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Mössbauer Spectroscopic Studies on Short 'Self-fenced' Porphyrinato Iron(III) Complexes. Evidence for the Absence of μ-Oxo-bridged Formation

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Abstract

Mössbauer spectra provide evidence for the existence of monomeric monohydroxo(porphyrinato)iron(III) complexes in solids formed under conditions where μ-oxo-bridged species might have been expected. The porphyrins studied in this work are all of the 'self-fenced' variety. It is demonstrated here that the presence of such fences is sufficient to deter the formation of μ-oxo-bis(porphyrinato)iron(III) complexes.

Introduction

The formation of μ-oxo-bridged (porphyrinato)iron(III) species has been a much researched topic in iron(III) porphyrin chemistry [1–7]. The factors responsible for inhibiting μ-oxo-bridged species have been of interest in designing porphyrinato iron(II) complexes capable of reversibly binding molecular oxygen [8–16].

In the last few years, various modified metalloporphyrin complexes have been synthesised as models of natural oxygen carriers such as haemoglobin and myoglobin. The 'picket fence' and the 'capped' iron porphyrin complexes synthesised by Collman *et al.* [14, 15] and by Baldwin *et al.* [8–10] respectively are examples. However, these porphyrins based on a steric inhibition of μ-oxo-bishaem formation strategy may be regarded as overkill. Vaska and Amundsen [17, 18] prepared (tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron(II) [$T(MeO)_3PPFe(II)$] and *meso*(tetrakis(2,4,6-triethoxy phenyl)porphyrinato)iron(II) [$T(ETO)_3PPFe(II)$] which are protected by smaller 'fences' on both faces. The products from exposure of the two compounds to O_2 could not be satisfactorily characterised although the authors did conclude that μ-oxo-dimer formation had not occurred. Recently a reinvestigation into the properties of these compounds using ^1H NMR spectroscopy has been untertaken [19]. Latos-Grazinski *et al.* [19] found that instead of μ-oxo-bridge formation a high-spin species which has the formulation [$T(MeO)_3PPFeOH$] is the product on exposure to oxygen. *meso*(Tetra(anthracenyl)porphyrinato)iron(II) [TAnPFe(II)] has been synthesised [20]. [$TAnPFe(II)(N\text{-}Me\text{-}Im)_2$] was converted under oxygen and at room temperature into an iron(III) species, but was oxygenated reversible at –20 °C [20]. The fences in this anthracyl porphyrin are also relatively small. Our studies on tetra(4-sulpho,1-naphthyl)porphyrinato iron(III) [TNPSFe(III)] [7] show that this complex does form a μ-oxo-bis haem.

We report here the Mössbauer spectra of the known complexes [$T(MeO)_3PPFeCl$] and [$T(MeO)_3PPFeOH$]. The latter was prepared under conditions which for non sterically hindered (porphyrinato)iron(III) complexes would have produced μ-oxo-bis haems. In addition we report the preparation of *meso*-tetraphenanthrenylporphyrin ($TPhPH_2$) and report the electronic absorption and Mössbauer spectra of two of its iron(III) complexes. We also report electronic absorption spectra for TAnPFe(III) complexes.

Experimental

Preparation of Porphyrins

The symmetric *meso*-substituted porphyrins listed in Table 1 were prepared from pyrrole (Aldrich) and the aldehyde (purchased from Aldrich and used as received) in refluxing propionic acid according to the method of Alder *et al.* [21]. The solution was stirred for 30 min cooled to room temperature and filtered. The resulting powder was washed with methanol. After drying the powder was dissolved in a minimal amount of chloroform and chromatographed on a 60 cm long neutral alumina (Aldrich) column with a chloroform/hexane mixture. The main purple band was collected for each porphyrin and the solvent was allowed to evaporate to dryness. $H_2T(MeO)_3PP$ and H_2TAnP have been prepared previously [17–20]. H_2TPhP was analysed by the Micro Analytical Laboratory, Department of Chemistry, University of

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TABLE 1. Electronic absorption spectra for free base porphyrins

Porphyrins prepared	Abbreviation	Electronic absorption maxima[a]				
		Soret	IV	III	II	I
meso(Tetra(2,4,6-methoxyphenyl)porphyrin	$H_2T(MeO)_3PP$	420(1)	514(0.09)	545(0.05)	590(0.05)	645(0.04)
meso(Tetra(anthracenyl)porphyrin	H_2TAnP	424(1)	516(0.13)	546(0.06)	592(0.06)	655(0.03)
meso(Tetra(phenanthrenyl)porphyrin	H_2TPhP	424(1)	515(0.08)	547(0.04)	588(0.04)	648(0.03)

[a] λ_{max} in nm. Relative intensities of the absorption bands are normalised to the Soret bands and appear in parentheses.

TABLE 2. Electronic absorption maxima (nm) for the porphyrinato iron(III) chlorides complexes in chloroform

Compound	Soret	Soret	IV	III	II	I	Reference
$[T(MeO)_3PPFeCl]$	390	421	510	578	656	689	this work
		422	508	578	658	686	23
[TAnPFeCl]	380	424	514	586	660	695	this work
[TPhPFeCl]	379	428	512	586	649	683	this work

Manchester. *Anal.* Found: C, 86.5; H, 4.9; N, 5.0. Calc. for $H_2TPhP \cdot 0.5C_6H_{12}$: C, 88.8; H, 4.92; N, 5.30%.

Preparation of Porphyrinato Iron(III) Complexes

A literature method was used to prepare the metalloporphyrins [22]. A refluxing solution of the porphyrin in dimethylformamide (DMF) was treated with ferrous chloride and the mixture refluxed until the reaction was complete. The progress of the reaction was monitored spectrophotometrically. The products were extracted with chloroform. Half of this chloroform solution was shaken with a few millilitres of concentrated hydrochloric acid in air to obtain the monomeric porphyrin Fe(Por)Cl. The remainder was stirred for 5 h in air with sodium hydroxide (50 ml, 25%) to obtain the μ-oxo-bridged species $O(FePor)_2$ or the monomeric porphyrin Fe(Por)OH. The chloroform layer was separated from the water layer and purified by chromatography. The complexes were identified by their electronic absorption spectra (Tables 2 and 3).

TABLE 3. Electronic absorption maxima (nm) for the porphyrinato iron(III) complexes in chloroform (with aqueous NaOH present). These are monomeric complexes (see text)

Compound	Soret	α	β	Reference
$[T(MeO)_2PFe(OH)]$	422	578	635	this work
	418	578	634	23
[TAnPFe(OH)]	424	581	636	this work
[TPhPFe(OH)]	425	580	634	this work

Physical Measurements

Instrumentation

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5G. The Mössbauer spectrometer has been previously described [24]. The pH measurements were carried out using a Philips PW 9409 digital pH meter and a glass electrode. A Perkin-Elmer model 1300 spectrophotometer was used to record IR spectra in the range 4000–400 cm^{-1} as Nujol mulls on NaCl discs. The instrument was calibrated by the polystyrene bands at 3027.9, 1601.8 and 906.9 cm^{-1}.

Mössbauer spectroscopy

Mössbauer spectra were recorded on solids at 78 K. The solids from effective high pH were prepared by removing solvent and drying. All spectra were computer fitted by a simple least-squares fitting program. All isomer shifts are referred to natural iron. Details of the apparatus, source, etc. have been published previously [2, 4, 7].

Results and Discussion

The electronic absorption spectra are presented in Table 1 for the free base porphyrins. These are listed with adoption of the numbering system (IV–I) for the visible bands used by Falk [25]. The possible transitions for those bands were previously discussed by Gouterman [26].

$H_2T(MeO)_3PP$ (Table 1) has an Eto-type electronic absorption spectrum. This type with band intensities in the ratio IV > II > III–I is found for example in

TABLE 4. ^{57}Fe Mössbauer spectroscopic data of monomeric porphyrinato iron(III) complexes at 78 K

Complex	δ (mm s^{-1})^{a}	Δ (mm s^{-1})^{a}	Γ (mm s^{-1})^{b}	Γ (mm s^{-1})^{b}
[T(MeO)$_3$PPeCl]	0.32(6)	0.62(11)	0.31(6)	1.20(7)
[T(MeO)$_3$PPFe(OH)]	0.35(5)	0.38(9)	0.25(12)	0.92(7)
[TPhPFeCl]	0.27(6)	0.48(7)	0.30(3)	1.15(6)
[TPhPFe(OH)]	0.32(8)	0.40(10)	0.13(5)	0.77(8)

^{a}The isomer shift and quadrupole splittings are difficult to computer fit as the spectra are asymmetric broad lines (see Fig. 1). Hence the large errors on the data. ^{b}Half-width at half-height.

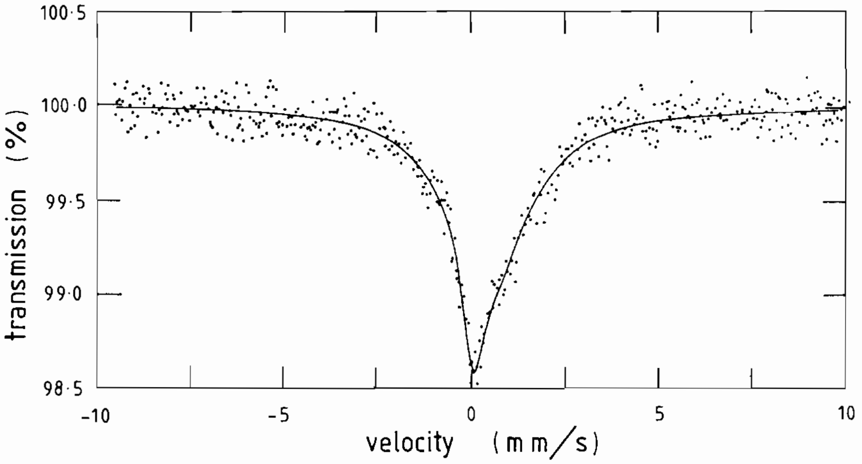

Fig. 1. ^{57}Fe Mössbauer spectra of [T(MeO)$_3$PPFeCl] at 78 K.

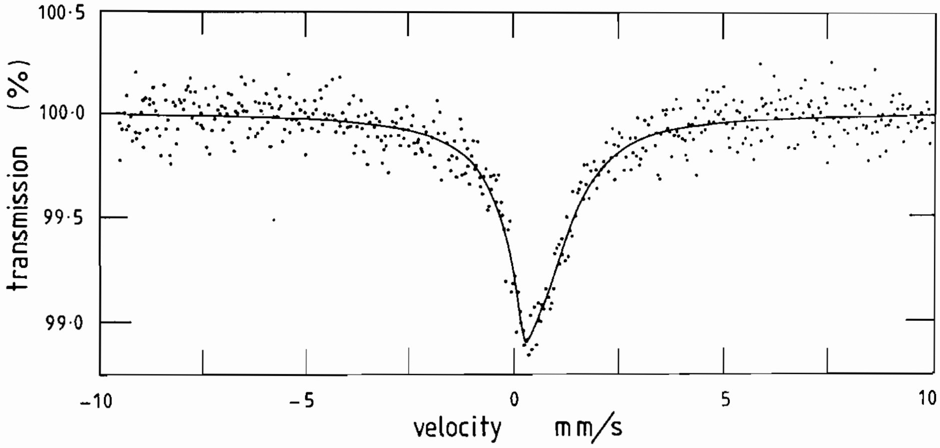

Fig. 2. ^{57}Fe Mössbauer spectra of [T(MeO)$_3$PPFeOH] at 78 K.

H_2TPP. The Mössbauer spectra of the compounds 1 and 2, [T(MeO)$_3$PPFeCl] and [T(MeO)$_3$PPFe(OH)] (Table 4) have isomer shifts that are typical of high-spin iron(III) porphyrins. The spectra are broad and asymmetric at 78 K for these compounds (Figs. 1 and 2). The electronic absorption spectra of these compounds are in good agreement with the literature spectra [23], as are the IR spectra which remain unaltered when the OH^- ion replaced the Cl^- ion in the region between 900–800 cm^{-1}. The shoulder on the Soret band present in these spectra is usually observed in the electronic absorption spectrum of the iron(III) porphyrin monomers. The differences in the Mössbauer parameters and the shifts in the electronic absorption spectra must reflect the effect of the axial ligand(s) on the electronic environment of the iron atom. $T(MeO)_3PPFe(III)$ is one of the self-fenced porphyrins and is ostensibly protected by fences on both faces. This compound was first prepared and studied by Vaska *et al.* [17, 18]. They postulated that the four trimethoxyphenyl substituents in $T(MeO)_3$-PPFe have no free rotation [17], unlike the phenyl in TPPFe whose rotation is only slightly hindered [17].

[TNPFeCl] and its μ-oxo-bishaem have been previously prepared [27]. The substituent on the *meso* position does not prevent the formation of a μ-oxo-bishaem but does make it less favourable [7]. This can be explained in either or both of the following ways. (i) The free rotation of the naphthalene groups allows all these groups to be on the same side of the porphyrin plane. (ii) The four possible isomers that exist in TNPSFe(III) rearrange between each other and form μ-oxo-dimers only where hindrance is a minimum.

In contrast, the An group like the trimethoxyphenyl groups are not free to rotate [20]. This is because of steric hindrances between H atoms in the An and the pyrrole protons in the transition state. In TAnPFeCl there is no evidence of μ-oxo-bridge formation in the presence of NaOH. The hydroxide group replaces the Cl ion as an axial ligand and forms [TAnPFe(OH)]. No changes were observed (when the hydroxide groups replaced the Cl^-) in the IR spectra of these compounds in the region between 900–800 cm^{-1}. The electronic absorption spectrum of [TAnPFe(OH)] is in good agreement with the spectra of Harel and Felton [28] and Cense and Le Quan [20] and is remarkably similar to that of high-spin Fe(III)TPP methoxide [29].

The phenanthrene (Ph) ring, unlike anthracene (An) has an asymmetrical shape when its aldehyde reacts with pyrrole to form a porphyrin ring. [TPhPFeCl] has four Ph groups substituted at the *meso* positions. The latter compound like [TNPFeCl] has four possible isomers. Because of the low percentage yield of this compound (0.5%–1.5%) no attempt was carried out to separate the isomers. The Mössbauer spectrum of [TPhPFeCl] has an isomer shift that is typical of high-spin (porphyrinato)iron-(III)Cl monomers. The spectrum is broad and asymmetric. For [TPhPFe(OH)] in the solid state, no evidence of dimerisation was found. For this compound a Mössbauer spectrum typical of an asymmetric high-spin (porphyrinato)iron(III) monomer was observed, and the IR spectrum does not change in the 900–800 cm^{-1} region when the OH group replaces the Cl ion in [TPhPFeCl]. In solution, the electronic absorption spectra of [TPhPFe(OH)] (Table 3) is very similar to that of [TAnPFe(OH)] and $[T(MeO)_3PPFe(OH)]$. To explain the solution spectra we suggest that the electronic absorption spectra belong to PorFe(III)(OH) species and are coincidently similar to those of μ-oxo-bishaems. In addition the discussion presented by Cheng *et al.* [23] on the similarity found for the electronic absorption spectra of $[(TPP)FeOCH_3]$ and [(TPP)-FeOFe(TPP)] also is evidence in favour of our suggestion.

Conclusions

We find no evidence for μ-oxo-bishaem species in these complexes. There was no evidence of asymmetric Fe–O stretching absorbances around 850 cm^{-1} in the IR spectra. The Mössbauer spectra of the two hydroxide species were asymmetric unresolved broad lines. In contrast, typical μ-oxo-bishaems contain antiferromagnetically coupled iron(III) centres which are manifest in their Mössbauer spectra by the presence of well resolved quadrupole splittings on symmetrical sharp lines [2, 7, 30].

In the $T(MeO)_3PPFe(III)$ complexes our findings are in good agreement with the conclusions of Amundsen *et al.* [17, 18] and Latos-Grazinski *et al.* [19].

It appears that relatively small fences on phenyl substituents on the *meso* carbons of porphyrinato iron(III) compounds are sufficient to deter the formation of μ-oxo-bishaems.

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