Inorganica Chimica Acta, 98 (1985) 11–17

Synthesis and Reactivity of some Fe(II) and Mn(II) Complexes with Hemiporphyrazine

I. COLLAMATI*

Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti die Coordinazione del C.N.R., Via Salaria Km 29,500, Casella Postale 10, 00016 Monterotondo Stazione, Rome, Italy

E. CERVONE and R. SCOCCIA

Dipartimento di Chimica, Università di Roma, P.le A. Moro 5, 00185 Rome, Italy

Received April 20, 1984

Abstract

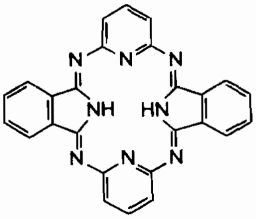
New paramagnetic Fe(II) and Mn(II) complexes with the divalent hemiporphyrazine (hpH_2) were isolated and characterized. Their formula are Mhp, $MhpH_2O$, MhpHCl, $Mhp(HCl)_2$ and $Fehp(\gamma\text{-pic})_2$. Of these, the HCl derivatives are true adducts of divalent metal complexes.

The H_2O and HCl derivatives were found to be thermally very stable. This arises, in addition to the coordination of oxygen or halogen to the metal, from an interaction between the protons of the coordinated molecules and the nearby nitrogen atoms of the macrocycles. A general tendency of the complexes to coordinate axially to give high spin derivatives is observed with this ligand. $Fehp(\gamma\text{-pic})_2$ gives a magnetic moment of 4.0 μB, suggesting the presence of an intermediate spin state. This is attributed to the weak and asymmetric ligand field of the macrocycle.

The reactivity of the complexes in the solid state and in solution was examined. Solutions of Fe(II) complexes were found to react with oxygen. It was determined spectroscopically that the reaction with O_2 is not reversible. Under anaerobic conditions, however, the oxidized species present in solution reacts back to the initial Fe(II) species. The addition of Ph_3P increases the velocity of the back-reaction.

Introduction

The study of porphyrin-like compounds, especially the interaction of iron complexes with such biologically important molecules as CO, O_2, NH_3, *etc.*, has been of interest to us for some time [1, 2]. More recently, much work has been carried out on the complexes with the first transition series metals of hemiporphyrazine (hpH_2, Scheme), a divalent macrocycle which resembles phthalocyanine with respect to the inner ring of 16 atoms, but not with respect to the symmetry and the π-conjugation extent. The results on the synthesis and the spectroscopic study of Co(II), Ni(II), Cu(II) and Zn(II) complexes [3, 4], together with some X-ray data [5], indicate for this ligand a rather peculiar coordination chemistry.



Among the metal complexes of the first transition series, much attention has been dedicated to the iron complex and its reactivity with O_2. When this part of our work was completed, the structural and magnetic study of an oxidized iron–hemiporphyrazine complex of formula $(FeOhp)_n$ was published [6]. This same compound was also isolated and characterized by us—even by X-ray. This led us to publish all our results on the chemistry and reactivity of the iron derivatives of hemiporphyrazine.

Here we report some new complexes of hpH_2 with Fe(II), together with additional results on Mn(II) complexes that in many ways are parallel to those obtained with the iron complexes. Of the Mn(II) derivatives, only the synthesis and the magnetic susceptibility of $MnhpH_2O$, were previously known [7]. The reactivity with oxygen of these complexes is also described.

Following this paper, our work on the Fe(IV)–hemiporphyrazine and the analogous compounds of molybdenum and vanadium will be presented.

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

Experimental

Reagents

Hemiporphyrazine was prepared as described previously [8]. The other materials and solvents were reagent grade. Pyridine and γ-picoline were refluxed on KOH and distilled before use. The synthesis of Fe(II) complexes and the preparation of Fe(II)-containing solutions were carried out under Matheson UHP nitrogen.

Preparation of the Complexes

α- and β-forms of Fehp(HCl)$_2$

$FeCl_2 \cdot 4H_2O$ (900 mg, 4.5 mmol) was added under N_2 to an air-free suspension of hpH_2 (1.6 g, 3.6 mmol) in DMF (60 ml). The reaction mixture was gently refluxed for 50 min. A red solid was collected by filtration, washed with DMF and CH_3OH and vacuum dried. It corresponds to the formula Fehp(HCl)$_2$, which we call the α-form (yield 80%). On prolonged heating of the reaction suspension, the red colour turned to brown, and after nearly 8 h the brown solid, collected by the above procedure, corresponded to the formula Fehp(HCl)$_2$, which we call the β-form.

Mnhp(HCl)$_2$

$MnCl_2 \cdot 4H_2O$ (550 mg, 2.8 mmol) was added to a suspension of hpH_2 (1 g, 2.3 mmol) in DMF (15 ml). The reaction mixture was refluxed for 3.5 h. Mnhp(HCl)$_2$ was collected as a red solid by filtration, washed with DMF and CH_3OH, and vacuum dried (yield 78%). Changing the reaction time or other reaction conditions did not result in other crystal modifications of this compound.

Fe(Mn)hpHCl

These brown mono-HCl compounds were obtained upon heating the red bis-HCl compounds at 300 °C, 10^{-2} torr (a 2 h heating was necessary for the conversion of 100 mg of the starting complex).

Fe(Mn)hpH$_2$O

A suspension of Mhp(HCl)$_2$ (1 g) in 0.5 M NaOH (100 ml) was stirred at room temperature for 1 h. After *ca.* 15 min., the suspension slowly turned greenish-brown. Solid compounds corresponding to the formula MhpH$_2$O were collected by filtration, washed with water and dried *in vacuo*. They were purified by sublimation (~450 °C, 10^{-2} torr). In this way anhydrous or partially hydrated compounds were obtained: upon exposure to air they are readily converted to the monohydrate compounds. FehpH$_2$O was also obtained by repeated sublimation (at least four times) of Fehp(HCl)$_2$ (~450 °C and 10^{-2} torr) and exposure to air. MnhpH$_2$O was also prepared starting from Mn(acetate)$_2$ as reported [7] and purified by sublimation. When sublimed, both the complexes were obtained as blue-violet needles. Powdered crystals were greenish-brown (Fe(II)) and greenish (Mn(II)).

Fe(Mn)hp

The thermal analysis shows that MhpH$_2$O compounds, undergo weight loss at about 250 °C, which is in agreement with the elimination of a H_2O molecule. However, samples sealed under vacuum upon heating at 250 °C show the presence of oxygen, as do samples taken from the sublimation apparatus in an inert environment. That anhydrous compounds are indeed obtained upon heating and that the presence of oxygen (from analytical data) is due to the high H_2O-reactivity of these compounds, was then clarified by following the water elimination and recombination *via* IR spectra. This was carried out using a special apparatus described below.

Fehp(γ-pic)$_2$

FehpH$_2$O (100 mg) in a quartz tube was heated at 250 °C under vacuum for 2 h. Anhydrous air-free γ-picoline (3 ml) was added and the tube sealed under vacuum and heated at 150 °C for 1 h. The tube was cooled, opened, and the greenish-black prismatic crystals obtained were filtered off and dried *in vacuo*.

Physical Measurements

Elemental analyses were performed by the Servizio Microanalisi, Area della Ricerca di Roma and by A. Bernhardt, Analytische Laboratorien, Elbach, W. Germany.

Thermogravimetric analyses were carried out under anhydrous N_2 on a Dupont 950 Thermoanalyser. IR and UV-visible spectra were recorded on Perkin Elmer spectrophotometers 580 B and 555, respectively.

An in-house IR cell was used to obtain the IR spectra of Mhp complexes and of their H_2O-interactions. It consisted of a cylinder provided with vacuum and gas-intake valves and NaCl windows; an IR window holder equipped with an electric resistance and a thermocouple could be inserted therein. The Mn(II) and Fe(II) complexes were sublimed directly onto NaCl disks which were inserted into the cylinder. The first spectrum recorded was that of MhpH$_2$O. The disk was then heated under vacuum and other spectra were recorded to follow the elimination of H_2O. The spectra of anhydrous compounds were then recorded at room temperature. Air was then admitted in the cylinder and the H_2O-absorption followed.

For the IR spectra in argon matrices the gas was passed through a coil in a liquid nitrogen cold trap. Fehp and Cohp were evaporated in a heated Quartz-Pyrex furnace at temperatures ranging from 520 to

550 K, and were co-deposited with argon on a CsI plate cooled at 13 K by a Displex CSA-202 (Air Products and Chemicals) closed cycle helium refrigeration system.

Magnetic susceptibilities were measured by the Gouy method. Susceptibility values of the Zn(II) complexes were used for the diamagnetic corrections [3]. The magnetic measurement of Fehp and Mnhp complexes were carried out on samples obtained after prolonged heating, at 250 °C under vacuum of the corresponding $MhpH_2O$ complexes. These samples were transferred under vacuum to a Braun dry box and sealed in appropriate tubes. Several samples, prepared by the same procedure, were used to ascertain the magnetic susceptibility values.

X-ray powder spectra were obtained with a Debye camera using Cu-Kα filtered radiation.

Results

When hpH_2 reacts with a slight excess of Fe(II) or Mn(II) halides, complexes of formula M(II)-hp$(HCl)_2$ are obtained.

Two crystal modifications are isolated when M = Fe. The complete elimination of HCl molecules from these complexes yields air-stable compounds corresponding to M(II)hpH_2O. A partial elimination is also possible and yields M(II)hpHCl compounds. The M(II)hpH_2O compounds give rise, upon heating at 250 °C under vacuum, to H_2O-sensitive M(II)hp complexes. A further adduct of Fe(II)hp obtained is metastable, high spin Fehp(γ-pic)$_2$.

We have found that the Mn(II) complexes are O_2-stable both in solid state and in solution. The Fe(II) complexes are O_2-stable in the solid state at room temperature. They are readly oxidized in the presence of oxygen, upon heating or in solution.

Fe(Mn)hp(HCl)$_x$ (x = 1,2)

Mhp$(HCl)_2$ are high spin compounds, thermally very stable as adducts. A first HCl molecule is eliminated at nearly 300 °C, as reported in Table I. Curiously, pure Fehp$(HCl)_2$, FehpHCl and MnhpHCl were also obtained by rapid sublimation at nearly 450 °C, 10^{-2} torr; the first sublimation usually affords a mixture of Mhp$(HCl)_2$, MhpHCl and MhpH_2O. Much lower stability was observed in solution where the HCl-adducts easily dissociate. Thus, Mnhp$(HCl)_2$ dissolved at room temperature in non-anhydrous γ-picoline to yield a precipitate of MnhpH_2O; in addition, the solutions were O_2-stable. Fehp$(HCl)_2$ dissolved in air-free nitrogen bases to yield green solutions identical to those obtained from FehpH_2O, also with regard to the UV-visible spectra. These spectra are due to the species Fehp(bases)$_2$. HCl molecules are also easily eliminated upon treatment with 0.5 M aqueous NaOH solution or addition of thallium acetate to a DMF suspension of the adduct. Similarly, the HCl adducts are readily recovered from the Mhp complexes, by stirring the latter in a 0.5 M HCl solution.

We have already described the analogous bis-HCl derivatives of Co(II), Ni(II), Cu(II) and Zn(II) complexes [3]. The first three have been found to form an isomorphic series and a different crystal modification of the Ni(II) and Co(II) complexes could be obtained by slightly changing the reaction conditions.

TABLE I. Analytical Data and some Physical Properties of Mhp Complexes.

Compound	Analytical data (calc)					μ_{eff} μB	T range and % of the weight loss[a]
	%C	%H	%N	%O	%Cl		
Fehp$(HCl)_2\alpha$	54.9	3.0	19.5		12.2	5.1	285–330 °C, 6%
Fehp$(HCl)_2\beta$	55.0 (55.04)	2.9 (2.82)	19.7 (19.76)		12.5 (12.53)	5.2	stable up to 360 °C
FehpH_2O	60.7 (60.94)	3.1 (3.13)	21.8 (21.87)	3.0 (3.03)		5.1	260–270 °C, 3%
Fehp(γ-pic)$_2$	67.0 (67.06)	4.0 (4.12)	20.3 (20.59)			4.0	150–215 °C, 27%
Fehp						5.0	
Mnhp$(HCl)_2$	56.0 (55.12)	2.9 (2.83)	20.3 (19.79)		11.9 (12.54)	6.0	295–350 °C, 6%
MnhpH_2O	60.9 (60.94)	3.2 (3.13)	21.6 (21.87)	3.0 (3.03)		6.0	240–255 °C, 3%
Mnhp						6.1	

[a] The thermal behaviour is observed up to 450 °C.

$Mnhp(HCl)_2$ and the red form (α-form) of $Fehp(HCl)_2$ are isomorphous with the Zn(II) analogue, whereas the brown form (β-form) of $Fehp(HCl)_2$ is isomorphous with the second crystal modification of the Ni(II) and Co(II) compounds. On the whole, for $Mhp(HCl)_2$ compounds the α-form occurs with Mn, Fe, and Zn, the β-form with Fe, Co and Ni, and another form (which we refer to as the γ-form) with Co, Ni and Cu.

Compounds of an isomorphic series have identical powder spectra and overlapping IR spectra. Going from one series to another, small but significant changes are detected in some regions of the IR spectra. Particular differences between the α- and β-forms of $Fehp(HCl)_2$: the β-form dissolves only with difficulty in N-bases and more forcing conditions, *i.e.* hot (80 °C) 0.5 M NaOH, are necessary to obtain $FehpH_2O$.

The compounds obtained by elimination of one HCl molecule from the bis-HCl derivatives, as indicated by thermal analysis gave IR and powder spectra identical with those of ZnhpHCl [3] and are therefore considered the isomorphous HCl-monoadducts of Fe and Mn complexes.

Compared with complexes which do not contain HCl, $Mhp(HCl)_x$ (x = 1,2) show additional bands in the region 3300–2700 cm^{-1}. They are assigned to NH bond vibrations, as originated from the interactions of HCl with the nitrogens of the macrocycle [3]. It is less easy to assign bands due to M–Cl moieties because in the diagnostic region, absorption bands are also shown by compounds not containing HCl. Nevertheless, this band can be assigned with some confidence in MnhpHCl (270 cm^{-1}), $Mnhp(HCl)_2$ (300 cm^{-1}) and α-$Fehp(HCl)_2$ (310 cm^{-1}).

Fe(Mn)hpH$_2$O

This formula represents the final state of anhydrous Fe(II) and Mn(II) hemiporphyrazinates to air or an imperfectly dry environment. They are high spin compounds isomorphous with the Zn(II) and Co(II) analogues [3]. Other significant common features are: the quite low OH stretching frequencies (*ca.* 3100 cm^{-1}) in the similar IR spectra and the high H_2O elimination temperature (see Table I).

$MnhpH_2O$ was already reported [6] as an insoluble compound. We have observed that in the presence of Cl^- ions (*e.g.* with LiCl) it dissolves slightly in DMF to yield an O_2-inert reddish solution. By evaporation or addition of EtOH the compound is recovered unchanged.

$FehpH_2O$ is quite soluble at room temperature in N-bases to yield (under N_2) green solutions which rapidly turn brown-yellow with traces of oxygen.

Fehp(γ-pic)$_2$

Because of the great instability of solutions of iron(II)–hemiporphyrazine complexes in N-bases, sealed-vial methods were used for the synthesis of this adduct. Even then, well dehydrated reagents had to be used to avoid formation of $FehpH_2O$.

$Fehp(\gamma\text{-pic})_2$, which is dark green when ground, is relatively stable to air, in which it slowly (*ca.* 1 month) exchanges the base with H_2O without oxidation.

The synthesis of $Fehp(\gamma\text{-pic})_2$ usually gives a mixture of two different polymorphs (α and β) with identical analytical composition but different IR and X-ray powder spectra. Occasionally the two crystal modifications can be obtained pure. They are isomorphous with the related α and β forms isolated and characterized for high spin $Cohp(\gamma\text{-pic})_2$ [9], whereas only the α form was obtained for high spin $Nihp(\gamma\text{-pic})_2$ [5].

The visible spectrum as a solution in γ-picoline is identical to that obtained when $FehpH_2O$ or $Fehp(HCl)_2$ are dissolved in the same solvent (Fig. 1; $\lambda_{max}(\epsilon)$: 686 (2.7×10^3); 628; 392; 346 (2.7×10^4)).

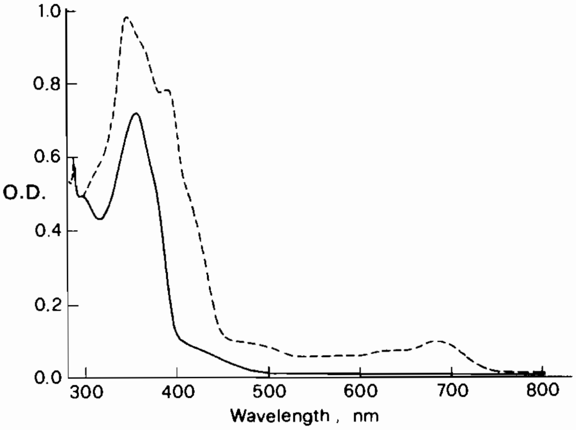


Fig. 1. Electronic spectra of solutions in γ-picoline of: hpH_2 2.4×10^{-5} M ——; $Fehp(\gamma\text{-pic})_2$ 3.7×10^{-4} M – – –; 1 mm cell.

The TG shows that weight loss occurs in the range 150–215 °C in two distinct steps, corresponding to elimination of the two γ-picoline molecules. Under N_2 or in vacuum, the final air-stable product is $FehpH_2O$.

Different samples of $Fehp(\gamma\text{-pic})_2$ give at room temperature a magnetic susceptibility corresponding to an average magnetic moment of 4.0 μB.

Fe(Mn)hp

These are high spin compounds as the corresponding hydrates. Figure 2 reports the IR spectra of Fehp and $FehpH_2O$. Only minor differences are apparent except for the absence of the OH absorptions in the former. The same feature is observed when the IR spectra of Mnhp and $MnhpH_2O$ are compared.

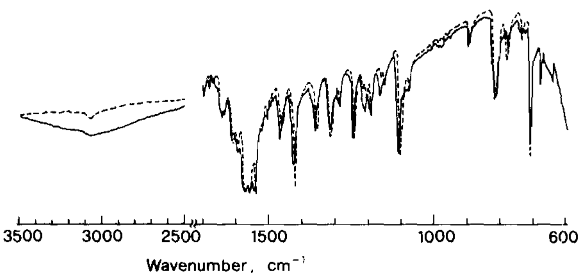


Fig. 2. Infrared spectra of sublimed $FehpH_2O$ ——; Fehp – – –; (window of NaCl).

The rapid H_2O absorption of these compounds when air is again admitted into the apparatus (1 min for the sublimates used for IR *in situ*) can be repeated reversibly if the heating to obtain anhydrous species again is carried out under vacuum. If traces of oxygen are present in this phase (*i.e.* during heating) Fehp oxidation occurs: new bands appear in the region 800–900 cm^{-1}.

The support for the existence of intermolecular interactions in these complexes (see Discussion) was sought by carrying out IR measurements of samples diluted in argon matrices. The results for Fehp and Cohp are shown in Fig. 3. The IR spectra of Cohp as a thin film and in an argon matrix are very similar. The frequencies and the number of absorption bands are almost unaltered; higher resolution of the medium-intensity band at 1210 cm^{-1} is noted. Conversely Fehp shows significant variations in the general spectral features.

Interaction of Fehp with O_2 in Solution

The best solvents for iron-hemiporphyrazine complexes are N-bases; γ-picoline was used for following spectrophotometric changes due to interaction with O_2.

Given that this interaction was monitored at [Fe] ~ 10^{-4} M and it is difficult even in dry solvent to reduce water concentration below 10^{-4} M, $FehpH_2O$ was used instead of Fehp. Bubbling O_2 into the solution caused colour changes from green to yellow-brown with consequent changes in the visible and UV regions. The spectral changes observed with time for 5 ml of a 3.7×10^{-4} M solution of Fe(II)hp on bubbling in *ca.* 1 ml of O_2 are illustrated in Fig. 4A. The bands in the visible region decrease in intensity and eventually disappear; the band at 346 nm also decreases in intensity. Good isosbestic points are given, and the final spectrum is characterized by a maximum at 390 nm. Prolonged oxygenation leads to no further spectral changes and the solution gave no EPR signal down to 100 K.

The interaction with O_2 is irreversible. Removal of dioxygen effected by bubbling pure dinitrogen through the solution or by freeze-thawing cycles do not reproduce the original spectrum. In anaerobic conditions, however, the spectrum with a maximum at 390 nm is not stable indefinitely; it depends on $[O_2]$ and inversely on the temperature. A completely oxidized iron–hp solution (~10^{-4} M) becomes green after *ca.* 24 h and shows the spectrum typical of $Fehp(\gamma\text{-pic})_2$ when the solution is first purged with N_2 and then left in a closed vessel at 33 °C (Fig. 4B). Under the same conditions the stability of the oxidized species abruptly drops (to 1 h) if a large excess of Ph_3P is added immediately after purging the solution with N_2.

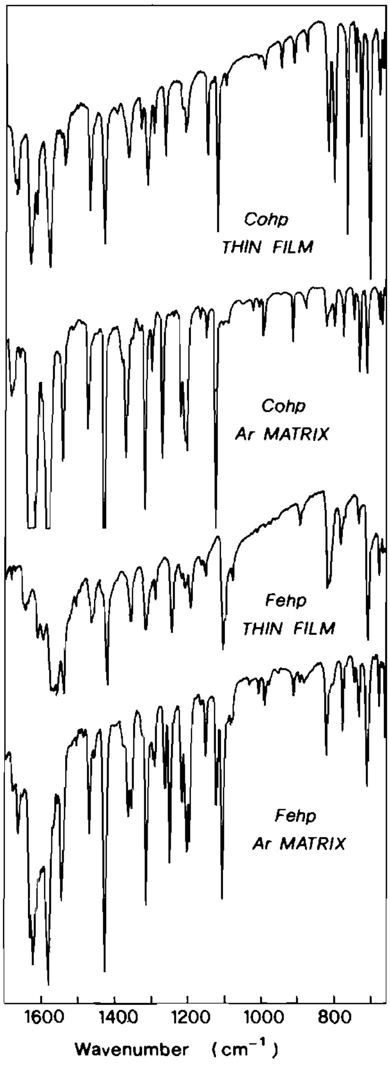


Fig. 3. Infrared spectra of Fehp and Cohp.

Experiments were then performed to identify the eventual formation of Ph_3PO. Following the above procedures, oxidized solutions of $Fehp(\gamma\text{-pic})_2$ in γ-picoline were deaerated *in vacuo*, Ph_3P added in 1:1 ratio and the tube closed and thermostatted at 33 °C. In parallel experiments the time required for complete reduction was found *via*

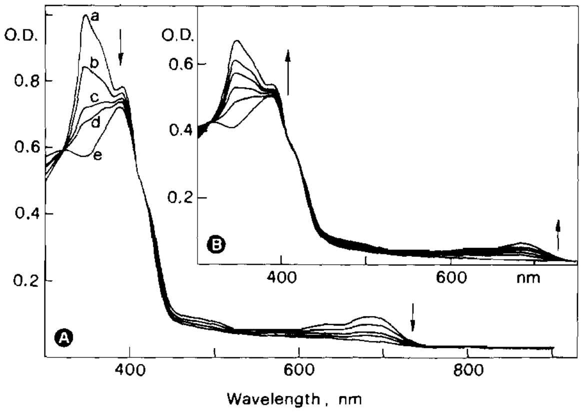


Fig. 4. A. Spectral changes over time of γ-picoline solution of Fe(II)hp, oxygenated as reported in the text: a) initial spectrum; b), c), d), e) after 15, 60, 90, 180 min; [Fe] = 3.7 × 10^{-4} M; 1 mm cell; T = 22 °C. B. Spectral evolution of an oxidized solution of Fehp in γ-picoline, under anaerobic conditions; [Fe] = 2.5 × 10^{-4}; 1 mm cell; T = 33 °C.

spectrophotometry. When reduction was complete the solvent was removed *in vacuo*, the residue was re-dissolved in toluene and the solution filtered and the toluene removed *in vacuo*. The IR spectrum of the residue was compared with that of Ph_3P: Ph_3PO mixtures of known concentrations. The oxidation of Ph_3P during manipulation in the absence of the iron complex was estimated *via* blanks and taken into account. No significant formation of Ph_3PO was evident under these conditions.

Discussion

The magnetic behaviour of tetracoordinated complexes formed by Fe(II) or Mn(II) with the related macrocyclic phthalocyanine and porphyrins apparently follows a generally reliable rule: if the metal lies in the plane of the macrocycle, the spin state of the complexes is intermediate, but it is high spin when the metal is out of the plane [10]. Thus, for the only iron complex of this kind, Fe(TpivPP), to which the high spin state is assigned, it is suggested that intermolecular interactions with oxygen atoms on the 'pickets' pull the metal out of the plane [11].

The comparison with the behaviour of Fe(II) and Mn(II) in the Fehp and Mnhp complexes must take into account the fact that the macrocyle ligand field is in this case weaker and less symmetrical. However, we believe that their high spin state is induced by significant intermolecular interactions which effectively changes the coordination number of the metal, perhaps also drawing the metal out of the plane.

We have reported [3] that high spin $CohpH_2O$ can lose H_2O to give Cohp as a low spin compound which is air-stable in the solid state and isomorphous with Nihp, and whose monomeric planar structure has been determined [12]. The conversion of high spin $CohpH_2O$ to low spin Cohp occurs with significant changes in the IR spectrum.

Fe(II) and Mn(II) complexes behave very differently from that of Co(II). Their monohydrate compounds have IR spectra which overlap with that of the isomorphous $CohpH_2O$, but undergo only slight changes when the complexes eliminate water. The anhydrous compounds immediately recover H_2O upon exposure to air and are high spin. These observations suggest that the structures of Fehp and Mnhp are very similar to those of the corresponding hydrate compounds, and adopt intermolecular interactions even in the absence of coordinated water.

This is supported by the comparison of IR spectra of Fehp and Cohp as thin films and in inert-gas matrices. Dilution causes no changes in the monomeric tetracoordinated Cohp. Conversely, Fehp dilution (*i.e.* separation of the molecules) significantly modifies the IR spectra which become comparable with those of the other tetracoordinated complexes with this ligand (Cuhp, Cohp, Nihp).

Very recent X-ray studies have been carried out on $CohpH_2O$, $ZnhpH_2O$, and $MnhpH_2O$ [13]. These are in agreement with previous conclusions [3]. The H_2O molecule coordinates *via* the oxygen to the metal ion, the hydrogen atoms being bonded to the nitrogens of two adjacent macrocycles. The presence of such H-ligand interaction (which is presumably also present in the isomorphous Fehp-H_2O) is responsible for the thermal stability of the adducts and the low-energy ν_{OH} band. It could also rationalize the fact that solid $MhpH_2O$ are stabilized in the presence of stronger donors such as pyridine or γ-picoline.

A similar N– –H interaction is clearly established in the IR spectra of $Mhp(HCl)_x$ (M = Fe, Mn; x = 1,2). In addition, the halogen coordinates to the metal. Hexacoordination of this type has previously been found for complexes with other metal ions [3]. HCl derivatives of Mn(II) and Fe(II) are thus assigned on the basis of the above isomorphic relationship. $Mhp(HCl)_x$ complexes are similar to $MhpH_2O$ complexes in that the HCl molecules can be eliminated from the adducts and recovered from the Mhp compounds.

Fehp(γ-pic)$_2$, like the related H_2O and HCl derivatives is paramagnetic. The value of the magnetic moment, 4.0 μB, is indicative of an intermediate spin state for the metal ion. Since related six-coordinate Fe(II) complexes are usually low spin [14], this result is not expected and requires further investigation. The high spin behaviour observed for the isomorphous Cohp(γ-pic)$_2$ (α and β forms) [9] has been ascribed to the weakness and asymmetry of the hp ligand field.

Interaction of Fehp Complexes with O_2

In contrast to the macrocyclic analogous, Mn(II)–hemiporphyrazine complexes are inert to O_2 even in solution. In this respect, the Fe(II) complexes show normal behaviour. Nevertheless, their extreme sensitivity to O_2 when dissolved in N-bases is noteworthy. It is known that Fe(II)–phthalocyanine gives solutions stable to O_2 when dissolved in neat N-bases and the reaction of Fe(II)–porphyrins with O_2 is strongly inhibited under these conditions [15].

All Fe(II)–hemiporphyrazine complexes mentioned give the same spectrum when dissolved in neat γ-picoline (Fig. 1).

Absorptions at 686 and 628 nm may be assigned to M → L charge transfer transition. Bands at 392 and 346 nm are more difficult to assign because of the presence of ligand bands (Fig. 1, $\lambda_{max}(\epsilon)$: 358 (3.0×10^4)). Interaction with O_2 causes spectral changes with appearance of isosbestic points (Fig. 4A). Thus, a single oxidized species is present in solution (together with the initial Fe(II) species) and this species is responsible for the maximum at 390 nm.

As regards the nature of this species, it is noteworthy that bubbling O_2 into concentrated solutions causes the same spectral changes but these are accompanied by the formation of a solid, identified as an oxoiron(IV) compound [6, 16]. When dissolved in γ-picoline under N_2 the latter again gives a spectrum with a maximum at 390 nm. The species present in solution seems therefore of oxidation state +4. This suggestion is supported by the absence of an EPR signal for oxygenated solutions (high and low spin Fe(III) species show characteristic EPR spectra [17]).

The oxidized species present in solution of γ-picoline, again transforms to Fe(II)hp(γ-pic)$_2$, in absence of O_2. Although we observed that this reduction was accelerated by the addition of Ph_3P, it was not possible to directly identify Ph_3PO. This may be due to the γ-picoline solvent itself, which is a potential oxygen acceptor; the insolubility of Fe(II) complexes did not permit the reaction to be followed in other solvents.

Acknowledgements

The Authors wish to thank Prof. M. Maltese for the IR spectra of complexes in argon matrices, Mr. G. Chiozzini for thermogravimetric analyses, Mr. F. Dianetti for elemental analyses, Mr. G. Frasca for technical assistance and Mr. M. Viola for drawings.

References

1 I. Collamati, *Inorg. Chim. Acta, 35*, L303 (1979).
2 F. Calderazzo, G. Pampaloni, D. Vitali, G. Pelizzi and I. Collamati, *J. Organomet. Chem., 191*, 217 (1980).
3 D. Attanasio, I. Collamati and E. Cervone, *Inorg. Chem., 22*, 3281 (1983).
4 D. Attanasio and I. Collamati, unpublished results.
5 E. Agostinelli, D. Attanasio, I. Collamati and V. Fares, *Inorg. Chem., 23*, 1162 (1984).
6 W. Hiller, J. Strähe, A. Datz, M. Hanack, W. E. Hatfield, L. W. Haar and P. Gütlich, *J. Am. Chem. Soc., 106*, 329 (1984).
7 C. L. Honeybourne and P. Burchill, *Inorg. Synth., 18*, 48 (1978).
8 C. L. Honeybourne and P. Burchill, *Inorg. Synth., 18*, 47 (1978).
9 An X-ray structure determination has been carried out on the β form of Cohp(γ-pic)$_2$. I. Collamati, G. Dessy and V. Fares, results to be published.
10 See ref. 14, page 456 onwards.
11 G. B. Jameson, W. T. Robinson, J. P. Collman and T. N. Sorrell, *Inorg. Chem., 17*, 858 (1978).
12 J. C. Speakman, *Acta Cryst., 6*, 784 (1953).
13 Shie-Ming Peng, private communication.
14 J. R. Sams, T. B. Tsin, in 'The Porphyrins' in D. Dolphin, (Ed.), vol. IV, p. 466, Acad. Press, N. Y. (1979).
15 J. O. Alben, W. H. Fuchsman, C. A. Beaudreau and W. S. Caughey, *Biochem., 2*, 624 (1968); J. P. Collman, *Acc. Chem. Res., 10*, 265 (1977); J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Albert, G. Land and W. T. Robinson, *J. Am. Chem. Soc., 97*, 1427 (1975).
16 I. Collamati, E. Cervone and R. Scoccia, paper to be submitted for publication.
17 J. D. Stong and C. R. Hartzell, *Bioinorg. Chem., 5*, 219 (1976).