--DATA SHEETS,CARD BLANKS AND PAPER TAPE

FILM FACTOR SCALING,LP AND OPTIONAL ABSORPTION CORRECTIONS
PREPARATION AND UPDATING FILE FOR INPUT TO L-S CALCULATIONS

ABSORPTION CORRECTIONS,SHARPENING FOR PATTERSON OR
NORMALISED STRUCTURE FACTORS,CORRELATION,SORTING,SCALING

DIRECT METHODS FOR PHASE DETERMINATION (SYMBOLIC ADDITION)

FOURIER SUMMATIONS INCLUDING PATTERSONS AND GENERAL PLANE

DERIVATION OF POSITIONAL COORDINATES OF ATOMS
IN RIGID GROUPS AND FROM PATTERSON MAPS

FULL-MATRIX LS REFINEMENT OPTIONALLY INCLUDING RIGID GROUPS

GENERAL FILE LISTING AND ANALYSIS OF WEIGHTING SCHEMES
CRYSTAL AND MOLECULAR GEOMETRY INCLUDING TABLES OF
DISTANCES,ANGLES AND FIGURES SUITABLE FOR PUBLICATION

FINDING A MOLECULE FROM A GENERAL ARRAY OF ATOMS

CALCULATIONS MAY PROCEED BY ANY SENSIBLE ROUTE WHICH DOES NOT PASS UPWARDS THROUGH A PROGRAM NAME OR AGAINST AN ARROW

SOME NECESSARY ILS,IED OR ATOM PARAMETER DATA SETS ARE INDICATED

* THESE PROGRAMS ARE NOT YET WORKING ON THE 360/44 PS

APPENDIX B

The University of Canterbury Computing System for X-ray Structure Analysis

The computer program configuration of the University of Canterbury Chemistry Department crystallography group as of November 1969 is shown in Table B1. Programs used in the structure determination in this work (Chapter 3) are listed in Table B2.

Calculations were carried out using an IBM 360/44 computer with 32K words of core storage and twin 2315 disc storage drives. A comprehensive range of computer programs has been adapted to this hardware. Diagrams were produced using an IBM 1620 computer to drive a Calcomp incremental plotter.

The author wishes to acknowledge in particular the contributions of G.J. Gainsford and R.J. Dellaca in the adaptation and development of many of the programs used in the course of the structure determination. Due largely to their efforts the present system of programs is sufficiently sophisticated for use by a person with a comparatively limited experience of computing techniques.

TABLE B2

COMPUTER PROGRAMS USED IN THE COURSE OF THE WORK IN CHAPTER 3

Local Name	Derived From	Authors
CELGLS	ORGLS	W.R. Busing, K.O. Martin and H.A. Levy, adapted by P.R. Ireland.
CORFFE	ORFFE-II	W.R. Busing, K.O. Martin, and H.A. Levy
CORLS	-	K. Emerson
CUCLS	NUGLS	R.J. Doedens and J.A. Ibers, adapted by R.J. Dellaca
DANTEP	ORTEP	C.K. Johnstone, adapted by R.J. Dellaca
FIDDLE	-	G.J. Gainsford
FILIST	-	P.R. Ireland
FORDAP	FORDAP	A. Zalkin
MEANPL	NRC-22	M.E. Pippy and F.R. Ahmed
RANGER	RANGER	P.W.R. Corfield
SAP SHNORM	NRC-4	S.R. Hall and F.R. Ahmed adapted by R.J. Dellaca
SUPIN LISUP	CUXR-2	W.M. Macintyre, M. Werkema, B.R. Penfold and F.W.B. Einstein.
SUPOUT	-	G.J. Gainsford
WABS	GNABS	G.W. Burnham and J.A. Ibers

APPENDIX C

STRUCTURE FACTOR LISTING FOR Pd(MMPM)$_2$

[illegible]

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THE COORDINATION CHEMISTRY OF DIPYRROMETHENE LIGANDS

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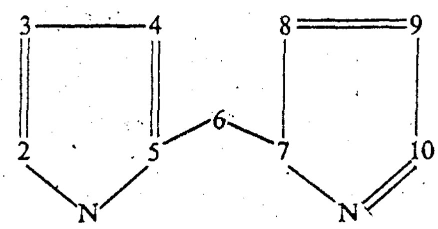
Tetrahedral complexes of composition ML_2 are readily obtained for Co(II), Ni(II), Cu(II) and Zn(II) with bidentate heterocyclic substituted dipyrromethene ligands MMPM,[1-5] MBrPM[4] and MClPM.

The tetrahedral stereochemistry is confirmed by both magnetic and electronic spectral data, and isomorphism of the Co, Ni and Zn compounds is apparent from X-ray powder photographs.



Ligand	2	3	4	8	9	10
MMPM	CH_3	CO_2Et	CH_3	CH_3	CO_2Et	CH_3
MBrPM	CH_3	CO_2Et	CH_3	CO_2Et	CH_3	Br
MClPM	CH_3	CO_2Et	CH_3	CO_2Et	CH_3	Cl

The structure of the Cu complex $Cu(MMPM)_2$ has been determined.[6] The mean planes of the two ligands are at 66° to each other rather than 90° as for exact tetrahedral coordination. The reason for the tetrahedral shape is the steric interaction of the substituents on C_2 and C_{10} between the two coordinated ligands.

It is more difficult to obtain complexes with the heavier metals. However, complexes have been obtained with MMPM for Pd(II)[2,3] and Cd,[2] and with MClPM for Pd(II), Cd, Hg, Ag(I) and possibly Ru(III) and Rh(III).

The diamagnetic ML_2 complexes have been studied by NMR and show interesting trends in the position of the methine proton resonance and the methyl proton resonances (Table 1). The changes in chemical shift from compound to compound correlate with the shift in the intense charge transfer band in the visible absorption spectra around 20,000 cm^{-1}.

The reactions of $Pd(NO_3)_2$ with MMPM and MClPM in the presence of acetate give the monomeric neutral complexes $Pd(MMPM)_2$[3] and $Pd(MClPM)_2$, respectively. These do not appear any different from other ML_2 complexes in their properties. When K_2PdCl_4 is treated with MClPM at least three products are obtained: $Pd(MClPM)_2$ in small amounts, $Pd_2(MClPM)_2Cl_2$ and a complex involving neutral MClPM rather than the usual anionic form. The relative yield of each product is pH dependent but the dimeric compound is the major species.

TABLE 1.

Ligand	Metal	Methine proton (ppm)	Methyl protons (ppm)
MMPM	—	6.98(1)	2.47(6), 2.59(6)
	Zn	7.38(1)	2.20(6), 2.60(6)
	Cd	7.38(1)	2.35(6), 2.61(6)
	Pd	7.38(1)	1.95(6), 2.57(6)
MClPM	—	7.88(1)	2.33(3), 2.47(3), 2.62(3)
	Zn	8.42(1)	2.27(6), 2.63(3)
	Cd	8.43(1)	2.30(3), 2.40(3), 2.63(3)
	Hg	8.41(1)	2.30(3), 2.52(3), 2.66(3)
	Pd	8.30(1)	2.22(3), 2.00(3), 2.58(3)

As it is not expected that the stereochemistry of Pd in PdL_2 would be tetrahedral, the complex $Pd(MMPM)_2$ was investigated by X-ray diffraction in order to see how the metal copes with a planar ligand having both stringent steric requirements and considerable π-delocalization. At the present stage ($R = 18{\cdot}9\%$) (i) the Pd stereochemistry is planar, (ii) the ligand is twisted about the methine carbon, (iii) the $NC_5C_6C_7NPd$ ring is not planar but bent giving a stepped arrangement of ligands around the metal. This suggests that the nitrogen atoms are more tetrahedral than trigonal planar.

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