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A Mössbauer Investigation of the Interaction of (Phthalocyaninato)iron(II) with Molecular Oxygen.
Evidence for only One Form of (μ-Oxo)bis(phthalocyaninato)iron(III) is found

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Abstract

Mössbauer data are presented for (μ-oxo)bis(phthalocyaninato)iron(III) [$(FePc)_2O$]. The quadrupole splitting is smaller than those found for other (μ-oxo)bis(porphyrin)iron(III) species. No evidence is found for a second (μ-oxo)bis(phthalocyaninato)iron(III) species in this work.

Introduction

Over the past few years we have made systematic studies of the chemistry of protoporphyrin IX iron(II)/(III) (PPIXFe) solutions and solids as models to aid in the understanding of the chemistry and properties of haem proteins [1–11]. In the course of this work we have studied two (μ-oxo) dimers (more correctly called oligomers); one found at high pH in (PPIXFe(III)) [3], solutions and the other in tetra (p-sulphophenyl) porphine iron(III) (TPPSFe(III)) [11]. Both these materials were water soluble and had similar quadrupole splittings of 0.53 mm s^{-1} for $(TPPSFe(III))_2O$ and 0.58 mm s^{-1} for $(PPIXFe(III))_2O$. Other workers have recorded similar quadrupole splittings for a range of μ-oxo-bridged porphyrins [12, 13].

Recently a paper has appeared discussing the interaction of (phthalocyaninato)iron(II) (PcFe(II)) with molecular oxygen in which two (μ-oxo)bis(phthalocyaninato)Fe(III) complexes were reported and characterised by a number of techniques [14]. As these were the first well characterised Fe(III) phthalocyaninato species we decided a study of the Mössbauer spectra would be useful, since the quadrupole splittings compared to the μ-oxo-bridged porphyrins should be changed, because of the differences in the phthalocyaninato molecule compared to the porphyrin molecule. Also as the two $(PcFe(III))_2O$ species are claimed to differ structurally their Mössbauer parameters should demonstrate these differences.

Results and Discussion

The Mössbauer results are presented in Table I and Figs. 1 and 2. The Infra-red spectra are in Fig. 3. The sample of μ-oxo 1 made by the method of Ercolani *et al.* [14] gives Mössbauer parameters

TABLE I. Mössbauer Parameters for Fe(II)Pc and μ-Oxo-bridged Dimers at 110 K.

	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})^a	Relative %Abs
Fe(II)Pc (at 298 K)	0.39(2)	2.60(2)	0.15(1)	
Fe(II)Pc	0.46(2)	2.65(2)	0.17(1)	100(2)
μ-oxo 1	0.34(2)	0.38(2)	0.17(1)	100(3)
μ-oxo 2(a)	0.34(2)	0.37(2)	0.15(1)	100(5)
μ-oxo $2(b)_{\text{Fit A}}$	0.34(2)	0.49(2)	0.18(1)	46(4)
	0.23(2)	1.31(2)	0.17(1)	54(4)
μ-oxo $2(b)_{\text{Fit B}}$	0.34(2)	0.38(2)	0.17(1)	35(3)
	0.23(2)	1.28(2)	0.19(1)	65(3)

^{a}Half width at half height.

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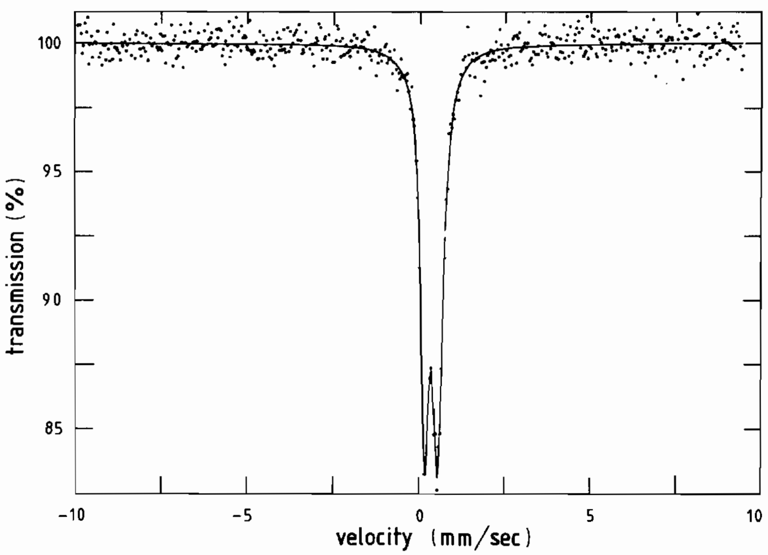

Fig. 1. Mössbauer spectrum of (μ-oxo)bis((phthalocyaninato)iron(III)) (μ-oxo 1).

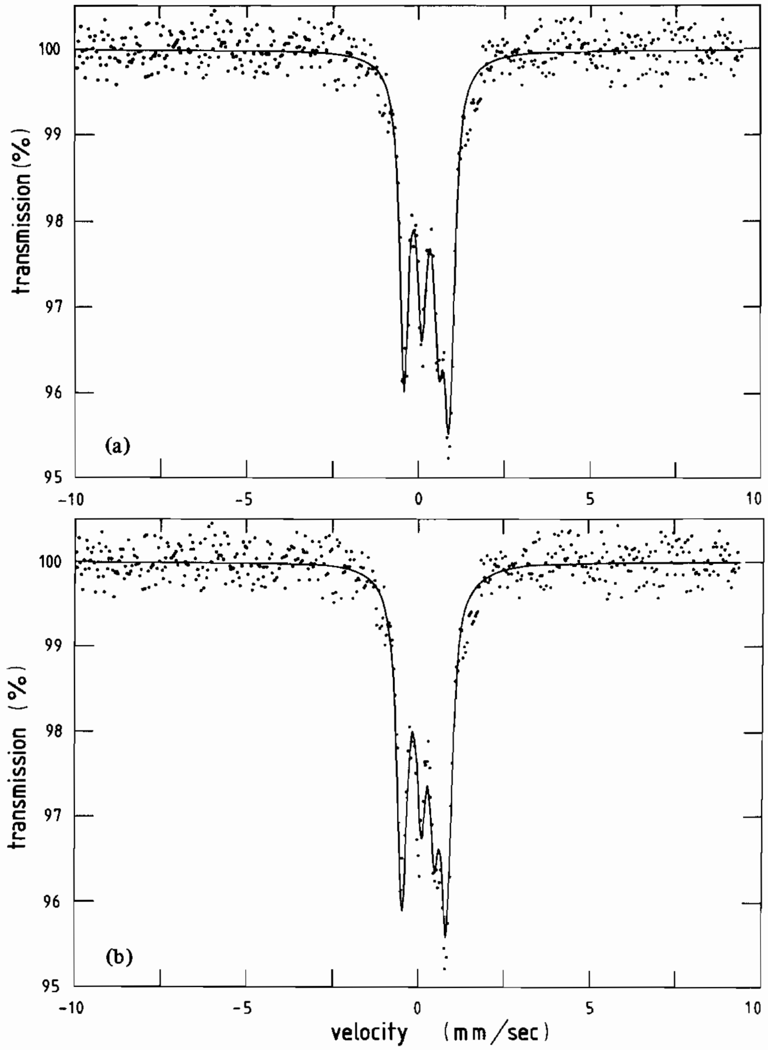

Fig. 2. Mössbauer spectrum of μ-oxo 2(b) prepared from 96% H_2SO_4, bubbling O_2 through solution, (i) Fit A, (ii) Fit B.

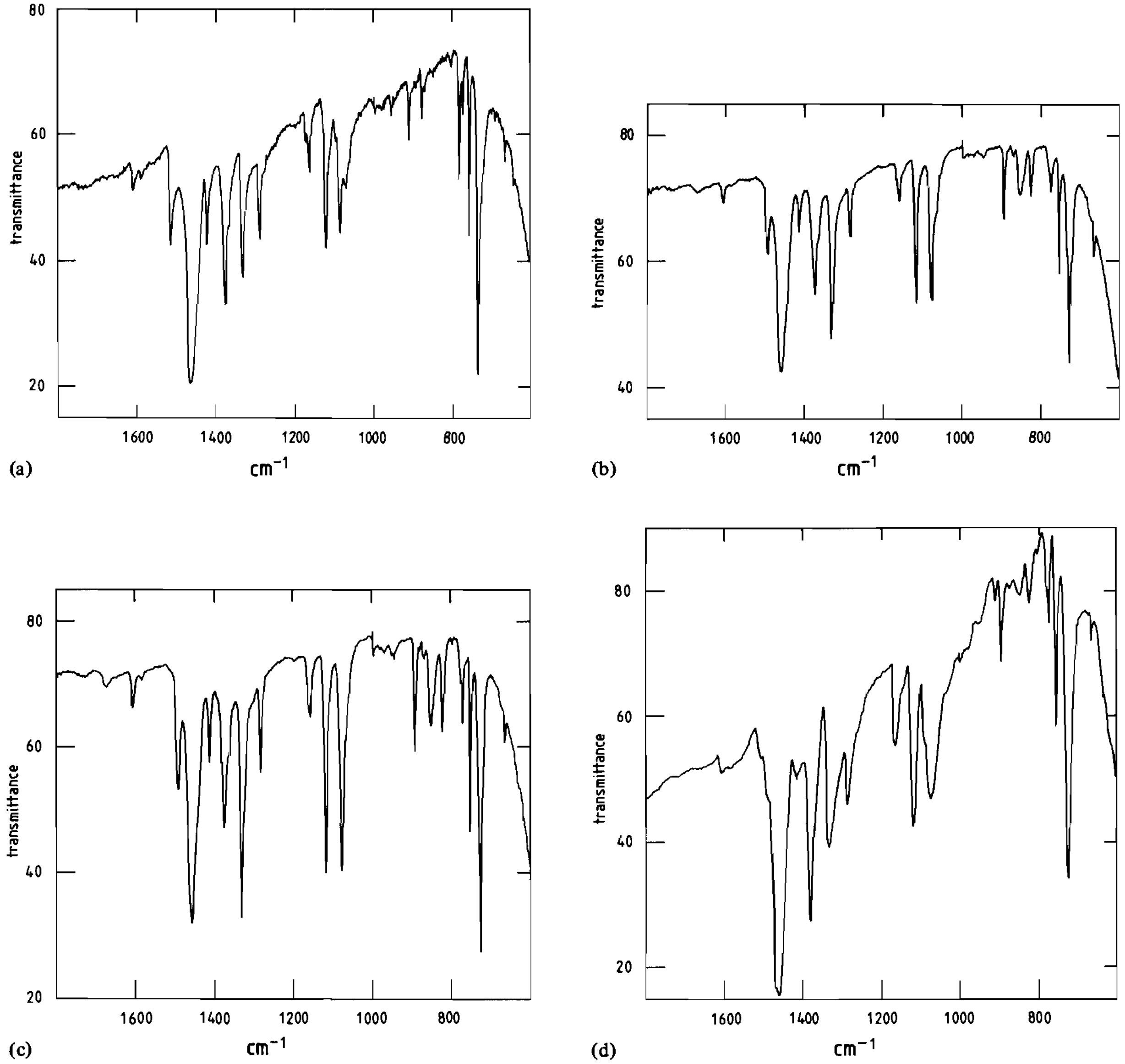

Fig. 3. Infra-red spectra of: (a) Fe(II) phthalocyanine; (b) (μ-oxo)bis((phthalocyaninato)iron(III)) μ-oxo 1; (c) (μ-oxo)bis-(phthalocyaninato)iron(III)) μ-oxo 2(a); (d) (μ-oxo)bis((phthalocyaninato)iron(III)) μ-oxo 2(b).

(Table I, Fig. 1) in keeping with the assignment of $(PcFe(III))_2O$ to this compound (IR Fig. 3b). The sample of μ-oxo 2(a) made according to the first suggested method of Ercolani *et al.* [14] gives Mössbauer parameters identical to that of μ-oxo 1 Table I (IR data Fig. 3c). The sample of μ-oxo 2(b) prepared by dissolving Fe(II)Pc in 96% H_2SO_4 and bubbling O_2 as described by Ercolani *et al.* gave an infrared spectrum very similar to that reported [14]. The Mössbauer spectrum of this sample (Fig. 2) shows the presence of two iron sites; one possibly the μ-oxo 1 dimer and the second an unknown low spin Fe(II) species. We will return to this spectrum below.

It is worth noting that the Mössbauer quadrupole splitting for $(PcFe(III))_2O$ presented here is the smallest found for a μ-oxo-bridged Fe dimeric species [12, 13]. This quadrupole splitting is generated by a modified electronic environment compared to the μ-oxo-bridged oligomers $(PPIXFe(III)_2O$ and $(TPPS(Fe(III))_2O$. The modification is caused by three principal factors:

(1) The phthalocyanine group's electronic effect on the Fe(III) environment.

(2) The angle of the Fe–O–Fe bond.

(3) The strength of the Fe–O–Fe bond.

There have been a number of Mössbauer studies of Fe(II)Pc [15–27]. These have established the fact that the iron is in an $S = 1$ state and the parameters are similar to those we present for Fe(II)Pc (Table I).

Amongst the Mössbauer studies two recent papers [28, 29] deal with Fe(II)Pc supported on carbon electrodes. These papers present spectra containing an oxidized Fe(III) species, some of which appears to fit the Mössbauer parameters of $(PcFe(III))_2O$. In addition, there is evidence for a species prepared in acid that has the same parameters to those we present for our second site in μ-oxo 2(b) (Fig. 2). Blomquist *et al.* [30] suggest this site is due to FePc bonded to the carbon electrodes. However, Scherson *et al.* [29] suggest it is due to a sulphonated phthalocyanine iron(II) species. The sample quoted by the latter authors was prepared in a similar manner to that suggested by Ercolani *et al.* [14] using H_2SO_4 and bubbling O_2 through the solution.

We agree with the suggestion of Scherson *et al.* [29] that this species with a quadrupole splitting of 1.28(2) mm s^{-1} is a tetrasulphonated phthalocyanine Fe(II) species, though disagree with these authors in that we believe that the parameters have been modified by the presence of SO_3^- groups and that these groups change the electronic distribution in the molecule affecting the entire phthalocyanine skeleton and being transmitted to the Fe(II) via the N atoms.

We have fitted the spectrum Table I, Fig. 2 μ-oxo 2(b) in two different ways. The first fit was carried out letting both sites vary and this fit yields an inner doublet with a quadrupole splitting of 0.49 mm s^{-1}. The second fit B had the inner site held to the parameters of μ-oxo 1, but the relative area of this site was allowed to vary. From the data in Table I, presented in Fig. 2 there is little to choose between these two fits. We suggest that the difference of 0.1 in the quadrupole splitting with no corresponding change in the chemical shift is not good evidence for a different μ-oxo dimer, and probably is due to the counting statistics.

A change of 0.1 mm s^{-1} in quadrupole splitting in a μ-oxo dimer prepared in H_2SO_4 would be expected, as this complex could well contain sulphonated phthalocyanine iron(III) rings. These would modify the quadrupole splitting relative to that of phthalocyanine rings (*cf.* $(TPPFFeIII)_2O$ and $(TPPSFeIII)_2O$ have quadrupole splittings of 0.62 mm s^{-1} and 0.53 mm s^{-1} respectively [11, 12].

We suggest that the material said to be μ-oxo 2 by Ercolani *et al.* [14] is in fact a mixture of the two species we present in Fig. 2, though not necessarily in the same ratio. Such a mixture could easily have been erroneously described as it would generate a very small magnetic moment if only a small amount of the μ-oxo 1 $(PcFe(III))_2O$ species were present along with a low spin Fe(II) species (the latter in excess).

We are currently attempting to fully characterise the low spin Fe(II) sulphonated phthalocyanine material.

Experimental

Preparation of Fe(II) Phthalocyanine and μ-Oxo-bridged Dimers

Fe(II) Phthalocyanine was prepared according to the method of Linstead *et al.* [31]. (μ-Oxo)bis((phthalocyaninato)iron(III)) was prepared by the method of Ercolani *et al.* [14].

Instrumentation

The Mössbauer spectra were recorded on an instrument previously described [32]. The source was ^{57}Co (10 mCi) in rhodium (Radiochemical centre, Amersham), at 20 °C. The spectrometer was operated in a saw tooth mode and the spectra computer fitted. The spectrometer was calibrated with a 25 μM thick natural iron reference absorber. All isomer shifts are referred to this as zero shift. Infra-red spectra were recorded as Nujol mulls with a Perkin-Elmer 225 spectrophotometer.

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