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Crystalline Isomerism in (μ-Oxo)bis[(phthalocyaninato)iron(III)]: Further Characterization of the Isomer Having a Linear or Quasi-Linear Fe–O–Fe Bond System (μ-Oxo(2))

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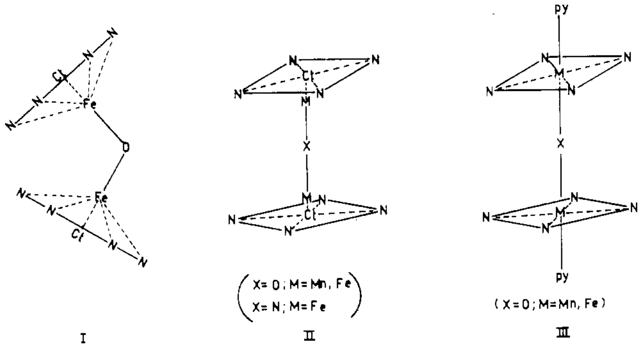
The crystalline isomer of (μ-oxo)bis[(phthalocyaninato)iron(III)], identified previously as μ-oxo(**2**), has been further investigated by means of magnetic susceptibility measurements and ESR and Mössbauer spectra. Susceptibility data taken on different samples of μ-oxo(**2**) in the temperature range 300–4 K are indicative of a high-spin ($S = {}^5/_2$, $S = {}^5/_2$) strongly antiferromagnetically coupled Fe(III) dimeric species. The observed coupling constant J (-195 cm^{-1}), significantly higher than that found for the alternative isomer, i.e., μ-oxo(**1**) (characteristic IR absorptions at 852 and 824 cm^{-1}, assigned as ν_{as}(Fe–O–Fe)), is in keeping with the presence of a linear or quasi-linear Fe–O–Fe moiety, as indicated by structural information. The Mössbauer spectra at 4.2 K of samples obtained by different methods of preparation give fairly clean single doublets with δ values (isomer shift) of 0.26 ($\pm$0.01) mm s^{-1} and ΔE_Q values (quadrupole splitting) of 1.27 ($\pm$0.01) mm s^{-1}. These values are intermediate between those found for the five-coordinate high-spin μ-oxo(**1**) complex and the related six-coordinate low-spin adduct of formula $[(py)PcFe]_2O$ and support the high-spin electronic structure suggested by the magnetic susceptibility data. Discussion and comments are extended to pertinent, partly incorrect, literature reports.

We have recently established that interaction of (phthalocyaninato)iron(II), PcFe (Pc = phthalocyaninato dianion, $C_{32}H_{16}N_8$ 2−), with dioxygen, in a variety of media, leads to the formation of (μ-oxo)bis[(phthalocyaninato)iron(III)], $(PcFe)_2O$, isolated and characterized in two different crystalline forms, i.e. μ-oxo(1) (characteristic IR bands at 852 and 824 cm^{-1}, assigned as ν_{as}(Fe–O–Fe)) and μ-oxo(**2**).[1a,b] These two crystalline isomers show different X-ray powder patterns, IR spectra, and room-temperatures magnetic moments.[1a,b] Their magnetic behavior within the temperature range 300–80 K is also different.[1b] Conversely, the visible spectrum in 96% H_2SO_4 solution and the spectral changes in this solvent and in the presence of molecular oxygen or in a nitrogen atmosphere are identical for both species,[1c] as also are the visible spectra in pyridine immediately after dissolution and the subsequent spectral changes in this solvent as a function of time[1b,d] (see also below). They also show identical spectroelectrochemical behavior when dissolved in pyridine.[2] The IR spectral and magnetic properties of μ-oxo(**1**) were correlated with those of other antiferromagnetically coupled high-spin ($S = {}^5/_2$) μ-oxo Fe(III) dimeric species.[1a,b] In fact, very recently, Kennedy et al.[3] have definitely established, by means of ESR, Mössbauer, and magnetic susceptibility data, that μ-oxo(**1**) is a strongly coupled Fe(III) high-spin ($S_1 = {}^5/_2$, $S_2 = {}^5/_2$) complex. On the basis of the previous available[1b] information on the two crystalline isomers, μ-oxo(**1**) was tentatively assigned the bent structure I (Scheme I) whereas in μ-oxo(**2**) the Fe–O–Fe moiety was assumed to be linear (II, Scheme I), as suggested by the magnetic behavior of this isomer in the temperature range 300–80 K and its isomorphism with the corresponding Mn–O–Mn analogue.[1b] Also, the isomorphism shown by μ-oxo(**2**) with the recently characterized μ-nitrido-bridged complex $(PcFe)_2N$[1e,4] has reinforced the assumption of a linear structure for the Fe–O–Fe moiety in μ-oxo(**2**). It appears, then, that μ-oxo(**2**) has a molecular conformation intermediate between that of μ-oxo(**1**) and that of $[(py)PcFe]_2O$ (III, Scheme I). The latter pyridine adduct, briefly mentioned elsehwere,[1b,d] is now fully characterized.[5] Since $[(py)PcFe]_2O$ contains the little-known low-spin Fe(III) centers, it seemed desirable to investigate μ-oxo(**2**) in order to establish whether its spin state approaches more that of high-spin ($S = {}^5/_2$) five-coordinate μ-oxo(**1**) (I) or, rather, that of the low-spin ($S = {}^1/_2$) six-coordinate adduct (III). In the present paper, we present a detailed investigation of μ-oxo(**2**) and assign oxidation number and spin state by use of Mössbauer spectra, magnetic susceptibility measurements, and ESR spectra.[1f] Recently, Frampton and Silver[6] investigated the Mössbauer spectra of $(PcFe)_2O$ and apparently were unable to identify μ-oxo(**2**). We comment here on this paper in relation to the present results and show that these authors probably did obtain μ-oxo(**2**) from PcFe in concentrated H_2SO_4 (in mixture with μ-oxo(**1**)) but that they formulated its structure incorrectly.

Scheme I



Experimental Section

Synthesis of μ-Oxo(1). μ-Oxo(**1**) was prepared from PcFe as previously reported.[1a,b]

Synthesis of μ-Oxo(2). This crystalline isomer was prepared from μ-oxo(**1**) in chloronaphthalene and 2-propylamine (method a) and from PcFe in 96% H_2SO_4 (method b) as described previously.[1b] A variation of method a was also used in which μ-oxo(**2**) was obtained by oxidizing PcFe as follows: Finely ground PcFe (200 mg) was added to a solution of 2-propylamine (0.75 mL) in chloronaphthalene (20 mL), and the

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(1) (a) Ercolani, C.; Rossi, G.; Monacelli, F. *Inorg. Chim. Acta* **1980**, *44*, L215–L216. (b) Ercolani, C.; Gardini, M.; Monacelli, F.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1983**, *22*, 2584–2589. (c) Ercolani, C.; Monacelli, F.; Rossi, G. *Inorg. Chem.* **1979**, *18*, 712–716. (d) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G. *J. Chem. Soc., Chem. Commun.* **1983**, 549–550. (e) Goedken, V. L.; Ercolani, C. *J. Chem. Soc., Chem. Commun.* **1984**, 378–379. (f) A preliminary account of this work, including Mössbauer data, electrochemistry, and visible spectral behavior in pyridine of μ-oxo(**1**) and μ-oxo(**2**) was given in the Proceedings of the XVIII Congresso Nazionale di Chimica Inorganica, Como, Italy, Sept 16–20, 1985; pp 64–67 (A8).

(2) Bottomley, L. A.; Ercolani, C.; Gorce, J.-N.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1986**, *25*, 2338–2342.

(3) Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W. *Inorg. Chem.* **1985**, *24*, 3302–3305.

(4) Bottomley, L. A.; Gorce, J.-N.; Goedken, V. L.; Ercolani, C. *Inorg. Chem.* **1985**, *24*, 3733–3737.

(5) Ercolani, C.; Gardini, M.; Murray, K. S.; Pennesi, G.; Rossi, G.; Zwack, P., manuscript submitted for publication.

(6) Frampton, C. S.; Silver, J. *Inorg. Chim. Acta* **1985**, *96*, 187–191.

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mixture was kept under stirring for 30 min. The mixture was then filtered, and the solution obtained was stirred in air for 16–20 h. The use of a wide-necked beaker facilitates the complete evaporation of 2-propylamine. The solid formed was separated from the mother liquors by filtration, washed with CH_3OH, and dried under vacuum (yield ca. 100 mg). In a variation of method b, μ-oxo(**2**) could also be obtained by using μ-oxo(**1**) in place of PcFe as follows: μ-oxo(**1**) (300 mg) was dissolved in 96% H_2SO_4 (40 mL) and the mixture kept under stirring for 10–15 min (longer times with exposure to air might start some decomposition of the phthalocyanine chromophore[1c]). After filtration and separation of any undissolved material, the solution was added, drop by drop, to cold (<5 °C) water (150 mL) with stirring. The solid that formed was separated from the mother liquors, washed abundantly with water to eliminate traces of acid, and dried under vacuum (10^{-2} mmHg, yield ca. 50%). In all cases the formation of μ-oxo(**2**), as also that of μ-oxo(**1**), was monitored by elemental analyses, IR spectra, and visible spectral behavior in pyridine.

Measurements of Molar Extinction Coefficients and Spectral Behavior in Pyridine as a Function of Time for μ-oxo(1) and μ-oxo(2). Both μ-oxo(**1**) and μ-oxo(**2**) are appreciably soluble in pyridine and exhibit an identical spectrum in the visible range immediately after dissolution, with a main visible absorption at ca. 620 nm. Quite often, an induction period of variable extension is observed before the spectral changes effectively start. This has allowed the measurement of the molar extinction coefficients for the two isomers. Since it is assumed that μ-oxo(**1**) and μ-oxo(**2**), although different in the solid state, form the same species in pyridine solution, i.e. $[(py)PcFe]_2O$, the ϵ values that were calculated should indeed be assigned to the latter species. The values measured for the molar absorptivity were $\epsilon_{620} = 1.54 \times 10^5$ and 1.57×10^5 for μ-oxo(**1**) and μ-oxo(**2**), respectively, i.e. practically identical, as expected. The pathway leading from $[(py)PcFe]_2O$ (blue solution) to $PcFe(py)_2$ (green solution, main visible absorption at 652 nm) takes place in two well-separated steps; the slope of the D_{620} vs. D_{652} plot reveals an evident discontinuity between the two sets of spectra. The kinetic behavior of this complex reaction is now under examination.[7]

Comments on the Reproducibility of μ-Oxo(2) Formation. In our previous paper[1b] the conditions were considered under which μ-oxo(**1**) or μ-oxo(**2**) could be obtained in solvents such as dimethyl sulfoxide or α-chloronaphthalene, in the absence or in the presence of aliphatic volatile N bases. Also, method a was described in detail as a route for the conversion of μ-oxo(**1**) to μ-oxo(**2**) by using α-chloronaphthalene and 2-propylamine, although at the time, a statistical approach to the synthesis of μ-oxo(**2**) was not performed. Recently, Frampton and Silver[6] attempted to describe the Mössbauer spectra of both μ-oxo(**1**) and μ-oxo(**2**). Apparently, however, these authors were unable to report the Mössbauer data on μ-oxo(**2**), since as they state,[6] they found no evidence for the formation of this isomer following our methods of preparation.[1b] They also concluded that μ-oxo(**2**) was not obtained by method b (from PcFe) and proposed that the sample obtained by this method was a mixture containing mostly a low-spin Fe(II) tetrasulfonated phthalocyanine. These conclusions were based on the Mössbauer spectrum obtained[6] and reference to literature reports.[8-10] No analytical data or experimental description was given. Assuming that Frampton and Silver's procedures were not too dissimilar from those reported previously by us,[1b] we must conclude that method a (from μ-oxo(**1**)) is subjected to some irreproducibility. This is perhaps not surprising, in view of the fact that μ-oxo(**1**) and μ-oxo(**2**) are simply structural isomers and thus their formation could well be sensitive to even subtle changes in the method used. Indeed, interchangeability of the two isomers under certain conditions was previously emphisized and irreproducibility widely pointed out.[1b] We confirm, however, by recent experiments in Rome and at Monash University that μ-oxo(**2**) can indeed be obtained by method a (from μ-oxo(**1**)). Moreover, by use of the variation of method a, using PcFe as starting material as described above, we obtained systematically μ-oxo(**2**) in more than 10 attempts. In the case of method b, which involves tedious washing procedures, we have recently reproduced this work successfully and obtained μ-oxo(**2**) (from PcFe) in good yield. The tendency to the formation of μ-oxo(**2**) (from PcFe) in 96% H_2SO_4 has now been proved also in our experiments of the conversion of μ-oxo(**1**) into μ-oxo(**2**) in this medium, as described above (three distinct experiments were fully accomplished).

Mössbauer Spectra, Magnetic Susceptibility Measurements, and ESR Spectra. Mössbauer spectra were measured at CAMEN (Pisa, Italy) and at Monash University (Melbourne, Australia). In Pisa the room-temperature spectra were measured as described elsewhere,[11] with no special precaution taken in the handling of the samples, due to the air stability of our materials. At Monash University variable-temperature Mössbauer spectra were taken as reported previously.[12] Magnetic susceptibility measurements in the temperature range 300–4 K were taken in Rome with a Faraday balance using $HgCo(CNS)_4$ as standard. The ESR spectra were obtained with a X-band Varian E-9 instrument.

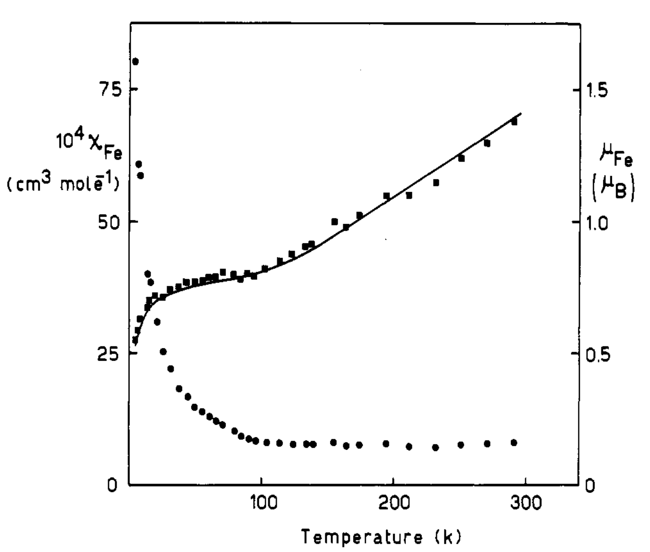

Figure 1. Plots of χ_{Fe} and μ against T in the temperature range 300–4 K. The best fit calculated curve for μ_{Fe} uses parameters given in the text.

Results and Discussion

It is clearly shown in the Experimental Section that μ-oxo(**2**) can be obtained in a number of ways. Different samples of μ-oxo(**2**) were prepared by using different starting materials, i.e. μ-oxo(**1**) or PcFe and methods a or b, and were examined by magnetic susceptibility, Mössbauer, and ESR measurements. Some of the measurements, particularly Mössbauer spectra, were made in two different laboratories and found to give practically identical results.

Magnetic Susceptibility, ESR, and Mössbauer Spectra. The room-temperature magnetic moments were measured in Rome on different samples of μ-oxo(**2**), and the values obtained were all found to be in the range 1.38–1.42 μ_B/Fe atom, in good agreement with the values previously reported.[1b] The temperature dependence of χ_{Fe} vs. T for the sample prepared by method a (from PcFe) is shown in Figure 1. Two other samples, prepared by using an alternative method or starting material, showed similar behavior. χ_{Fe} exhibits a gentle decrease in the range 300–200 K, as expected for a strongly coupled $S = {}^5/_2$ dimer, followed by a constant trend in the range 200–80 K, before increasingly rapidly between ca. 80 and 4.7 K. The rapid increase in χ_{Fe} at low temperatures is due to the presence of traces of a monomeric high-spin impurity. This is quite a common feature in the susceptibilities of μ-oxo Fe(III) complexes, although the sample previously examined,[1b] which showed a much steeper decrease of χ_{Fe} vs. T, probably contained almost undetectable amounts of such an impurity.

The low value of χ_{Fe} at 300 K suggests an antiferromagnetic constant, J, in excess of -150 cm^{-1}. In order to fix the χ_{Fe}/T data, a model similar to that used to interpret the data for μ-oxo(**1**)[3] was employed, which includes a ${}^5/_2$–${}^5/_2$ dimer (χ_1) and a zero-field split monomer contribution (χ_2) to the observed susceptibility, viz.

$$\chi_{obsd} = \alpha\chi_1 + (1 - \alpha)\chi_2$$

with α being the fraction of the dimer present. The impurity,

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[7] Ercolani, C.; Monacelli, F.; Pennesi, G.; Rossi, G., unpublished results.

[8] Melendres, C. A. *J. Phys. Chem.* **1980**, *84*, 1936–1939.

[9] Blomquist, J.; Moberg, L. C.; Johansson, L. Y.; Larsson, R. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2287–2292.

[10] Sherson, D. A.; Yao, S. B.; Yeager, E. B.; Eldridge, J.; Kordesch, M. E.; Hoffmann, R. W. *J. Phys. Chem.* **1983**, *87*, 932–943.

[11] Calderazzo, F.; Frediani, S.; James, B. R.; Pampaloni, G.; Reimer, K. J.; Sams, J. R.; Serra, A. M.; Vitali, D. *Inorg. Chem.* **1982**, *21*, 2302–2306.

[12] Mitchell, A. J.; Murray, K. S.; Newman, P. J.; Clark, P. E. *Aust. J. Chem.* **1977**, *30*, 2439–2455.

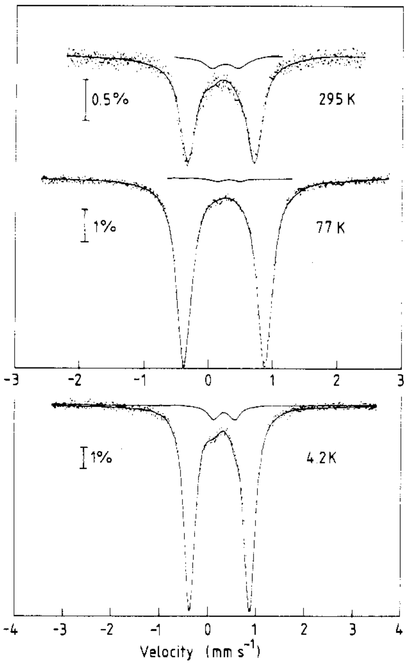

Figure 2. Mössbauer spectra of μ-oxo(**2**) (Sample A, Table I) at 295, 77, and 4.2 K.

which could not be detected either by IR or by Mössbauer spectra (see below), is clearly evident in the X-band ESR spectrum of μ-oxo(**2**), which shows lines at $g \sim 6$ and $g \sim 4.3$, typical of tetragonally and rhombically distorted Fe(III) ($S = {}^5/_2$) monomeric species. A small component of μ-oxo(**1**), detected in the Mössbauer spectrum of the μ-oxo(**2**) sample (A, vide infra), could be safely ignored in the susceptibility calculations, since it makes no contribution in the low-temperature region and has virtually no effect in the high-temperature region.

Some general effects quickly emerged from the fitting attempts, as would be expected when combining a small χ_1 value from a majority dimer species with a relatively large χ_2 value from a minor monomer species. Thus, the size of J determined the shape of the high-temperature region while the size of D, the axial zero-field splitting parameter, determined the shape of the low-temperature region. The fraction of the dimer, α, modulated the magnitude of χ_{Fe} over the whole temperature range. Susceptibility values at intermediate temperatures were the most difficult to simulate precisely. The best fit parameters obtained from the fitting program were $J = -195 \pm 5$ cm^{-1}, $D = 20 \pm 5$ cm^{-1}, and $\alpha = 0.983 \pm 0.001$. The calculated μ_{Fe}/T curve is compared with the experimental curve in Figure 1. The J value for μ-oxo(**2**) is larger than that obtained for μ-oxo(**1**),[3] as expected for a linear Fe–O–Fe bridge (Scheme I).

The Mössbauer spectral parameters obtained on the various samples of $(PcFe)_2O$ are given in Table I. The spectrum of one sample of μ-oxo(**2**) (A), at 295, 77, and 4.2 K, is shown in Figure 2. The 4.2 K spectra of samples A, B, C, and D are compared in Figure 3. It is important to note that the room-temperature values for μ-oxo(**1**) and μ-oxo(**2**), measured in our two different laboratories, are practically coincidental for both the isomer shift δ ($\pm$0.01 mm s^{-1}) and the quadrupole splitting ΔE_Q ($\pm$0.01 mm s^{-1}).

The spectra of the four samples of μ-oxo(**2**) all show at 4.2 K an intense symmetrical doublet with parameter values $\delta = 0.26 \pm 0.01$ mm s^{-1} and $\Delta E_Q = 1.27 \pm 0.01$ mm s^{-1} arising from the predominant μ-oxo(**2**) species. Sample A shows a small amount of μ-oxo(**1**) present, while samples C and D show a similar percentage of μ-oxo(**1**) together with additional small quantities of other species. The line shapes for C and D are generally similar. In order to reproduce the shoulders on the main doublet, a doublet with ΔE_Q of ca. 1.9 mm s^{-1} and a percentage area of ca. 6% was included in the line-fitting analysis. Such splittings have been observed in six-coordinate low-spin species[5] although the δ values

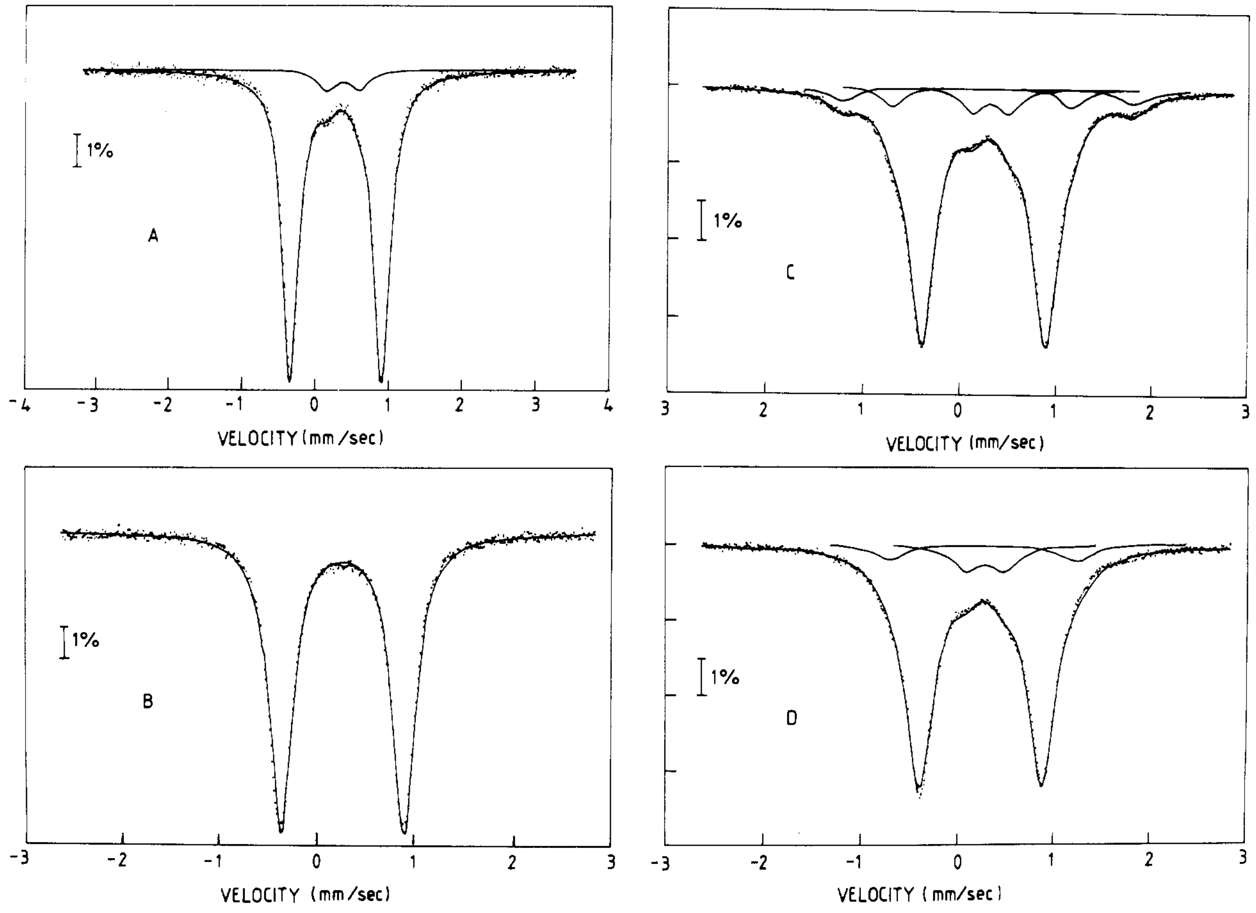

Figure 3. Low-temperature (4.2 K) Mössbauer spectra of different samples of μ-oxo(**2**) (A–D as specified in Table I).

Table I. Mössbauer Parameters for Various Samples of $(PcFe)_2O$

sample[a]	T, K	δ,[d] mm s^{-1}	ΔE_Q, mm s^{-1}	Γ,[b] mm s^{-1}	area, %	ref
μ-oxo(**2**),A	295	0.18	1.04	0.15, 0.15	90.6	*e*
		0.25[c]	0.42	0.15, 0.15	9.4	*e*
	77	0.25	1.26	0.14, 0.14	98.8	*e*
		0.32[c]	0.35	0.11, 0.11	1.2	*e*
	4.2	0.26	1.25	0.13, 0.13	93.4	*e*
		0.35[c]	0.44	0.14, 0.14	6.6	*e*
μ-oxo(**2**),B	295	0.18	1.05			*f*
	4.2	0.26	1.26	0.14, 0.14	100	*e*
μ-oxo(**2**),C	4.2	0.25	1.28	0.17, 0.17	83.1	*e*
		0.32[c]	0.37	0.13, 0.13	6.3	*e*
		0.30	3.02	0.17, 0.17	5.2	*e*
		0.24	1.85	0.13, 0.13	5.4	*e*
μ-oxo(**2**),D	4.2	0.25	1.27	0.18, 0.18	84.9	*e*
		0.29[c]	0.40	0.17, 0.17	8.6	*e*
		0.28	1.95	0.20, 0.20	6.5	*e*
μ-oxo(**1**)	295	0.26	0.40			*f*
	295	0.25	0.42	0.22, 0.22		3
	77	0.36	0.44	0.16, 0.16		3
	4.2	0.37	0.44	0.17, 0.17		3
μ-oxo(**1**)	110	0.34	0.38	0.17, 0.17		6
μ-oxo(**2b**)	110	0.23	1.28	0.19, 0.19		6

[a] μ-Oxo(**2**),A: prepared by method a from PcFe. μ-Oxo(**2**),B: method a, from μ-Oxo(**1**). μ-Oxo(**2**),C: method b, from PcFe. μ-Oxo(**2**),D: method b, from μ-oxo(**1**). [b] Half-width at half-maximum height. [c] μ-Oxo(**1**) impurity. [d] Referred to metallic iron. [e] Monash University. [f] Pisa.

are generally a little lower than that deduced here. The outer doublet shown in Figure 3C is symptomatic of ca. 5% of an intermediate-spin ($S = {}^3/_2$) species[13] being present in sample C. No evidence was found in samples prepared by method a of Mössbauer lines due to a monomeric high-spin Fe(III) impurity indicated by the magnetic and ESR data to be present in ca. 1.6% concentration. This is not surprising in view of the detection limits of the Mössbauer effect technique.

A number of features can be inferred from Figures 2 and 3 and Table I. The spectra of samples A and B (Figure 3), prepared by route a from chloronaphthalene/2-propylamine solutions, are generally similar in their intensities and line widths, as are C and D prepared by route b from concentrated H_2SO_4 solutions, but A and B are distinct from C and D. Samples A and B are generally prepared in a more crystalline form than C and D, which precipitate in a fine semicolloidal manner from H_2SO_4. The nature of the crystalline state therefore seems to influence the appearance of the spectrum. Nevertheless, the values of the μ-oxo(**2**) Mössbauer parameters of all samples examined are identical, and as it is also shown below, they are clearly consistent with an oxidation state of +3 on Fe and with a strong intradimer antiferromagnetic interaction.

Samples A and B show a clear variation in the size of both δ and ΔE_Q as a function of decreasing temperature. An increase of 0.05 mm s^{-1} in δ is commonly observed and is assigned to the second-order Doppler shift. The increase in ΔE_Q (ca. 0.20 mm s^{-1}), in the range of temperature explored (300–4.2 K), is a little larger than is commonly observed and might relate to the occurrence of some structural/bonding modification.

The isomer shift value for μ-oxo(**2**) at 4.2 K (0.25 mm s^{-1}) is only slightly smaller than that observed for μ-oxo(**1**) ($S = {}^5/_2$). Instead, it seems to approach those observed in other Fe(III) phthalocyanine species of different spin states, such as $[PcFe(OPh)_2]^-$ (low-spin, $S = {}^1/_2$), or PcFeCl (intermediate spin/spin admixed, $S = {}^5/_2, {}^3/_2$).[13] Thus, from the isomer shift alone the ground state in μ-oxo(**2**) would not be easily assigned. If we consider the ΔE_Q value for μ-oxo(**2**) (1.25 mm s^{-1}), it is observed that it is significantly higher than that of μ-oxo(**1**) (0.44 mm s^{-1}) and of some known Fe(III) porphyrin μ-oxo species,[14] and it approaches those of other known high-spin Fe(III) μ-oxo dimers,[15] including the two complexes of formula $[Fe_2O(bbimae)_2X_2](NO_3)_2$ (bbimae = 2-(bis(benzimidazol-2-(methyl)amino)ethanol, X = Cl or CNS) recently characterized by X-ray work[16] and containing a linear Fe–O–Fe bond system and of various high-spin monomers.[14,17] Furthermore, it is much smaller than the values found for complexes having low-spin ($S = {}^1/_2$, ΔE_Q = 2.2–2.6 mm s^{-1}) or intermediate-spin states ($S = {}^3/_2$, ΔE_Q = 2.9–3.2 mm s^{-1}).[13] Thus, the observed Mössbauer parameters appear to be strongly diagnostic of a high-spin ($S = {}^5/_2$) ground state of Fe(III) in this isomer, in keeping with indications from the magnetic results.

The Mössbauer parameters for μ-oxo(**1**) and μ-oxo(**2**) can be compared to those for the six-coordinate species $[(L)PcFe]_2O$ (where L = py, 4 Me-py, pip, etc.), for which the information available[5] (e.g. L = py, δ = 0.18 mm s^{-1}, ΔE_Q = 1.75 mm s^{-1} at 4.2 K) points to a low-spin configuration on the Fe atoms. The pyridine adduct is isostructural with the analogous complex, $(pyPcMn)_2O$,[18] which is known from X-ray work to have a linear M–O–M bridge and to have the metal strictly in the N_4 plane of Pc. The continuous trend in the Mössbauer parameters in going from μ-oxo(**1**), through μ-oxo(**2**), to the six-coordinate adducts gives strong support for the corresponding structures I–III shown in the Scheme I. The fact that μ-oxo(**2**) is still high-spin, and therefore, closer to μ-oxo(**1**) than to $[(py)PcFe]_2O$, may be indicative of very weak external axial interactions on the Fe atoms of the dimer, which then remain essentially five-coordinate. The Fe atom is likely to be closer to the center (C_t) of the Pc plane in μ-oxo(**2**) (II) than in μ-oxo(**1**) (I) (see for example the variation of the C_t–Fe distance in bent $(TPPFe)_2O$[19] compared to linear $(TPPFe)_2N$[20]).

The Mössbauer parameters for the predominant species present in the sample prepared by Frampton and Silver[6] using our method b from PcFe (named μ-oxo(**2b**)) are also included in Table I. It is immediately seen that these parameters are practically coincidental with those found by us for μ-oxo(**2**), and indeed, there seems to be little doubt that μ-oxo(**2b**)[6] mainly consisted of μ-oxo(**2**). We regret that these authors did not report the elemental analyses of the isolated solid material to support their assignment of μ-oxo(**2b**) as consisting mainly of tetrasulfonated low-spin Fe(II) phthalocyanine ($TSPcFe^{II}$), nor did they give its visible spectrum in 96% H_2SO_4 or in pyridine, both of which would have easily allowed them to distinguish between the unsubstituted species PcFe or, rather, $(PcFe)_2O$ (see ref 1b–d and above). Frampton and Silver's assignment is certainly incorrect for a number of reasons additional to those given above:

(a) $TSPcFe^{II}$, which is not low spin in the solid state,[21] is sensitive to molecular oxygen, and this has made its preparation and characterization particularly intriguing.[22] Thus it seems unlikely that $TSPcFe^{II}$ can be isolated from 96% H_2SO_4 after the suggested[1b] prolonged bubbling of dioxygen.

(b) Our direct experience[1c] and literature reports[23] exclude the possibility of a sulfonation reaction occurring at the peripheral benzene rings of PcFe after dissolution, at room temperature, in 96% H_2SO_4, where rather protonation reactions occur.[23,1c]

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(13) (a) Kennedy, B. J.; Brain, G.; Murray, K. S. *Inorg. Chim. Acta* **1984**, *81*, L29–L31. (b) Kennedy, B. J.; Murray, K. S.; Zwack, P.; Kalz, W.; Homborg, H. *Inorg. Chem.* **1986**, *25*, 2539–2545.

(14) Sams, J. R.; Tsin, T. B. *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. IV, p 425.

(15) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1–35.

(16) Takahashi, K.; Nishida, Y.; Maeda, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 2375–2380.

(17) Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, 100, 6354–6362.

(18) Vogt, L. H., Jr.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1725–1730.

(19) Hoffmann, A. B.; Collins, D. M.; Day, V. W.; Fleisher, E. B.; Srivastava, T. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 3620–3626.

(20) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623–6628.

(21) Weber, J. H.; Bush, D. H. *Inorg. Chem.* **1965**, *4*, 469–471.

(22) McLendon, G.; Martell, A. E. *Inorg. Chem.* **1977**, *16*, 1812–1813.

(23) (a) Gaspard, S.; Verdaguer, M.; Viovy, R. *J. Chim. Phys.* **1972**, 1740–1747. (b) Berezin, B. D. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1959**, *2*, 165. (c) Ledson, D. L.; Twigg, M. V. *Inorg. Chim. Acta* **1975**, *13*, 43–46. (d) Gaspard, G.; Viovy, R.; Bregeault, J.; Jarjour, C.; Yolou, S. *C. R. Seances Acad. Sci., Ser. C* **1975**, *281*, 925–928.

(c) TSPcFe^{II} is known to be water-soluble. Thus, it appears improbable that it can be precipitated from 96% H_2SO_4 by dilution with water and isolated as a solid after repeated washings necessary for the removal of excess of acidity,[1b] also because acidity would be an intrinsic property of the suggested material.

(d) No bands of the SO_3H groups are present in the expected region of the IR spectrum reported.[6]

Conclusions. $(PcFe)_2O$ represents, to our knowledge, a unique example of a μ-oxo-bridged Fe(III) porphyrin-like molecule for which two solid crystalline isomers have been isolated and characterized. μ-Oxo(**1**) and μ-oxo(**2**) show different X-ray powder patterns, IR and Mössbauer spectra, and magnetic susceptibility behavior. Both of them are strongly antiferromagnetically coupled Fe(III) high-spin dimeric systems ($S = {}^5/_2$). The higher J value found for μ-oxo(**2**) (-195 cm^{-1}) with respect to that of μ-oxo(**1**) ($J = -120$ cm^{-1}; bent Fe–O–Fe moiety) is suggestive of a linear or quasi-linear Fe–O–Fe bond system, in keeping with the available crystallographic information. Finally, although μ-oxo(**2**) has very likely an intermediate structure between that of high-spin five-coordinate μ-oxo(**1**) and that of low-spin $[(py)PcFe]_2O$, it still shows a high-spin ($S = {}^5/_2$) ground state, very likely associated with a retained essentially five-coordinate environment with very weak or insignificant axial external contacts for Fe(III).

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Note Added in Proof. While the present paper was in press, we learned of a recent report on $(PcFe)_2O$ referring to Frampton and Silver's work[6] and to ours[1] on the same subject (see ref 24, as well as ref 25, a previous report by the same author). In a reelaboration of mostly previously published material, the author seems to support the existence of two Fe(III)-containing crystalline materials, as clearly established by us previously.[1b] The two isomers are renamed FePcoxyg$_1$ (i.e. μ-oxo(**1**)) and FePcoxyg$_2$ (i.e. μ-oxo(**2**)) (previously identified as S and B species, respectively,[25] S being changed into P and a mysterious imidazole derivative of P being labeled M in a later short report by the same author[26]), with little gain, throughout the paper, from the point of view of the exact chemical formulation of the species and no contribution to the clarification of the molecular and electronic structure of the two individual isomers. For other marginal details these reports[24-26] will be eventually referred to elsewhere.

Registry No. μ-oxo(**2**), 74353-48-3.

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(24) Collamati, I. *Inorg. Chim. Acta* **1986**, *124*, 61-66.
(25) Collamati, I. *Inorg. Chim. Acta* **1979**, *35*, L303-L304.
(26) Collamati, I. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 69-73.

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Highly Electroconductive Tetrathiafulvalenium Salts of Copper Halides

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The redox reaction of copper(II) halides with excess tetrathiafulvalene (TTF) yielded a variety of electroconductive mixed-valence complexes in different solvents: $(TTF)_2CuCl_2$ (the powder electrical conductivity was 14 S cm^{-1} at 300 K) in methanol, $(TTF)_7(CuCl_2)_3$ (10 S cm^{-1}) in acetonitrile, $(TTF)_5(CuBr_2)_3$ (1.5 S cm^{-1}) in methanol, $(TTF)_4(CuBr_2)_3$ (0.3 S cm^{-1}) in tetrahydrofuran, and $(TTF)_6CuBr_4$ (14 S cm^{-1}) in acetonitrile. Electron spin resonance, infrared, and X-ray photoelectron spectroscopic studies indicated that, in each compound, the copper atoms are in the Cu^I state and TTF moieties carry a fractional charge equally. The magnetic susceptibilities suggested that unpaired electrons are extensively delocalized over the TTF lattices.

Introduction

Tetrathiafulvalene (TTF) and its analogues have been found to form highly electroconductive donor–acceptor complexes.[2,3] Their electrical properties can be varied over a wide range by changing the nature of the acceptor species. The use of metal chelates as acceptors is expected to be a versatile route for the preparation of a wide variety of conductive TTF complexes that exhibit different electrical properties, because various types of metal chelate anions can be employed with different geometries and oxidation states of the central metal ion. On this basis, several metal complexes involving TTF or its analogues have been prepared.[4] An important compound that has been prepared recently is $(BEDT\text{-}TTF)_2AuI_2$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene), which undergoes a transition to a superconducting state at ca. 5 K.[5]

One of the common features of the conducting donor–acceptor complexes is that the constituent molecules are in a mixed-valence (or partial-oxidation) state.[2,3,6] Accordingly, the preparation of conductive TTF complexes requires the use of appropriate oxidants that can oxidize TTF^0 partially to TTF$^{n\bullet+}$ ($n < 1$). Copper(II) chelates are expected to function as oxidants with respect to TTF^0 under appropriate conditions, because they have low standard-electrode-potential values and are readily converted to the corresponding Cu^I chelates.[7] Copper(II) halides have been reported to oxidize TTF^0 readily to TTF$^{\bullet+}$ or TTF^{2+};[8,9] the resulting

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(1) (a) Universidad de Sonora. (b) University of Arizona.
(2) "Proceedings of the International Conference on Low-Dimensional Conductors", *Mol. Cryst. Liq. Cryst.* **1982**, *79*, *85*, *86*.
(3) "Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals", *Mol. Cryst. Liq. Cryst.* **1985**, *119*, *120*.
(4) (a) Interrante, L. V.; Browall, K. W.; Hart, H. R., Jr.; Jacobs, I. S.; Watkins, G. D.; Wee, S. H. *J. Am. Chem. Soc.* **1975**, *97*, 889. (b) Wudl, F. *J. Am. Chem. Soc.* **1975**, *97*, 1962. (c) Kistenmacher, T. J.; Rossi, M.; Chiang, C. C.; Van Duyne, R. P.; Cape, T.; Siedle, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 1958. (d) Kondo, K.; Matsubayashi, G.; Tanaka, T.; Yoshioka, H.; Nakatsu, K. *J. Chem. Soc., Dalton Trans.* **1984**, 379.
(5) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nuñez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465.
(6) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.
(7) Meites, L.; Zuman, P.; Narayanan, A.; Fenner, T. L.; Jandík, J. *CRC Handbood Series in Inorganic Electrochemistry*; CRC: Boca Raton, FL, 1981; Vol. II.
(8) Siedle, A. R.; Candela, G. A.; Finnegan, T. F.; Van Duyne, R. P.; Cape, T.; Kokoszka, G. F.; Woyciejes, P. M.; Hashmall, J. A. *Inorg. Chem.* **1981**, *20*, 2635.
(9) Honda, M.; Katayama, C.; Tanaka, J.; Tanaka, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41C*, 197.