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Some μ-oxo Compounds of Iron–Hemiporphyrazine. Synthesis and Properties

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Abstract

Details of the conditions necessary for preparing the recently reported μ-oxo-ironhemiporphyrazinate compounds $(Fe(IV)hpO)_n$ and $[(Fe(III)hp)_2O]H_2O$ are given. Two further homologous μ-oxo Fe(III)-hemiporphyrazinates are described: an amorphous μ-oxo dimer and a μ-oxo dimer HCl adduct. The thermal and spectroscopic (UV–Vis, IR, Mössbauer, XPS) properties and magnetic susceptibilities of these compounds have been investigated. The reducibility of these species in solution, in the presence and absence of O_2, has been monitored. The results do not indicate a change in oxidation state of the iron in $(FehpO)_n$. Attempts to obtain the hemiporphyrazinato Fe(III) chloride are described.

Introduction

Two μ-oxo compounds of the hemiporphyrazine iron complex (Fehp) are known. Single crystal X-ray analysis has shown that one has a polymeric structure –Fehp–O–Fehp–O– (compound **1**) [1], and the iron was designated Fe(IV) $S = 1$, whereas the other has a dimeric structure Fehp–O–Fehp–OH_2 (compound **2**) [2] in which the iron is a high spin Fe(III).

We obtained both products by oxidizing Fe(II) hemiporphyrazine with gaseous O_2 in N-base solution at room temperature. The variable that determines which of the two compounds is formed is the presence or absence of traces of H_2O. Under anhydrous conditions μ-oxo **1** is obtained, whereas in the presence of H_2O dimer **2** is given. The two products can also be obtained under other conditions, but the factor that distinguishes **1** and **2** is always the same, *i.e.*, H_2O.

Before the structure of **1** was known, an extensive characterization of the two compounds was carried out by thermal analysis, spectroscopic analysis, Mössbauer and ESCA measurements. However, the two compounds were found to be very similar and there was no evidence for a different iron oxidation state. For this reason, after the structure of **1** appeared and before the structural results of **2** became available, we thought that **2** was also an Fe(IV) hemiporphyrazine compound. The same assumption was made for the iron of two other compounds obtained by us having similar properties as **1** and **2**: an amorphous μ-oxo compound (compound **3**) derived from **2** by heating under vacuum, and a μ-oxo–HCl adduct (compound **4**) obtained by the interaction of **1** or **2** (or **3**) with dilute aqueous HCl.

With this in mind, in a recent article we mentioned that other Fe(IV) hemiporphyrazine compounds would be reported [3]. In reality, our structural determination of **2** showed without doubt that it contains Fe(III), and gives the same oxidation state as the iron in compounds **3** and **4**. Here we report all the experimental data collected on the synthesis of compounds **1**, **2**, **3** and **4**, their characterization by thermal spectroscopic and magnetic analysis and some data on their reactivity.

Experimental

Preparation of the Compounds

hpH_2, $FehpH_2O$, $Fehp(HCl)_2$, $Fehp(\gamma\text{-pic})_2$ were prepared as described previously [3]. The other materials were reagent grade. Solvents were purified by conventional methods. Syntheses and manipulations in an inert atmosphere were carried out using prepurified Matheson HP nitrogen.

Fehp μ-oxo, 1

The first samples of the compound described as $(FeOhp)_n$ were obtained by us as a brown microcrystalline precipitate by bubbling oxygen in a solution of Fe(II)hp *ca.* 5×10^{-3} mol dm^{-3} in γ-picoline at room temperature and under anhydrous conditions. $\nu FeOFe = 898$ cm^{-1}. An optimized preparation of the compound was carried out as follows.

100 mg of $FehpH_2O$ (or 120 mg of $Fehp(HCl)_2$) were added under N_2 to 20 ml of anhydrous γ-picoline and the temperature raised to 80–100 °C. After 10 min, O_2 was introduced and bubbled in for 90 min. After cooling under O_2, the dark brown suspension was filtered to give 80 mg of μ-oxo **1** as dark brown microcrystals (reddish when ground). The compound was washed with γ-pic and toluene.

1 could be obtained more simply in air by heating at the boiling point suspensions of $FehpH_2O$ (300 mg) in DMF, γ-picoline, nitrobenzene (NB) (10 ml). After *ca.* 40 min filtration of the hot suspensions gave pure microcrystalline μ-oxo **1** (*ca.* 200 mg from nitrobenzene).

The oxidation of Fe(II) comes about by the action of ambient O_2 even when the solvent used is nitrobenzene. Fe(II)hp closed under vacuum in a tube with nitrobenzene remains unchanged, even after heating at 200 °C for an hour.

The compound may be recrystallized from nitrobenzene, as long as cooling of the clear solutions is carried out in strictly dry air. Crystals in the form of thin elongated prisms suitable for X-rays are obtained.

Fehp μ-oxo dimer monohydrate, Fehp–O–Fep–H_2O, 2

This is obtained in place of μ-oxo **1** both in the first two preparations above if the γ-pic is not anhydrous or if traces of water are added intentionally. It can also be obtained from the mother liquors of **1** when exposed to moisture. Very thin brown needles slowly separate; after 24 h the solid is filtered, washed with γ-pic or DMF and then vacuum dried. It is light brown when ground; νFeOFe = 878 cm^{-1}.

The compound **2** is also obtained by simply shaking **1** in air at room temperature, N-base, DMF or nitrobenzene as solvents. The transformation **1** → **2** can be followed by monitoring a change in colour of the suspension from reddish to brown. Because of the low solubility of **1** in DMF, this solvent needs more than two days stirring.

2 may be recrystallized as **1** as long as contact with humidity is assured during cooling of the clear, boiling hot solutions; otherwise **1** is obtained.

Regardless of the solvent from which it is separated, **2** always has the same crystalline form and X-ray powder spectrum, but it contains a different chlathrated solvent, shown more clearly by TG and by IR spectrum than by elemental analysis. In particular, the compound obtained by NB allows the identification of weak absorption bands in the IR spectrum due to free NB at 850, 1350 and 1520 cm^{-1}, and it shows a loss in weight between 130 and 150 °C of ~7%. (Calculated for 0.5 NB + $1H_2O/[(Fehp)_2O]H_2O\cdot(NB)_{0.5}$ = 7%). When obtained from py, γ-pic, or DMF, only small quantities of H_2O are chlathrated, because only a loss in weight varying from 2.0 to 3.5% can be identified in TG. (Calculated for $H_2O/[(Fehp)_2O]H_2O$ = 1.76%).

Fehp μ-oxo dimer amorphous, 3

This was obtained as a brown compound by heating **2** at 150 °C, 10^{-2} torr (*ca.* 1 h for 50 mg). νFeOFe = 848 cm^{-1}.

Fehp μ-oxo dimer, HCl adduct, $[(Fehp)_2O](HCl)_5(H_2O)_6$, 4

1 or **2** (100 mg) was stirred with HCl (0.5 mol dm^{-3}, 10 ml) for 30 min. The brown suspension turns reddish; the reddish brown solid, separated by filtering, was dried at 50 °C in vacuum for 3 h. νFeOFe = 846 cm^{-1}. *Anal.* Calc. for $C_{52}H_{45}N_{16}O_7Cl_5Fe_2$: C, 48.07; H, 3.47; N, 17.26; Cl, 13.67. Found: C, 47.90; H, 3.20; N, 17.15; Cl, 13.40%.

Attempt to obtain Fe(III)hpCl

Compound **4** was heated in vacuum at various temperatures. This treatment easily led to iron reduction, and $Fe(II)hp(HCl)_2$ was obtained [3]. Nevertheless, in various experiments carried out at 200 °C, a compound, **5**, was obtained that did not show an Fe–O–Fe absorption in the IR spectrum and showed absorption at ~340 cm^{-1} attributable to a Fe–Cl bond. Its chlorine content was close to that expected for FehpCl. Moreover, compound **5** was recovered unchanged after treatment with 0.5 mol dm^{-3} NaOH. This shows that the chlorine content cannot be ascribed to adduct HCl molecules [3, 4].

Various kinds of measurements were carried out; absorption and Mössbauer spectra showed mainly that these samples were impure and contained Fe(II) in varying quantities. Therefore, it was difficult to define the compound with certainty as being Fe(III)-hpCl.

Reduction of μ-oxo compounds 1 *and* 2

To highlight the reducibility of the oxidized complexes **1** and **2** by γ-pic and by PPh_3, the following experiments were carried out. Portions of 20 mg of **1** were added to tubes containing, respectively: (a) toluene (5 ml); (b) γ-pic (2 ml); (c) toluene (2 ml) + PPh_3 (200 mg); (d) nitrobenzene (1 ml) + PPh_3 (200 mg). The tubes were sealed in vacuum and maintained at 150 °C for 48 h. Under these conditions, the solid always remained present as such. After cooling, the tubes were opened and the contents rapidly filtered. The resulting solid was **1** in (a); $Fe(II)hp(\gamma\text{-pic})_2$ in (b); $Fe(II)hpH_2O$ in (c) and (d). Similarly, with $[(Fehp)_2O]H_2O$ in place of **1**, no reduction took place in (a) and Fe(II) compounds were obtained in (b), (c) and (d).

Physical Measurements

The elemental and thermal analyses, magnetic susceptibility measurements, X-ray powder spectra, and UV and IR absorption spectra were carried out as described previously [4, 5]. The Mössbauer spectra were recorded in the constant acceleration mode with a ^{57}Co(Rh) source held at room temperature. The velocity scale was calibrated using a thin metallic iron foil and all isomer shifts were referred to the centre of the spectrum of an α-Fe absorber. Lorentzian lineshapes were used for the least-squares fitting of the experimental data. The X-ray photoelectron spectra were recorded on the VG ESCA 3Mk2 of the Servizio ESCA, Area della Ricerca di Roma del CNR. The exciting source was the Al K$\alpha_{1,2}$ radiation.

Results and Discussion

Structures of μ-oxo Compounds 1 *and* 2

Let us briefly look back to the fundamentals of the structures of 1 and 2 [1, 2]. 1 is described as being formed of parallel rows of polymers –Fehp–O–Fehp–O– (Fig. 1). The bridging oxygen is not found on the axis of the chain, but in two positions about the axes, to which there are different Fe–O–Fe angles. The Fe–O (bridge) distance is long (~2 Å). The distances Fe–Nisoind and Fe–Npy that define the coordination cavity, as well as the deviation from planarity of the macrocycle, are comparable with those found in diamagnetic Nihp [6]. The iron is considered tetravalent with a spin state S = 1 on the basis of the absence of an ESR signal and of a good fitting of magnetic data with an appropriate model. The Mössbauer spectrum is asymmetric and reveals that two iron sites are present. This is interpreted as arising from the oxygen disorder.

2 is formed of asymmetrical μ-oxo Fe(III) dimers FeB–O–FeA–OH_2. Two Fe–O (bridge) distances exist; the shortest, 1.738 Å, is with the pentacoordinated iron FeB, and the longest, 1.782 Å, is with hexacoordinated FeA. The dimers are co-axially Facing to form tetramers H_2O–FeA–O–FeB···FeB–O–FeA–H_2O. These are repeated in the crystal generating a two-dimensional network due to the hydrogen bonds between the H_2O molecules of a tetramer and the external nitrogens of macrocycles coordinated to FeB of adjacent tetramers (Fig. 2). Structural parameters, IR, and magnetic behaviour are in line with those observed in μ-oxo dimers of Fe(III) S = 5/2, [7] and by analogy this state is ascribed to the iron in 2.

Thermal Behaviour of 1 *and* 2. *The Obtaining of an Amorphous μ-oxo Fehp Compound (Compound* 3*)*

The thermal behaviour of the compounds was examined, and IR spectra and X-ray powder patterns were run as a check. In Fig. 3a the thermogravimetric curve of 1 only shows the weight loss corresponding to the elimination of oxygen at ~370 °C*. This is confirmed by the behaviour of 1 when it is heated in vacuum. This compound remains unchanged up to 350 °C, at which temperature it becomes Fe(II)hp (in air Fe(II)hpH_2O) [3] and sublimes.

The first weight loss in the TG (130–150 °C) curve of 2 represents loss of solvent and is somewhat variable (see 'Experimental'). Beyond this step the curve is identical to that of 1 (Fig. 3b, c). If 2 is heated in vacuum (10^{-2} torr) and the temperature increased up to $T < 150$ °C, the compound remains unchanged; for $150 < T < 300$ °C the new compound 3 is given; for $T \geq 310$ °C 1 is obtained. At ~350 °C the same behaviour is observed as for 1.

Compound 3 is characterized by an IR spectrum very similar to that of 1 apart from the position of the Fe–O–Fe band at ~850 cm^{-1}. Its X-ray powder

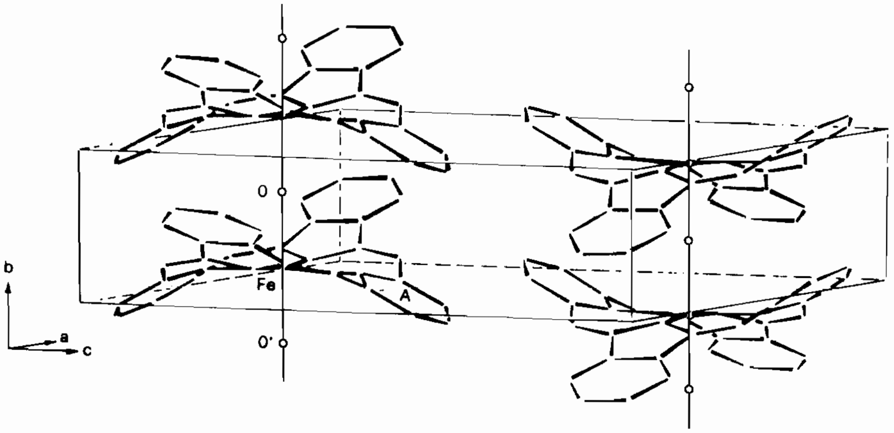

Fig. 1. Structure of μ-oxo 1 (reprinted from ref. 1).

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*Although it is true that oxygen analysis results must be treated with caution, this determination was carried out on five samples of compound 1, four of which were formed of well-shaped crystals. The values found were fairly different and lower than that expected: 2.2, 2.7, 1.8, 2.1 and 3% (expected 3.2%). In addition, the IR spectrum of the sample with the higher oxygen content showed, in the region 4000–3000 cm^{-1}, a very weak absorption remininscent of that presented by the μ-oxo monohydrate 2.

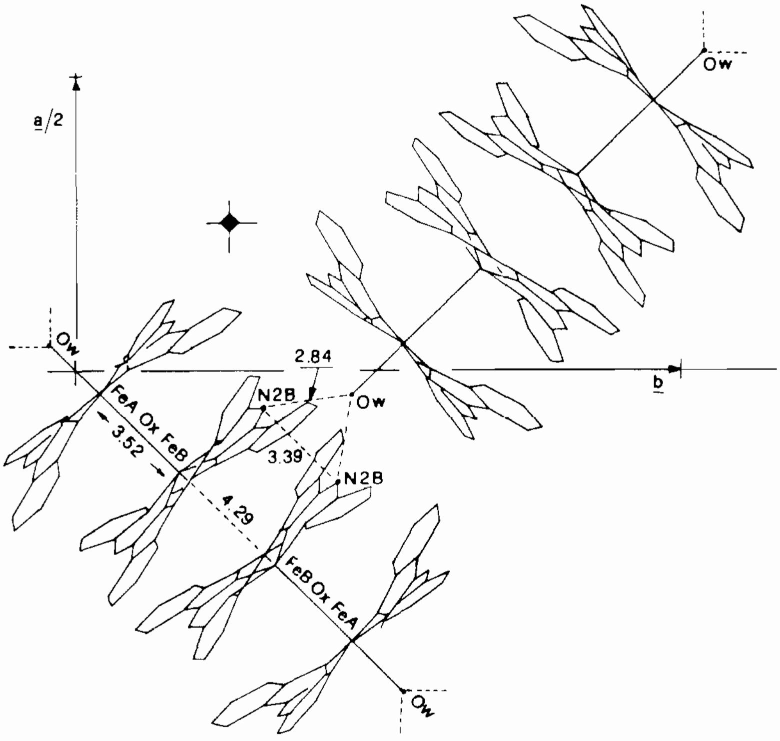

Fig. 2. Structure of $[(Fehp)_2O]H_2O$ (reprinted from ref. 2).

pattern indicates that the compound is amorphous. Its nujol mulls are not stable in air and, with time, show a partial transformation to **2**. The complete transformation $\mathbf{3} \rightarrow \mathbf{2}$ is obtained by simple reflux in H_2O in which both compounds appear insoluble. The behaviour of **3** indicates that it is a μ-oxo dimer, obtained from dimer **2** by eliminating the solvent, that readily takes up H_2O to give **2**. The thermal analysis of **3** is identical to that of **1** (Fig. 3d). If the thermoanalysis is interrupted at 300–310 °C, one finds that **3** has become **1**. The transformation $\mathbf{3} \rightarrow \mathbf{1}$ occurs without any variation in weight and without involving thermal processes (Fig. 3d and 3d'). **3** was also heated in O_2 for 1 h at various temperatures. The IR spectra of the samples treated in this way showed that the compound remains practically unchanged up to ~260 °C, at which temperature decomposition starts.

Further research on the thermal behaviour of **2** was carried out by interrupting the thermal analyses at various temperatures. It was found that: (i) at $T < 150$ °C the compound results unchanged; (ii) at $150 < T < 300$ °C a mixture of **1** and **3** was obtained; (iii) at $T \geqslant 310$ °C **1** was obtained. **2** was placed in N_2 in a closed vessel and made to undergo prolonged heating at 150 °C. Samples taken at successive intervals showed a slow but direct transformation of **2** into **1**. The same result was obtained by heating **2** at 150 °C sealed in a vacuum tube. Lastly, suspensions of **2** in inert solvents, like toluene, chlorobenzene, or nitrobenzene, were sealed in vacuum tubes that were heated for 24 h at 170 °C. **1** was obtained.

The main points of this examination seem to be:

(a) In conditions that should not permit a variation in the oxidation state of the metal, crystalline **2** (*i.e.*, the dimer Fe(III)μ-oxo monohydrate) gives **1**.

(b) The transformation can be direct (even if slow) at 150 °C. When heating in a N_2 flow (thermal analysis) or under pump vacuum, **2** gives **1** via a compound **3**, which we attribute as being an amorphous Fe(III) μ-oxo dimer.

(c) The transformation $\mathbf{3} \rightarrow \mathbf{1}$ that is seen at 300 °C (i) occurs without any variation in weight; (ii) does not involve a thermal process; (iii) is not favoured by O_2.

Reaction of Compounds **1**, **2** *and* **3** *with HCl: the Obtaining of μ-oxo HCl Adduct* **4**

Reaction with HCl is the classic procedure for obtaining chloroferric(III) compounds starting from Fe(III) μ-oxo dimers. The μ-oxo compounds **1**, **2** and **3** behave in the same way when treated under various conditions with HCl. In the presence of an organic solvent, they (nearly) always give Fe(II)hp-$(HCl)_2$. The reduction is avoided in a reproducible way if the compounds are stirred at room temperature with dilute aqueous HCl in absence of organic solvent. The compound obtained in these conditions

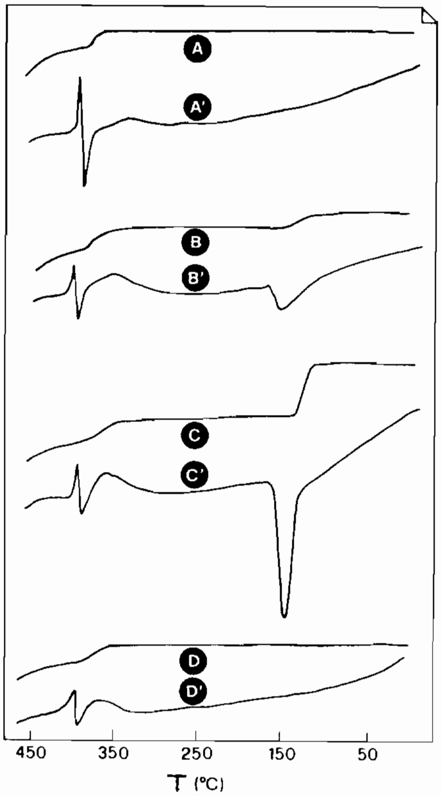

Fig. 3. Thermal analysis (TGA, DTA) of: μ-oxo, **1** (a, a'); $[(Fehp)_2O]H_2O$ obtained from DMF or γ-pic (b, b'); $[(Fehp)_2O]H_2O$ obtained from nitrobenzene (c, c'); amorphous μ-oxo, **3** (d, d').

(compound **4**) is easily characterized as a HCl adduct of a μ-oxo dimer compound because:

(1) simple washing with H_2O gives the μ-oxo dimer **2** once more.

(2) the compound is antiferromagnetic (see below) and shows an IR band between 800 and 900 cm^{-1} (846 cm^{-1}) as expected for compounds containing the group Fe–O–Fe [7].

(3) the IR spectrum also shows absorption in the NH region, always seen for the HCl adducts of Mhp compounds [3, 4]. Absorptions attributable to Fe–Cl bonds are missing.

For the IR characteristics of the compound, the HCl present in **4** is thought to interact essentially with the ligand through formation of hydrogen bonds H– – – – –N with the external nitrogens of the macrocycle. This (ligand)N– –HCl interaction was previously seen in $Fe(II)hp(HCl)_2$ [3], as in the other $M(II)hp(HCl)_2$ [4] adducts (in which, in addition, the halogen coordinates to the metal). Consistent with the resulting stronger interaction of the HCl– –M(II) hemiporphyrazine complex, a treatment with NaOH 0.5 mol dm^{-3}, instead of only H_2O, is necessary to eliminate the acid molecule from $M(II)hp(HCl)_2$ compounds.

Compound **4** contains more HCl, on the basis of the previously isolated compounds, than is considered to interact with the two macrocycles of the μ-oxo dimer (5 instead of 4); we cannot exclude that some HCl points towards the oxygen bridge.

Its thermal analysis between 60 and 300 °C shows a nearly continuous weight loss. What happens when the compound is heated in vacuum (10^{-2} torr) at temperatures <300 °C is described in 'Experimental'. On heating at 325 °C (10^{-2} torr) it sublimes and Fe(II)hp is obtained.

TABLE I. Magnetic Data

Compound	μ_{eff} (μ_B)	T (K)
μ-oxo **1**	1.68 0.62	300 87
μ-oxo **2**	2.09 1.48	294 83.5
μ-oxo **3**	2.16 1.56	293 78.5
μ-oxo **4**	2.34 1.83	288 78.5

TABLE II. Mössbauer Spectral Parameters

Compound	T (K)	δ ($mm\ s^{-1}$)		ΔE_Q ($mm\ s^{-1}$)
$Fe(II)hpH_2O$	78		0.966(3)	1.457(2)
μ-oxo **1**	78	site 1	0.359(5)	1.725(4)
		site 2	0.392(5)	1.415(4)
	300	site 1	0.25(1)	1.68(1)
		site 2	0.29(1)	1.43(1)
$[(Fehp)_2O]H_2O$	78		0.388(2)	1.656(2)

Magnetic, Mössbauer and ESCA Measurements

The magnetic moments of the μ-oxo compounds **1**, **2**, **3** and **4** measured at room temperature and at temperatures near 80 K are reported in Table I. All the compounds show the presence of antiferromagnetic interaction between the iron centres. The values found by us for **1** agree with those previously reported by Hiller *et al.* who carried out a complete and detailed magnetic study of the compound [1].

In the Table II are reported the Mössbauer data measured at 300 K and 78 K for **1**, **2** and $Fe(II)hpH_2O$. Their spectra are reported in Fig. 4. The δ and ΔE values of the high-spin $Fe(II)hpH_2O$, when compared with those of high-spin Fe(II) complexes with similar ligands, [8], show a relatively low value for ΔE. Both high and low symmetric environments have been found to give such low ΔE

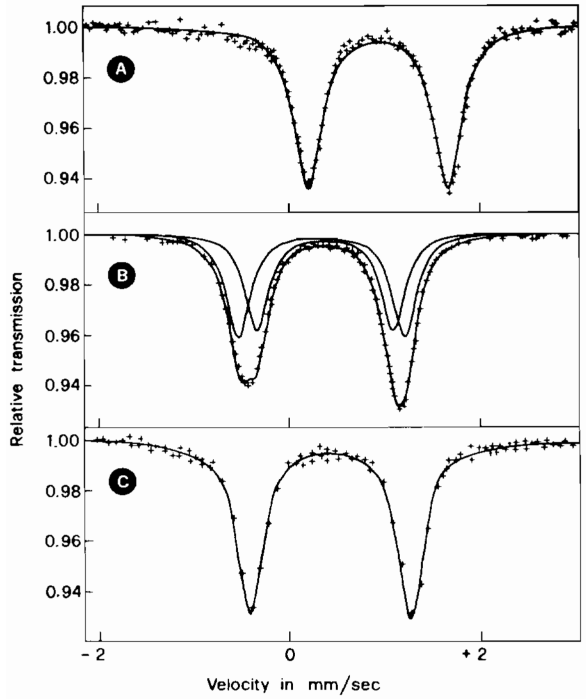

Fig. 4. Mössbauer spectra at 78 K of: (A) Fe(II)hpH_2O; (B) μ-oxo 1: (C) [$(Fehp)_2O$]H_2O.

values [9]. With hp as ligand, the first case certainly does not occur, and the low value of ΔE again supports its high asymmetry [10, 11].

The two pairs of δ and ΔE data obtained by us from the asymmetric spectrum of compound **1**, even though they were obtained at slightly different temperatures, agree with those reported by Hiller *et al.* [1]. These δ and ΔE values do not appear in line with the values found for the Fe(IV) complexes ascertained to date [12]. Characteristics for such an oxidation state seem, in fact, to be an isomer shift of about 0 mm/s in addition to a rather large quadrupole splitting. The values found for **1** are close to those expected for a high-spin Fe(III) monomer or a Fe(III) μ-oxo dimer [8], taking into account that the asymmetry of the environment, due to this macrocycle, can lead to an increase of the ΔE value for Fe(III) compounds. This is verified by the values of δ and ΔE measured for the Fe(III) dimer **2** which, in addition, are completely comparable to those of μ-oxo **1**. So, with Mössbauer spectroscopy the two compounds **1** and **2** are not differentiated.

Finally, it was possible to measure an X-ray photoelectron spectrum on the compounds **1** and **2** and on the compound Fe(II)hpH_2O. The binding energies of Fe2p3/2 levels found are: 710 eV for Fe(II)hpH_2O, 711 eV for **1** and 711.5 eV for **2**. Although these data are to be considered with caution in that they are due to a single determination ($\Delta = \pm 0.2$ eV), the value found for Fe(II)hpH_2O is close to those of Fe(II) compounds and the values found for μ-oxo **1** and **2** (comparable within measuring errors) are those expected for Fe(III) compounds [13].

Spectrophotometric Behaviour and Stability in Solution of μ-oxo Iron–Hemiporphyrazine Compounds

The IR spectra in the 1000–600 cm^{-1} region for the four μ-oxo compounds are reported in Fig. 5. We notice that the Fe–O–Fe group of **2** gives only one absorption, whereas the Fe–O–Fe group of **1** shows an asymmetric band clearly originating from more than one absorption.

As reported in 'Experimental', **1** or **2** can be obtained by bubbling gaseous O_2 in a Fe(II)hp solution in γ-pic (anhydrous or wet). If the concentration of the iron(II) hemiporphyrazine solution does not exceed 10^{-3} mol dm^{-3}, we can record the absorption spectrum before and after the formation of solids resulting from the passage of O_2. Qualitative spectra are shown in Fig. 6. The initial green solution has the spectrum of the Fe(II)hp(γ-pic)$_2$ species (spectrum A) [3]. The final spectrum recorded on the yellow–brown solution, obtained by filtering the reaction suspension, is characterized by a maxi-

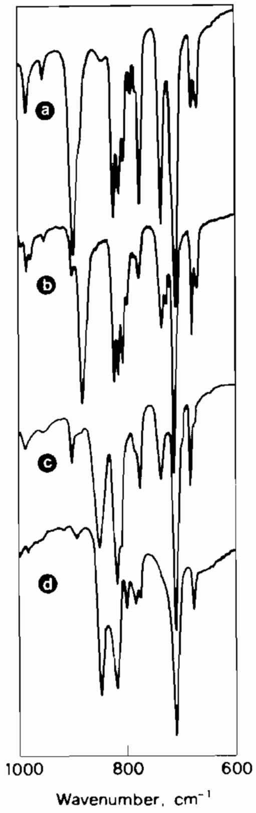

Fig. 5. Infrared spectra, as nujol mulls, of: (a) μ-oxo, **1**; (b) [$(Fehp)_2O$]H_2O, **2**; (c) amorphous μ-oxo, **3**; (d) μ-oxo, **4**.

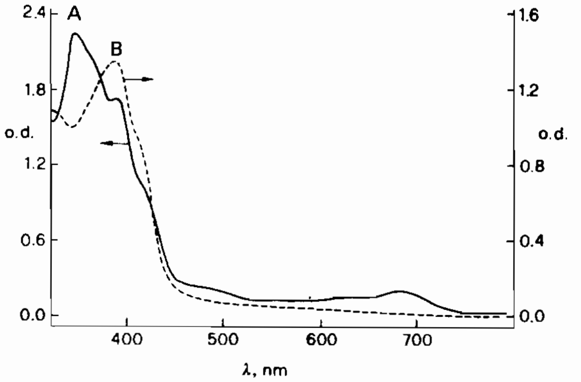

Fig. 6. Absorption spectra of: A, Fe(II)hp in γ-pic, under N_2 (left hand ordinate); B, the same solution, in presence of μ-oxo **1** or μ-oxo **2**, after bubbling O_2 (right hand ordinate). (1 mm cells).

mum at 390 nm (spectrum B) when the precipitate is formed either by **2** or **1**. The same spectra A and B have been reported to represent the initial and final stages of the irreversible interaction of Fe(II)hp with O_2 in γ-pic solution [3].

When the μ-oxo solids **1** and **2** as well as **3** and **4** are brought in solution in γ-pic in N_2, one observes that compound **1** dissolves with difficulty. The dissolution occurs more easily on heating at ~80 °C. The solution thus obtained presents the spectrum B. At room temperature, compound **2** dissolves more easily than **1**. Its spectrum is still B. **3** and **4** dissolve more easily and always give the same spectrum, B.

The spectrophotometric observations show that the same species is present in solution, whether the dimer or μ-oxo **1** separates from it, and is re-obtained on dissolving either. Before the structure of the dimer was resolved, these observations led us to think that in solution this species was an Fe(IV) species [3]. This is no longer tenable; it seems more likely that it is an Fe(III) compound, probably μ-oxo, given the absence of an ESR signal presented by the solution up to 100 K.

The yellow–brown solutions obtained by dissolving μ-oxo compounds, like those resulting from the interaction of O_2 with Fe(II)hp, in the complete absence of air are not stable; they slowly go green and the spectrum of Fe(II)hp(γ-pic)$_2$ is obtained. The entire behaviour can be summarized as follows:

$$\begin{tikzcd}
\text{Solid Fe(II)hp} \arrow[r, "\gamma\text{-pic}", "N_2"'] & \text{green solution of Fe(II)hp}(\gamma\text{-pic})_2 \; \lambda_{max}\ 346\text{ nm} \arrow[r, "O_2"] & \text{yellow solution } \lambda_{max}\ 390\text{ nm} \arrow[r, "O_2\text{ absent}"] \arrow[d, shift right] & \text{green solution } \lambda_{max}\ 346\text{ nm} \\
 & & \text{solid } \mu\text{-oxo } \mathbf{1} \text{ or solid } \mu\text{-oxo } \mathbf{2} \text{ (if } \gamma\text{-pic non anhydrous)} \arrow[u, shift right, "\gamma\text{pic}\ N_2"'] &
\end{tikzcd}$$

The time necessary to complete the reduction to Fe(II) depends on the concentration of the solution and decreases as the temperature increases. Furthermore, it is notably influenced by the addition of PPh_3.

Further evidence for the reduction that occurs in solution by the action of a substrate comes from the experiments carried out with **1** and **2** in vacuum-sealed tubes (see 'Experimental'). The time and the temperature at which they were carried out were chosen to take into account the low solubility of the complexes in toluene, even in the presence of a strong excess of PPh_3. The reduction does not occur in pure toluene or nitrobenzene, but does occur in toluene + PPh_3, in nitrobenzene + PPh_3, and in pure γ-pic. From the latter, the Fe(II) complex formed is isolated as solid Fe(II)hp(γ-pic)$_2$. The formation of solid Fe(II)hpH_2O in the other two cases indicates that Fe(II)hp from the reduction does not form stable solid adduct with PPh_3 and in air gives the stable Fe(II)hpH_2O.

Reduction to Fe(II) can also occur in air. We have seen that the μ-oxo **1** or [(Fehp)$_2$O]H_2O interact in air with aqueous dilute HCl to give the μ-oxo HCl adduct, **4**. If **4** is simply stirred in air with DMF, a colouring of the solvent is observed with separation of a solid that is found to be Fe(II)hp(HCl)$_2$. This same Fe(II) product can be directly obtained starting from **1** or **2** (as reported in 'Experimental'), if dilute HCl is added after they have been suspended in DMF (the latter result is also obtained with C_2H_5-OH instead of DMF).

$$\begin{tikzcd}
 & \text{[(Fehp)}_2\text{O](HCl)}_5(\text{H}_2\text{O})_6 \arrow[dr, "\text{DMF}"] & \\
\text{Comp. 1, [(Fehp)}_2\text{O]H}_2\text{O} \arrow[ur, "\text{aqueous HCl}"] \arrow[rr, "\text{HCl+ DMF}"'] & & \text{Fe(II)hp(HCl)}_2
\end{tikzcd}$$

Conclusions

The molecular structure of iron μ-oxo dimer Fehp–O–Fehp–OH_2 unequivocally ascribes the oxidation state 3+ to iron and forms the basis for an identical attribution for iron in analogous compounds: the amorphous μ-oxo iron–hemiporphyrazine and the μ-oxo iron–hemiporphyrazine HCl adduct. The conditions in which the μ-oxo dimer $[(Fehp)_2O]H_2O$ and the μ-oxo compound **1** are formed, their thermal and spectroscopic behaviour, and Mössbauer and ESCA data do not agree with a change to 4+ of the iron oxidation state in **1**.

Some further observations can be made on the structural data of this first stable solid Fe(IV) compound. The distances found for the coordination cavity of the ligand ($Fe-N_{isoind}$ = 1.91 Å, $Fe-N_{py}$ = 2.135 Å), when compared with the corresponding ones obtained for other hemiporphyrazine complexes (1.863 Å and 1.998 Å for the diamagnetic Nihp [6], 1.97 Å and 2.18 Å for high-spin $Nihppy_2$ [9], and 1.985 Å and 2.195 Å for the high-spin $[(Fehp)_2O]H_2O$ [2]), can indeed support the presence of an empty $d_{x^2-y^2}$. However, the Fe–O (bridge) distance, ~2 Å, seems long for a covalent bond with an empty d_{z^2} orbital, as in Fe(IV) S = 1. An axial Fe–O distance of ~2 Å has recently been found but for a coordinated H_2O molecule in a low spin Fe(III) porphyrin [14]. The same distance for a covalent Fe–O has, nevertheless, been found in μ-hydroxy bridges high-spin Fe(III) compounds [15] in which the d_{z^2} orbital is singly occupied.

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