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Molecular and Electronic Structure of Six-Coordinate Low-Spin Oxo-Bridged Dimers Formed by the Interaction of (μ-Oxo)bis((phthalocyaninato)iron(III)) with Nitrogen Bases

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Crystalline bisadducts of general formula [(N-base)PcFe]$_2$O have been prepared by the interaction of (μ-oxo)bis((phthalocyaninato)iron(III)) with vapors of liquid or liquid N-bases (pyridine, 4-methylpyridine, piperidine, 1-methylimidazole). Additional occluded molecules of the N-bases are also found present in the crystal lattice of these complexes. The molecular and electronic structure of the N-base adducts has been examined mainly on the basis of structural information and Mössbauer and magnetic susceptibility measurements. A six-coordinate structure and a low-spin ($S = {}^1/_2$) electronic configuration is assigned to Fe(III) in these μ-oxo dimers, with a weak antiferromagnetic coupling between the iron pairs of the dimer. The stereochemistry and spin state on the iron centers contrast with those of the more common five-coordinate high-spin Fe(III) centers in other μ-oxo dimers.

Introduction

Interaction of haem-like N$_4$ macrocycles with molecular oxygen has been widely investigated for comparison with more complex biological processes[1] and for an understanding of dioxygen activation in oxidative catalysis of organic substrates.[2] In our previous[3a] and more recent[3b,c,4] studies it has been established that interaction of (phthalocyaninato)iron(II), PcFe,[3f] with dioxygen, in air, at room temperature, and in a variety of media leads ultimately to the formation of (μ-oxo)bis((phthalocyaninato)iron(III)), (PcFe)$_2$O, as the final oxygen-containing species (reaction 1A).

$$2\mathrm{PcFe} + {}^1/_2\mathrm{O}_2 \rightarrow (\mathrm{PcFe})_2\mathrm{O} \qquad (1\mathrm{A})$$

Reaction 1A can be reversed in the presence of N-bases (i.e. pyridine[3b,d]), and (PcFe)$_2$O is reconverted into the original Fe(II) species, in the form of its corresponding bisadduct, PcFe(N-base)$_2$, with associated releasing of the oxygen atom. A similar redox process has also been observed with some tetrakis(alkylsulfonamido)-substituted iron phthalocyanines.[5] To our knowledge, there is no counterpart of this Fe(III)–Fe(II) reduction process for the large number of known Fe(III) μ-oxo-bridged species containing different N$_4$ macrocycles, i.e. porphyrins, or other related multidentate ligands such as Schiff bases, ethylenediaminetetraacetic acid, etc. Indeed, the reverse generally occurs; i.e., the presence of an N-base normally accompanies the uptake of O$_2$ by the macrocyclic Fe(II) species leading irreversibly to a μ-oxo species of the type written in eq 1A.[1]

Stoichiometric oxygen atom transfer to PPh$_3$ can be obtained from (PcFe)$_2$O, at room temperature and pressure, in toluene in the presence of pyridine (reaction 1B).[3d]

$$(\mathrm{PcFe})_2\mathrm{O} + \mathrm{PPh}_3 \xrightarrow[\text{room temp}]{\text{py}} 2\mathrm{PcFe(py)}_2 + \mathrm{OPPh}_3 \qquad (1\mathrm{B})$$

Our recent results also show that "uptake of molecular oxygen" (reaction 1A) followed by "oxygen atom transfer" to an external substrate (PPh$_3$) (reaction 1B) can be cycled catalytically by using either PcFe or PcFe(N-base)$_2$ at room temperature and at p_{O_2} = 60–70 atm, in toluene.[3e] Both reactions 1A and 1B very likely involve multistep pathways, where metal–oxo intermediates, believed to be active oxygen atom donors, are likely to be formed.

Isolation of intermediates can be useful to a better understanding of the mechanism through which the overall process develops. In examining reaction 1B, we observed that stable N-base adducts are formed by contact of (PcFe)$_2$O with various N-bases (py, 4-Mepy, pip, 1-Meim), obtainable as solid species of general formula [(N-base)PcFe]$_2$O. The synthesis and structural, magnetic, and spectroscopic characterization of these complexes are described here. Their visible spectral behavior in pyridine[3d,4] indicates that these complexes can be considered as precursors of the intermediate active oxygen atom transfer agents suggested as responsible for the stoichiometric[3d] and catalytic[3e] oxidation of PPh$_3$ (reaction 1B). They also represent a rare class (if not unique) of μ-oxo dimers containing six-coordinate low-spin Fe(III).

Experimental Section

PcFe (Eastman Kodak Co.) was purified by sublimation under vacuum (400 °C, 10^{-2} mm). (PcFe)$_2$O, in the form of μ-oxo(**1**)[3a,b] (characteristic IR bands at 852 and 824 cm^{-1}), was easily obtained from PcFe in DMF or THF in the presence of air. The alternative isomer of (PcFe)$_2$O, i.e. μ-oxo(**2**), was prepared from μ-oxo(**1**) or PcFe as previously reported.[3b,4] PcFe(1-Meim)$_2$·1-Meim was prepared by direct contact of PcFe with 1-Meim for 1–2 h. The suspended adduct was then separated from the solution by filtration, washed with benzene, and dried under vacuum. Anal. Calcd for C$_{47}$H$_{37}$N$_{11}$Fe: C, 69.6; H, 4.6; N, 19.0. Found: C, 69.2; H, 4.45; N, 18.3. PcMn was prepared by the method of Barrett et al.[6] and purified by sublimation under vacuum (400 °C, 10^{-2} mm). N-bases were freshly distilled before use.

Preparation of the Complexes of Formula [(N-base)PcFe]$_2$O. All the complexes described below were prepared from (PcFe)$_2$O and the appropriate N-base. Unless differently specified (vide infra), (PcFe)$_2$O was always used in the form of μ-oxo(**1**). Two methods were developed for the preparation of the complexes: (A) contact of solid (PcFe)$_2$O with the vapors of the N-base; (B) dissolution of (PcFe)$_2$O in the liquid N-base followed by precipitation of the N-base adduct by addition of a nonsolvent mixture.

[(4-Mepy)PcFe]$_2$O. Contact of solid (PcFe)$_2$O with 4-Mepy vapors requires 3–4 days for the formation of [(4-Mepy)PcFe]$_2$O. In this case,

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as well as for the other N-bases, the absorption of 4-Mepy can be easily followed by observing the decrease in intensity of the 852- and 824-cm^{-1} bands (ν_{as}(Fe–O–Fe)) present in the IR spectrum of μ-oxo(**1**). Anal. Calcd for $C_{76}H_{46}N_{18}Fe_2O$: C, 68.2; H, 3.46; N, 18.8. Found: C, 67.6; H, 3.5; N, 18.5. In the solid–vapor interaction the amount of 4-Mepy absorbed is in keeping with expectation (13.9%) or is only slightly higher (14–15%). Complete elimination of 4-Mepy can be obtained by heating the adduct under vacuum (10^{-2} mm) at 160–170 °C for 1 h. Invariably, μ-oxo(**2**) is the desolvated product obtained, as confirmed by its Nujol mull IR spectrum or visible spectrum in pyridine solution (maximum ca. 620 nm).[3b]

Use of method B is exemplified as follows: 500 mg of $(PcFe)_2O$ was dissolved (partly) in 4-Mepy (20 mL), with stirring. To the filtered solution were added hexane (40 mL) and acetone (25 mL). The purple crystalline precipitate that formed was washed, after filtration, with a mixture of hexane and acetone and dried under vacuum (350 mg). The 4-Mepy adduct obtained by method B generally contains occluded solvent in larger amounts with respect to the formula given above. Elemental analyses (Anal. Calcd for $C_{88}H_{60}N_{23}Fe_2O$: C, 69.3; H, 4.0; N, 18.4. Found: C, 68.5; H, 4.0; N, 18.1) and thermograms indicate that the amount of 4-Mepy corresponds to the value expected for 4 molecules of 4-Mepy/mol of μ-oxo species (calcd 23.8%, found ca. 23%). In both methods A and B prolonged contact with the N-base converts $(PcFe)_2O$ into $PcFe(4\text{-}Mepy)_2$. Elimination of the N-base by heating under vacuum (160 °C, 10^{-2} mm) gives μ-oxo(**2**).

$[(pip)PcFe]_2O$. For the preparation of this complex by method A interaction of $(PcFe)_2O$ with piperidine was maintained for 24 h. Thermograms show that $[(pip)PcFe]_2O$ loses piperidine at 100–130 °C and the amount of the N-base absorbed is normally around the value expected (12.9%) for the formula given. The samples prepared by method B usually contain more occluded solvent, up to 20% of the total weight (expected for 3 piperidine molecules 18.1%: Anal. Calcd for $[(pip)PcFe]_2O(pip)$, $C_{79}H_{65}N_{19}Fe_2O$: C, 67.4; H, 4.65; N, 18.9. Found: C, 66.9; H, 5.0; N, 18.5). The adduct gives μ-oxo(**2**) by heating under vacuum (10^{-2} mm) at 140 °C for 1 h.

$[(1\text{-}Meim)PcFe]_2O$. Solid–vapor interaction takes several days to determine the complete conversion of $(PcFe)_2O$ into $[(1\text{-}Meim)PcFe]_2O$. This latter can be more conveniently prepared by method B as follows: $(PcFe)_2O$ (500 mg) is suspended, with stirring, in a solution containing 1 mL of 1-Meim in 10 mL of acetone, for 2 h. The solid is separated from the solution by filtration, washed with acetone, and brought to constant weight under vacuum (450 mg). Anal. Calcd for $C_{72}H_{44}N_{20}Fe_2O$: C, 65.7; H, 3.4; N, 21.3. Found: C, 65.2; H, 3.4; N, 20.7. Thermograms show that 1-Meim is lost in two steps (90–110 and 160–180 °C). The total amount of the N-base normally corresponds to that expected for the formula given. Due to the tendency to form $PcFe(1\text{-}Meim)_2$ in the presence of an excess of the N-base, $[(1\text{-}Meim)PcFe]_2O$ often contains small amounts of the monomeric Fe(II) bisadduct as contaminant, as also observed in the case of the pyridine complex (see below and Discussion).

$[(py)PcFe]_2O$. This complex can be prepared by exposing $(PcFe)_2O$ to pyridine vapors for 18–20 h and then brought to constant weight under vacuum at room temperature for 1–2 h.[3b] Anal. Calcd for $C_{74}H_{42}N_{18}Fe_2O$: C, 67.9; H, 3.2; N, 19.2. Found: C, 66.7; H, 3.2, N, 19.1. In a similar manner a sample of the same pyridine adduct was prepared from μ-oxo(**2**). More prolonged contact of the oxo species with the vapor of the N-base leads to the formation of $PcFe(py)_2$, as also occurs when $(PcFe)_2O$ is suspended in toluene–pyridine or in pure pyridine.[3b,d]

By method B, 500 mg of $(PcFe)_2O$, either polymorph (i.e. μ-oxo(**1**) or μ-oxo(**2**)), was dissolved (partly), with stirring, in pyridine (20 mL) at room temperature and the solution separated by filtration from the undissolved material. Precipitation of the pyridine adduct from the solution was obtained by addition of hexane (50 mL) after ca. 20 min from the contact of the solid $(PcFe)_2O$ with the N-base. The crystalline solid was separated from the mother liquors by filtration, washed with hexane, and dried under vacuum for 1–2 h. Anal. Found: C, 67.2; H, 3.6; N, 18.75. Often small amounts of $PcFe(py)_2$ contaminate the samples of $[(py)PcFe]_2O$ (see Discussion). Complete elimination of pyridine from $[(py)PcFe]_2O$ can be obtained by heating at 130–140 °C under vacuum (10^{-2} mm) for 2 h. The loss of pyridine reproducibly results in the formation of μ-oxo(**2**) for all the samples examined.

Oxo-Bridged Complexes of Formula $[(N\text{-}base)PcMn]_2O$. $[(py)PcMn]_2O$ was prepared by following the description given elsewhere.[7] The preparation of the pip and 1-Meim complexes was carried out by dissolving PcMn in the appropriate N-base and O_2 bubbled into the solution (a) up to the complete evaporation of the N-base (pip) or (b) for a long time and then precipitating the complex by addition of hexane and acetone (1-Meim). These adducts all show an intense visible absorption in solution of the respective N-base at ca. 625 nm, as expected.[7] The 4-Mepy derivative, which had not been described previously,[7] was prepared similarly, i.e. prolonged O_2 bubbling into the solution of PcMn in 4-Mepy, followed by evaporation of the solution to dryness at room temperature under vacuum (10^{-2} mm). As for the other Mn N-base adducts, a solution spectrum in 4-Mepy of $[(4\text{-}Mepy)PcMn]_2O$ also shows a very intense peak at 621 nm, typical of these Mn–O–Mn species. Anal. Calcd for $[(4\text{-}Mepy)PcMn]_2O\cdot2(4\text{-}Mepy)$, $C_{88}H_{60}N_{20}Mn_2O$: C, 69.4; H, 4.0; N, 18.4. Found: C, 69.1; H, 3.85; N, 17.7.

Physical Measurements. Magnetic susceptibility measurements were taken both in Montelibretti (Italy) and at Monash University (Australia) in the range 300–4 K with good agreement between the results. The Mössbauer spectra were measured at Monash University as already described.[8] X-ray powder photographs were obtained with a Debye powder camera (114.6 mm in diameter) with a Cu Kα (Ni filtered) radiation. Thermogravimetric analyses were performed with a Du Pont 950 thermogravimetric analyzer under a stream of N_2 (0.5 L/min). Visible solution spectra were run on a Perkin-Elmer 330 spectrophotometer.

Results and Discussion

Synthesis and Structural Information. $(PcFe)_2O$, recently described in two different crystalline modifications, i.e. μ-oxo(**1**)[3b] (bent Fe–O–Fe) and μ-oxo(**2**)[3b,4] (linear or quasi-linear Fe–O–Fe), is representative of the widely investigated class of oxo-bridged dimeric systems containing square-pyramidal, high-spin ($S = {}^5/_2$), antiferromagnetically coupled Fe(III).[9] $(PcFe)_2O$ shows a marked tendency to react with N-bases. Under controlled conditions, N-base adducts of definite composition are formed. As discussed below, two molecules of N-base ligate to the oxo species to give complexes of formula $[(N\text{-}base)PcFe]_2O$ (N-base = 4-Mepy, pip, 1-Meim, and py), with additional solvent molecules occluded in the crystal lattice of these complexes (4-Mepy, pip). Common chemical features of these N-base adducts are (a) Fe(III) → Fe(II) reduction, with formation of the monomeric adducts of formula $PcFe(N\text{-}base)_2$ by prolonged exposure to vapors of, or contact with liquid, N-base (as pointed out in the Experimental Section this reduction reaction can lead to some contamination of the μ-oxo adducts with small amounts of the monomeric Fe(II) species (1-Meim, py)) and (b) formation of μ-oxo(**2**) by elimination of the N-base by heating under vacuum.

To establish whether the N-base molecules in the present complexes are indeed coordinated or, rather, dispersed in the crystal lattice may appear a trivial problem. As a matter of fact, five-coordinate, square-pyramidal Fe(III) stereochemistry in μ-oxo porphyrin dimers and other related systems appears to be the stable structural form.[10] The reluctance to further coordinate donor molecules at the external axial sites of Fe(III) to give six-coordinate species has been pointed out.[9b,10–13] There are examples in the literature in which solvent molecules, although firmly retained in the crystal lattice, are not coordinated to the metal ion, thus leaving the five-coordinate stereochemistry of Fe(III) preserved in these complexes. X-ray work has shown, for instance, that in the complexes $[(salen)Fe]_2O\cdot CH_2Cl_2$,[14] $[(salen)Fe]_2O\cdot 2py$,[10] $(C_{22}H_{22}N_4Fe)_2O\cdot CH_3CN$,[15] and the porphyrin dimer of formula $(C_{89}H_{56}N_{10}O)Fe_2O\cdot H_2O$[16] additional solvent molecules

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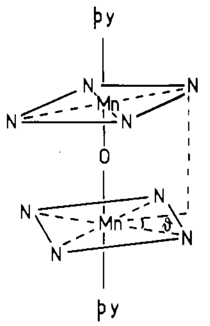

Figure 1. Schematic representation of $[(py)PcMn]_2O$ ($\vartheta = 49°$).[17]

Table I. Mössbauer Parameters for $[(N\text{-base})PcFe]_2O$ Adducts

L	T, K	δ,[a] mm s^{-1}	ΔE_Q, mm s^{-1}	$\Gamma_1 = \Gamma_2$,[b] mm s^{-1}	area, %
4-Mepy	295	0.12	1.81	0.14	85.9
		0.15	0.48	0.19	14.1[c]
	77	0.19	1.75	0.15	97.9
		0.19	0.25	0.10	2.1[c]
	4.2	0.20	1.76	0.15	100
pip	4.2	0.19	1.61	0.16	95.7
		0.32	0.33	0.15	4.3[c]
1-Meim	4.2	0.17	1.58	0.14	79.3
		0.30	1.68	0.15	20.7[d]
py[g]	4.2	0.18	1.73	0.14	56.0
		0.33	1.97	0.10	17.7[e]
		0.26	1.26	0.12	21.3[f]
		0.36	0.40	0.12	4.9[c]

[a] Referred to metallic iron. Errors: $\delta = \pm 0.01$ mm s^{-1}; $\Delta E_Q = \pm 0.01$ mm s^{-1}. [b] Half-width at half-maximum (hwhm). [c] For this minor inner doublet, most likely due to μ-oxo(**1**), errors are $\delta = \pm 0.05$ mm s^{-1} and $\Delta E_Q = \pm 0.05$ mm s^{-1}. [d] Assigned to $PcFe(1\text{-Meim})_2$; see text for the parameter values measured on $PcFe(1\text{-Meim})_2 \cdot 1\text{-Meim}$. [e] Assigned to $PcFe(py)_2$ (see also ref 18 and 19). [f] Assigned to μ-oxo(**2**) (see ref 4). [g] This sample prepared by route A, i.e. solid μ-oxo(**1**) + py vapor. Another sample, prepared by route B, gave, at 4.2 K, the following parameters: $[(py)PcFe]_2O$, $\delta = 0.18$ mm s^{-1}, $\Delta E_Q = 1.75$ mm s^{-1} (area 56.2%); $PcFe(py)_2$, $\delta = 0.32$ mm s^{-1}, $\Delta E_Q = 1.95$ mm s^{-1} (area 34.4%); μ-oxo(**1**), $\delta = 0.134$ mm s^{-1}, $\Delta E_Q = 0.43$ mm s^{-1} (area 9.4%).

are interstitial[10,14,15] or particularly located,[16] but definitely not coordinated to Fe(III). For the present complexes some information could be achieved by establishing a structural correlation between these complexes and $[(py)PcMn]_2O$[17] and the analogous Mn complexes (N-base = pip, 1-Meim, and 3-Mepy), of similar structure, described by Lever et al.[7] In $[(py)PcMn]_2O$, X-ray work has shown[17] that the molecular structure, schematically represented in Figure 1, consists of two oxo-bridged phthalocyanine rings twisted in a staggered position with respect to one another and containing six-coordinate, in-plane Mn(III) atoms, with the pyridine molecules ligated at the external axial sites of the μ-oxo dimer. Because of the isomorphism of this complex with that of the corresponding Fe(III)-containing species described here,[3b] it is definitely established that the same structure is present in $[(py)PcFe]_2O$. The manganese and iron 4-Mepy derivatives are also isomorphous. Indeed, isomorphism has not been found for the 1-Meim adducts, and comparison could not be made between the two piperidine derivatives because of the very poor X-ray powder spectrum of the manganese species. Thus, X-ray information is incomplete; nevertheless, it seems to be strongly indicative of a six-coordinate structure for the present complexes with an implied effective axial ligation of the N-base molecules. Mössbauer spectral studies and magnetic susceptibility measurements fully support this indication.

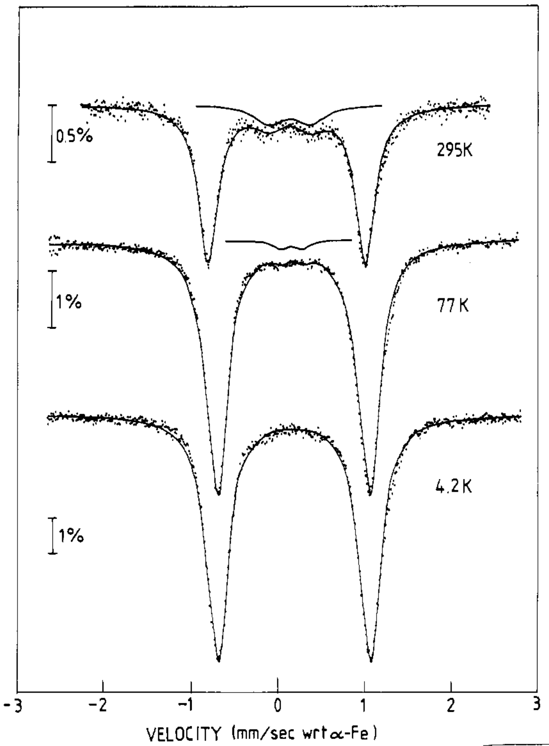

Figure 2. Mössbauer spectra in zero applied field of $[(4\text{-Mepy})PcFe]_2O$.

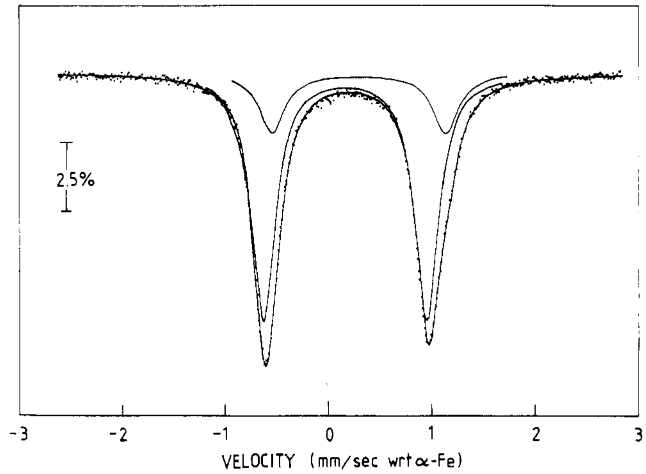

Figure 3. Mössbauer spectrum at 4.2 K of $[(1\text{-Meim})PcFe]_2O$ showing the component doublets used to fit the spectrum (see Table I).

Mössbauer Spectral Studies. Zero-field Mössbauer spectra were measured for all the complexes at low temperature (4.2 K) (Table I). For $[(4\text{-Mepy})PcFe]_2O$ the spectra were also measured at room temperature and at 77 K. These are displayed in Figure 2, where it can be seen that a symmetrical quadrupole doublet is observed at each temperature together with a very weak inner doublet at 295 and 77 K, due, most likely, to traces of μ-oxo(**1**). The intensities of the spectra increase as the temperature decreases from 295 K down to 4.2 K. The spectra also show a variation in the size of both δ and ΔE_Q as a function of decreasing temperature. An increase of 0.08 mm s^{-1} in δ is commonly observed and is assigned to the second-order Doppler effect. There is a small decrease in ΔE_Q between 295 and 77 K (0.06 mm s^{-1}).

The piperidine adduct also showed a sharp symmetrical doublet, while the 1-Meim complex showed a small asymmetry in both the line widths and intensities of the components of the quadrupole doublet. In fact, in the latter case the best least-squares fit of the spectrum utilized two doublets in ca. 4:1 relative area, with small differences in the δ and ΔE_Q values (Figure 3). The minor doublet, with $\delta = 0.30$ mm s^{-1} and $\Delta E_Q = 1.68$ mm s^{-1}, is due to the presence of small amounts of the Fe(II) bisadduct in the sample. Independent synthesis and Mössbauer measurements at 4.2 K on a sample of $PcFe(1\text{-Meim})_2 \cdot 1\text{-Meim}$ gave parameter values of $\delta = 0.31$ mm s^{-1} and $\Delta E_Q = 1.71$ mm s^{-1}, identical, within the experimental error, with those above and similar to those

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observed previously for $PcFe(Im)_2$.[18,19] It is perhaps a little surprising that the δ and ΔE_Q values for $PcFe(N\text{-base})_2$ and $[(N\text{-base})PcFe]_2O$ are so similar, but this presumably arises essentially because of the rather similar ligand arrangements in these low-spin d^6 and d^5 iron centers (vide infra).

The Mössbauer spectrum of the μ-oxo pyridine adduct was measured on a number of samples, and there was clear evidence of more than one quadrupole doublet being present, although the major doublet in each case was due to $[(py)PcFe]_2O$ with parameter values $\delta = 0.18$ mm s^{-1} and $\Delta E_Q = 1.73$ mm s^{-1}. The other spectral features, seen as a shoulder on the main doublet in the purest sample, prepared by method A, are assigned to the presence of $PcFe(py)_2$[18,19] and μ-oxo(**2**).[4] We have described above the difficulties faced in obtaining samples of the pyridine complex free from $PcFe(py)_2$. The actual concentration of this bisadduct in the sample listed in Table I is most likely less than the 17.7% deduced from Mössbauer spectral areas, since the latter are well-known not to equate with concentrations because of differing Debye–Waller factors. Further, the intensity of the visible spectral band of a pyridine solution of this sample (shoulder at ca. 653 nm), due to $PcFe(py)_2$, is very small (similar arguments on relative concentrations apply to the 1-Meim system). The only reasonable explanation for the calculated doublet having $\delta = 0.26$ mm s^{-1} and $\Delta E_Q = 1.26$ mm s^{-1} and being assigned to μ-oxo(**2**) is the presence of a small amount of this isomer in the original sample of μ-oxo(**1**). The other feature in Table I deserving of comment is the variation in parameter values of weak lines observed in some spectra and assigned to traces of μ-oxo(**1**). This is simply a result of line-shape analyses attempting to adequately incorporate such a weak, broad central feature and has no other significance.

The observed values of the isomer shift and the quadrupole splitting at 4.2 K for all the complexes examined are within the ranges 0.17–0.20 and 1.58–1.76 mm s^{-1}, respectively. These values are significantly different from those observed for the five-coordinate crystalline isomers μ-oxo(**1**) ($\delta = 0.37$ mm s^{-1}, $\Delta E_Q = 0.44$ mm s^{-1}) and μ-oxo(**2**) ($\delta = 0.25$ mm s^{-1}, $\Delta E_Q = 1.27$ mm s^{-1}).[4,20] These differences are reasonably explained on the basis of the axial perturbation produced by the ligation of the N-base to Fe(III) and the formation of the six-coordinate environment. Moreover, the δ and ΔE_Q values show a regular trend in going from μ-oxo(**1**) (bent Fe–O–Fe) through μ-oxo(**2**) (linear or quasi-linear Fe–O–Fe) to the present adducts (for the structural changes see the proposed Scheme I in ref 4). The problem arising, then, is as to whether, in the six-coordinate adducts, the implied in-plane location of the metal atom and the ligand field strngth of the phthalocyanine chromophore will induce a low-spin configuration or, rather, Fe(III) will retain the high-spin structure ($S = {}^5/_2$) observed in their two crystalline precursors. The extreme of this trend is represented by the recently reported monomeric, six-coordinate, low-spin ($S = {}^1/_2$) Fe(III) phthalocyanines containing two identical ligands, such as $PcFe(OH)_2^-$ ($\delta = 0.18$ mm s^{-1}, $\Delta E_Q = 2.22$ mm s^{-1}).[21] Thus, our adducts and these monomeric species show practically identical isomer shifts and only slightly different quadrupole splittings. These comparisons, taken in conjunction with other physical data (vide infra), strongly imply that the Fe(III) centers in these adducts are six-coordinate and low-spin. Comparison with the available Mössbauer data on pertinent oxo-bridged Fe(III) dimers formed with alternative multidentate ligands confirms the spin-state assignment, although not in an entirely unambiguous way. In the six-coordinate complexes $Na_4(FeEDTA)_2O{\cdot}12H_2O$, $enH_2(FeEDTA)_2O{\cdot}6H_2O$, and $[Fe_2O(bbimae)_2X_2](NO_3)_2$ (X = Cl, CNS) in which EDTA and bbimae are acting as pentadentate ligands, thus allowing attainment of six-coordination,[22-24] Fe(III) has been assigned a high-spin structure ($S = {}^5/_2$) mainly on the basis of UV–visible and Mössbauer spectral and magnetic susceptibility behavior. The isomer shifts of the present complexes are definitely lower than those found for the EDTA or bbimae complexes, whereas the quadrupole splittings are comparable to those of the EDTA complexes but higher than those found for the complexes containing bbimae. The oxo-bridged dimer $[Fe_2O(tsalen)_2]{\cdot}py$ is the only other known μ-oxo species that has been assigned a low-spin configuration, also on the basis of Mössbauer and magnetic susceptibility data.[25] This complex, however, shows a higher δ value and a lower ΔE_Q value than those observed here. Instead, both these data compare reasonably with those of the already mentioned six-coordinate high-spin bbimae complexes.[24]

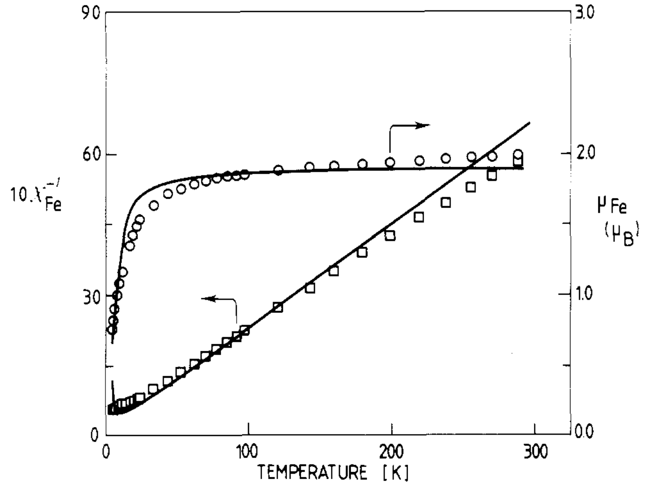

Figure 4. Magnetic moments (○) and reciprocal susceptibilities (□) as a function of temperature for $[(4\text{-Mepy})PcFe]_2O$. The solid lines are calculated by using the parameters given in Table II.

Magnetic Susceptibilities. The room-temperature magnetic moments of the complexes are all in the range 1.86–2.16 μ_B per Fe atom. These values have not been corrected for any contaminating μ-oxo(**1**) (or μ-oxo(**2**)) or $PcFe(N\text{-base})_2$, the former having negligible effect because of the similar magnetic moment[3b,4,20] and the latter leading to an underestimation of the susceptibility by an amount directly proportional to the actual concentration of the diamagnetic $PcFe(N\text{-base})_2$. The observed values of the magnetic moment could be indicative of strongly antiferromagnetically coupled (i.e. $J \approx -100$ cm^{-1}) high-spin Fe(III) pairs, as found in the many μ-oxo Fe(III) systems mentioned,[9a,10,14-16,22-24] and would be expected to decrease rapidly with the temperature. Alternatively, moments of this magnitude would be expected for weakly coupled, low-spin ($S = {}^1/_2$, $S = {}^1/_2$) Fe(III) pairs.

The temperature dependence of μ_{Fe} was found to be similar for all the complexes and shows a reasonably constant value in the range 300–90 K followed by a gradual decrease to a value of ca. 0.8 μ_B at liquid-helium temperatures. This behavior is displayed in Figure 4 for a representative complex, $[(4\text{-Mepy})PcFe]_2O$. The corresponding χ_{Fe} values are Curie–Weiss-like but display a leveling off of the susceptibilities near 4.2 K. The latter feature can be seen in the χ_{Fe}^{-1}/T plot as a deviation from the otherwise linear dependence ($\Theta = 22$ K). The plots, shown in Figure 4, are quite different from those observed for μ-oxo(**1**)[20] and μ-oxo(**2**)[4] and many other $S = {}^5/_2$ μ-oxo dimers.[9a,10,14-16,22-24] They are more reminiscent of the corresponding plots for low-spin monomeric Fe(III) phthalocyanines, such as $PcFe(OH)_2^-$, except that the

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Table II. Magnetic Parameters for $[(\text{N-base})\text{PcFe}]_2\text{O}$ Complexes[a]

N-base	μ_{Fe} (295 K)	g (±0.1)	J, cm^{-1} (±0.2)
4-Mepy	1.99	2.2	−5.9
pip	2.11	2.4	−6.3
1-Meim	2.16	2.35	−5.5
py	1.86	2.16	−5.5

[a] The formula assigned to the particular samples used for these measurements, on the basis of elemental and thermogravimetric analyses, were $[(\text{4-Mepy})\text{PcFe}]_2\text{O}\cdot 2(\text{4-Mepy})$, $[(\text{pip})\text{PcFe}]_2\text{O}\cdot\text{pip}$, $[(\text{1-Meim})\text{PcFe}]_2\text{O}$, and $[(\text{py})\text{PcFe}]_2\text{O}$; correspondingly, diamagnetic corrections used were 5.52×10^{-4} (4-Mepy), 5.33×10^{-4} (pip), 4.78×10^{-4} (1-Meim), and 5.05×10^{-4} cgsu (py).

latter uncoupled species do not display such a large decrease in μ_{Fe} at low temperatures.[21]

The data for the present adducts are qualitatively consistent with a weak antiferromagnetic coupling occurring between low-spin Fe(III) centers. Fitting of the data to a simple $-2J\bar{S}_1\cdot\bar{S}_2$ model (where $S_1 = S_2 = {}^1/_2$)[26] gave reasonable fits for J of ca. -6 cm^{-1}, although the calculated maximum in χ_{Fe} at ca. 10 K was not observed but rather the leveling off/inflection described above. The best-fit g and J values of this model are given in Table II. There are a number of possible reasons for the divergencies of the observed and calculated values noted in Figure 4. First, the simple spin–spin coupling model employed is not rigorously applicable to $S = {}^1/_2$ Fe(III) systems which have formally degenerate $^2T_{2g}$ ground states. However, the splitting of these states by spin–orbit coupling and rhombic ligand field effects is likely to be large enough to render the ground state an effective ^2A state and should therefore lead to reasonable agreement especially at low temperatures. Nevertheless, an orbital model, similar to that recently described for related orbitally degenerate systems, should strictly be used.[27-29] Second, it is possible that small concentrations of "monomeric" impurities, commonly observed in μ-oxo dimeric species, could be present and responsible for the divergence at low temperatures. Indeed, it is possible to reproduce the low-temperature inflection in χ_{Fe}^{-1} by including a $S = {}^1/_2$ monomer contribution, although in concentrations much higher than other measurements would sensibly suggest. The presence of small quantities of the Fe(II) bisadduct in the 1-Meim and py complexes would lead to a small reduction in χ_{Fe} at all temperatures and would only affect the g values. The small quantities of μ-oxo(**1**) present in the pip and 4-Mepy complexes will have negligible effects on the J values. Despite these subtleties in the fitting procedure, the data are clearly compatible with a weak antiferromagnetic exchange interaction occurring across the Fe–O–Fe bridge of these binuclear adducts. The only other known low-spin μ-oxo complex, i.e. $[\text{Fe}_2\text{O}(\text{tsalen})]\cdot\text{py}$,[25] shows a behavior similar to that of the present complexes. A J value of -4.5 cm^{-1} was deduced in that case.[25]

The reason for the low values of J in the present linearly bridged μ-oxo species is probably related to the disposition of the magnetic orbitals on Fe in relation to the p orbitals of the oxo oxygen. The relative orientation of the two cofacial PcFe planes will also be important. It is likely that the unpaired electron in the (N-base)PcFe$^+$ moieties of the present μ-oxo dimers will occupy the d_{yz} orbital, as has been suggested also for the complexes PcFe(X)_2^- ($X = \text{OH}^-$, N_3^-, etc.) by ESR spectra.[21] The d_{yz} orbital will overlap only very weakly with the oxygen p_z orbital and a little more strongly with the p_y orbital (the Fe–O–Fe axis is defined as z and the Fe–N$_{Pc}$ directions as x and y). Thus, only weak antiferromagnetic coupling would be expected for eclipsed geometries and even weaker coupling for staggered rings. In the latter situation, which is most likely occurring in our complexes, the Fe(d_{yz})–O(p_y) overlap at one end is mismatched in relation to the Fe(d_{yz}) orbital at the other. Overall, a combination of dipole–dipole and weak antiferromagnetic exchange coupling would be predicted from this simple superexchange model, as is, in fact, observed.

Further Comments and Conclusions. Coordination of N-bases such as py, 4-Mepy, pip, and 1-Meim at the external axial sites of $(\text{PcFe})_2\text{O}$ has led to a new series of stable N-base adducts of formula $[(\text{N-base})\text{PcFe}]_2\text{O}$. These complexes appear to be a homogeneous and rare class of six-coordinate low-spin Fe(III) oxo-bridged dimeric species, as has been established by structural information and Mössbauer and magnetic susceptibility data. A detailed examination of the magnetic data does not show significant differences in the series as a function of the nature of the N-base. Also, from the Mössbauer data of Table I it can be seen that the isomer shift values at 4.2 K vary very little as the N-base is varied. A similar lack of variation was observed in the N-base adducts of PcFe of the types PcFeL_2[18,19] and PcFe(CO)L[30] (L = heterocyclic or aliphatic N-base). There is more variation in the quadrupole splitting ΔE_Q, which decreases in the order 4-Mepy ≈ py > pip > 1-Meim. This contrasts with the order found in PcFeL_2, viz. pip > 4-Mepy > py > im. Since the pK_a values of the N-bases are in the order pip > im > 4-Mepy > py, a reasonable increase correlation with the σ-donor capacity of the N-base appears to be applicable to the present compounds, as proposed by Dale et al.[18] for the PcFe adducts. However, the exact d-orbital energy level distribution in the present low-spin trans O–Fe–(N-base) axially ligated Fe(III) phthalocyanines will influence the electric field gradient at Fe and hence also the ΔE_Q values. Detailed structural features may also be important. Presently, however, difficulties are being encountered in the preparation of single crystals suitable for an X-ray determination. When crystals are obtained, they diffract X-rays very poorly and the resulting peaks are very broad. Similar difficulties were found with crystals of $(\text{PcFe})_2\text{O}$.[3b] Attempts are still being carried out, particularly with the 1-Meim and py adducts.

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Note Added in Proof. Just prior to the publication of the present paper we successfully examined by X-rays single crystals formed from solutions of $[(\text{1-Meim})\text{PcFe}]_2\text{O}$ in a mixture of 1-Meim and acetone and having the composition $[(\text{1-Meim})\text{PcFe}]_2\text{O}\cdot[\text{PcFe}(\text{1-Meim})_2]\cdot 3(\text{CH}_3)_2\text{CO}$. As regards the structure of the μ-oxo dimer, X-ray data on these crystals are fully in agreement with the content of the present paper with regard to the coordination number and environment of the two Fe atoms, the geometry of the Fe–O–Fe moiety, and the relative position of the phthalocyanine rings. Details of this important X-ray work will be given in a forthcoming paper (Rossi, G.; Goedken, V. L.; Ercolani, C.; Dzugan, S., manuscript in preparation).

Registry No. $(\text{PcFe})_2\text{O}$, 74353-48-3; $[(\text{4-Mepy})\text{PcFe}]_2\text{O}\cdot 2(\text{4-Mepy})$, 109975-53-3; $[(\text{pip})\text{PcFe}]_2\text{O}\cdot\text{pip}$, 109975-55-5; $[(\text{1-Meim})\text{PcFe}]_2\text{O}$, 109996-02-3; $[(\text{py})\text{PcFe}]_2\text{O}$, 86308-25-0; $\text{PcFe}(\text{4-Mepy})_2$, 16702-08-2; PcFe(py)_2, 20219-84-5; PcMn, 14325-24-7; $[(\text{4-Mepy})\text{PcMn}]_2\text{O}$, 109996-03-4; $\text{PcFe}(\text{1-Meim})_2$, 55925-76-3; PcFe, 132-16-1.

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