X-Ray Crystal Structure of μ-Oxo-bis[(1-methylimidazole)-phthalocyaninatoiron(III)] and Comments on the Molecular Structure and Chemistry of Oxo-bridged Iron Phthalocyaninate Dimers†

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Single-crystal X-ray work has been carried out on crystals containing the 1-methylimidazole adduct of μ-oxo-bis[(phthalocyaninato)iron(III)], [{Fe(pc)(mim)}$_2$O]·[Fe(pc)(mim)$_2$]·3Me$_2$CO. The crystals are monoclinic, space group *C*2/*c*, with *a* = 35.236(5), *b* = 14.173(2), *c* = 23.220(3) Å, β = 103.56(10)° and *Z* = 4. The structure was solved and refined using all data including zero intensities (5739). Only the atoms of the μ-oxo dimer were refined anisotropically because of data limitations. The Fe atoms in [{Fe(pc)(mim)}$_2$O] are nominally centred in the phthalocyanine plane, with an average Fe–N(pc) of 1.92(3) Å and six-co-ordinate, with Fe–O 1.749(1) Å and Fe–N(mim) 2.039(7) Å. The Fe–O–Fe angle is 175.1°. X-Ray data for [Fe(pc)(mim)$_2$] are as expected for six-co-ordinate low-spin nitrogen-containing base adducts of [Fe(pc)]. The crystal data are discussed in the light of similar results on [{Fe(pc)(mim)}$_2$C] and related compounds.

Two different crystalline isomers of the μ-oxo dimer [{Fe(pc)}$_2$O] (pc = phthalocyaninate), *i.e.* μ-Oxo(1) and μ-Oxo(2), having a bent and a linear or quasi-linear Fe–O–Fe bond system, respectively, can be isolated as final products of the reaction of [Fe(pc)] with dioxygen.[1a–h] Both μ-Oxo(1) and μ-Oxo(2) contain highly antiferromagnetically interacting pairs of five-co-ordinate high-spin Fe^{III}.[1b,2] Interaction of [{Fe(pc)}$_2$O] with nitrogen-containing bases leads to the formation of adducts of formula [{Fe(pc)L}$_2$O] [L = pyridine (py), 4-methylpyridine (4Me-py), 1-methylimidazole (mim) or piperidine (pip)] in which the base is co-ordinated.[1b,h] These adducts have been characterized, mainly on the basis of magnetic susceptibility data and Mössbauer spectra, as containing weakly antiferromagnetically interacting pairs of six-co-ordinate low-spin Fe^{III}.[1h] It is worth noting that no examples have so far been reported of six-co-ordinate low-spin μ-oxo dimers formed with porphyrin or porphyrin-like macrocycles or similar multidentate ligands.

Crystallographic information, obtained exclusively by X-ray powder diffraction, provided additional support for the presence of a linear or quasi-linear Fe–O–Fe moiety in μ-Oxo(2) and the adducts [{Fe(pc)L}$_2$O] and direct ligation of the base at Fe in the latter series since: (*a*) μ-Oxo(2) is isomorphous with the Mn–O–Mn analogue[1b] and with the corresponding μ-nitrido species [{Fe(pc)}$_2$N],[3] very likely containing a linear Fe–N–Fe, as is the case for [{Fe(tpp)}$_2$N] (tpp = 5, 10, 15, 20-tetraphenylporphyrinate);[4] (*b*) [{Fe(pc)(py)}$_2$O] is isomorphous with [{Mn(pc)(py)}$_2$O],[1b] known from X-ray study to have a linear Mn–O–Mn system and py co-ordinated at the axial sites;[5] (*c*) isomorphism has also been observed for [{Fe(pc)(4Me-py)}$_2$O] and its manganese analogue,[1h] which should be structurally very similar to the py-containing species, since, presumably, the change from py to 4Me-py should not influence significantly the essential features of the structure.

Attempts to prepare single crystals suitable for X-ray work have been systematically carried out by us in the past on both series of compounds, *i.e.* [{Fe(pc)}$_2$O][μ-Oxo(1) and μ-Oxo(2) isomers] and the corresponding adducts [{Fe(pc)L}$_2$O].[1b,h] We present here the single-crystal X-ray work carried out on the species [{Fe(pc)(mim)}$_2$O]·[Fe(pc)(mim)$_2$]·3Me$_2$CO **1**, following that recently briefly reported for the isomorphous species containing the 1-methylimidazole adduct of μ-carbido-bis[phthalocyaninato)iron(III)], [{Fe(pc)(mim)}$_2$C]·[Fe(pc)-(mim)$_2$]·3Me$_2$CO **2**.[6] We also discuss several aspects of the structure of these and related species and comment on previous work by us and others on the same subject.

Experimental

Data Collection, Structure Solution and Refinement Details.—Product **1** was obtained in the form of single crystals suitable for X-ray crystallographic work by dissolving [{Fe(pc)}$_2$O] in a solution of mim, acetone and hexane, filtering and slowly evaporating in a Petri dish. In the presence of the mim, slow partial conversion of the μ-oxo-iron(III) dimer to the monomeric iron(II) bis adduct occurs.[1h] Crystals of **1** must be isolated as soon as they are formed, otherwise the reduction process continues and the well formed crystals disintegrate within hours.

A metallic purple polyhedral crystal of **1** having approximate dimensions 0.30 × 0.30 × 0.30 mm was mounted on a glass fibre in a random orientation. The crystal data, data collection and refinement details are summarized in Table 1. Preliminary examination and data collection were performed with Mo-Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal incident-beam monochromator. Cell constants and an

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Experimental data for the X-ray diffraction analysis of compound 1

Formula	$C_{72}H_{44}Fe_2N_{20}O{\cdot}C_{40}H_{28}FeN_{12}{\cdot}C_9H_{18}O_3$
M	2223.5
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	35.236(5)
b/Å	14.173(2)
c/Å	23.220(3)
β/°	103.56(10)
U/Å^3	11 272.8
Z	4
F(000)	4 600
D_c/g cm^{-3}	1.31
Scan width/°	1.3
2θ scan range/°	2–40
Standard reflections	3
Least-squares parameters	549
Data parameters	10

orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $7 < 2\theta < 15°$, measured by the computer-controlled diagonal-slit method of centring. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was 0.65° with a take-off angle of 2.8°, indicating poor crystal quality. The systematic absences and intensity distribution indicated the most probable space group to be $C2/c$ which was confirmed by the successful refinement. The data were collected at 23 ± 1 °C using the θ–2θ scan technique. The scan rate was 2° min^{-1}. Data were collected to a maximum of $2\theta = 40.0°$. The scan range was determined as a function of θ to correct for the separation of the $K\alpha_1\alpha_2$ doublet. A total of 5739 unique reflections were collected of which 5709 having $I > 2\sigma(I)$ were used in the refinement. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient μ(Mo-Kα) was 5.7 cm^{-1}. No absorption correction was made and an extinction correction was judged to be unnecessary.

The solution and refinement of this structure presented a number of problems, even after the announcement of the structure solution (see Note Added in Proof in ref. 1*h*), and encountered also with the crystals of compound **2**,[6] and with the X-ray work on μ-Oxo(1) and μ-Oxo(2).[1b] Although individual crystals of **1** were, as indicated, well formed, and visually impressive, they diffracted poorly. Reflections in some regions of reciprocal space had excessive half-widths resulting in some overlap of diffracted intensities as well as problems with including all of the intensity for some reflections with the permitted scan widths. There were no observable reflections above $2\theta = 40°$ and less than 50% of the data within the 40° shell had intensities greater than $2\sigma(I)$. The structure was solved using the Patterson heavy-atom method which revealed the positions of the Fe atoms.* The remaining atoms were located in succeeding Fourier difference syntheses. The atoms of the solvent molecules appeared as extremely diffuse areas of electron density in the large cavities created by the packing of the monomer and dimer molecules. Some of the molecules appeared to be present at fractional occupancies and were refined with occupancy factors of 0.5.

Hydrogen atoms were calculated at their expected positions and added to the structure-factor calculations but their positions were not refined. In the final refinement all non-hydrogen atoms of the μ-oxo dimer were refined with anisotropic thermal parameters. The atoms of the monomer and solvent molecules were refined isotropically due to limitations of the data set. The structure was refined by full-matrix least-squares techniques where the function minimized was $w(|F_o| - |F_c|)^2$ and $w = 1/\sigma^2|F_o|$. At convergence the final agreement values were $R = 0.179$ and $R' = 0.118$ for all data. A final difference Fourier map was featureless except for peaks of 0.6 e Å^{-3} in the vicinity of the solvent atoms. The final positional parameters are listed in Table 2.

As a result of the loose packing in **1**, large thermal motion of portions of the iron phthalocyanine moieties was observed, even more remarkable for the solvent molecules. As is immediately evident from the ORTEP view of the μ-oxo dimer (see below), and also for the monomer species, large thermal excursions of the mim atoms are present. The iron, oxygen and core atoms of the phthalocyanine ring have reasonable thermal parameters and nearly spherical ellipsoids. The thermal motion increases toward the periphery of the phthalocyanine rings, although not in a uniform manner. Portions of the phthalocyanine ring appear to exhibit motion perpendicular to the plane while some rotational motion within the plane is also apparent. While the data are limited in both quality and quantity, it is reassuring that the size and shape of the thermal ellipsoids are largely consistent within themselves and within chemical expectations.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

X-Ray Work.—Iron phthalocyanine compounds for which single-crystal X-ray work has been carried out are not numerous, and include [Fe(pc)] itself,[7] [Fe(pc)(4Me-py)$_2$]·2(4Me-py),[8] [Fe(pc)(dmso)$_2$]·2dmso, (dmso = dimethyl sulphoxide)[9] [Fe(pc)(CO)(dmf)]·dmf (dmf = dimethylformamide),[10] [{Fe(pc)Cl}$_2$I$_2$] and [Fe(pc)I],[11] [N(PPh$_3$)$_2$][Fe(pc)(CN)$_2$],[12] and the species **2** recently reported by us.[6] The present X-ray work on compound **1** is the first involving an iron phthalocyanine μ-oxo dimer.

Species **1** consists of an oxo-bridged dimeric species, [{Fe(pc)(mim)}$_2$O] located on a two-fold rotation axis passing through the oxygen atom, a monomeric species of formula [Fe(pc)(mim)$_2$], located on an inversion centre, and disordered solvent molecules scattered throughout the lattice voids.

A view of the μ-oxo dimer is shown in Fig. 1, together with the labelling scheme. Fig. 2 views the molecule approximately down the Fe–O–Fe bond axis and illustrates the rotation of the two phthalocyanine molecules relative to one another. A view of the co-ordination sphere, approximately normal to the Fe–O–Fe bond axis, is shown in Fig. 3; pertinent bond distances and angles are presented in Tables 3 and 4, together with those of [Fe(pc)(mim)$_2$]. The unit-cell contents for **1** (Fig. 4) and an ORTEP plot of the [Fe(pc)(mim)$_2$] molecule (Fig. 5) are also shown.

The most salient features of the co-ordination sphere of the μ-oxo dimer are summarized as follows: (*i*) in-plane location of the six-co-ordinate iron centres (displacement less than 0.02 Å towards the oxygen atom), with the mim molecules ligated *trans* to the Fe–O bonds of the Fe–O–Fe moiety; (*ii*) quasi-linear Fe–O–Fe bond system (175.1°); (*iii*) staggered position of the two phthalocyanine rings within the dimer (relative rotation 45°), with minimization of the non-bonding interactions between the benzene rings; and (*iv*) eclipsed orientation of the plane of the co-ordinated mim molecules with respect to the N(pc)–Fe–N(pc) equatorial axis. Noticeably, strictly similar features have been observed for the μ-carbido dimer in **2**,[6] as already anticipated.[13] Moreover, strong analogies are also observed with the dimer [{Mn(pc)(py)}$_2$O].[5] X-Ray data for these μ-oxo dimers are given in Table 5 together with those of three other pertinent μ-oxo dimers, and those of the

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* All computations were performed on a PDP 11/34 computer with the aid of the structure determination crystallographic program library obtained upon purchase of the X-ray equipment.

Table 2 Positional parameters and their estimated standard deviations (esds)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.987 97(4)	0.247 9(1)	0.172 58(6)	C(15A)	0.296 0(3)	0.235 3(7)	0.183 6(4)
Fe(2)	0.250	0.250	0.000	C(16A)	0.298 2(3)	0.224 6(7)	0.122 1(4)
O	1.000	0.242 6(7)	0.250	C(17A)	0.206 8(4)	0.078(1)	−0.038 7(6)
N(1)	0.965 3(2)	0.123 6(6)	0.169 8(3)	C(18A)	0.217 1(4)	−0.023(1)	0.035 8(6)
N(2)	0.937 2(2)	0.301 3(6)	0.171 5(3)	C(19A)	0.237 1(4)	0.061(1)	0.048 4(7)
N(3)	1.010 6(2)	0.369 5(6)	0.174 5(3)	C(20A)	0.172 6(6)	−0.083(2)	−0.055 8(9)
N(4)	1.037 5(2)	0.193 7(6)	0.169 6(4)	C(31)	1.087 3(3)	0.088 8(9)	0.172 2(5)
N(5)	0.899 0(2)	0.162 1(6)	0.170 7(4)	C(32)	1.046 4(3)	0.101 9(8)	0.170 5(5)
N(6)	0.953 7(2)	0.465 5(6)	0.176 5(3)	C(3)	0.963 5(3)	−0.128 1(7)	0.176 7(5)
N(7)	1.076 9(2)	0.330 9(6)	0.173 8(3)	C(4)	0.932 0(4)	−0.180 1(8)	0.177 4(6)
N(8)	1.021 8(2)	0.029 6(6)	0.170 6(4)	C(5)	0.896 7(4)	−0.147 6(8)	0.178 4(6)
C(1)	0.984 8(3)	0.040 0(7)	0.171 3(4)	C(6)	0.891 5(3)	−0.050 5(9)	0.177 1(5)
C(2)	0.958 6(3)	−0.035 4(7)	0.173 5(5)	C(11)	0.834 6(3)	0.308 5(8)	0.170 5(5)
C(7)	0.923 2(3)	0.002 9(7)	0.174 2(5)	C(12)	0.811 9(3)	0.385 8(9)	0.169 7(5)
C(8)	0.928 5(3)	0.103 9(7)	0.171 4(4)	C(13)	0.827 7(3)	0.473 2(9)	0.173 7(5)
C(9)	0.904 0(3)	0.254 5(8)	0.172 1(4)	C(14)	0.867 4(3)	0.487 5(8)	0.176 6(5)
C(10)	0.872 6(3)	0.319 3(7)	0.171 6(5)	C(19)	1.013 9(3)	0.621 9(8)	0.179 2(4)
C(15)	0.888 6(3)	0.406 4(7)	0.174 1(4)	C(20)	1.046 3(3)	0.677 5(7)	0.181 1(5)
C(16)	0.929 6(3)	0.395 9(7)	0.173 0(4)	C(21)	1.081 8(3)	0.637 6(8)	0.177 9(4)
C(17)	0.990 4(3)	0.452 8(7)	0.175 1(4)	C(22)	1.086 3(3)	0.543 8(7)	0.176 0(4)
C(18)	1.017 7(3)	0.528 7(6)	0.177 2(4)	C(27)	1.141 4(3)	0.185 7(9)	0.174 5(6)
C(23)	1.053 3(3)	0.492 7(7)	0.175 7(4)	C(28)	1.162 3(3)	0.106(1)	0.174 0(7)
C(24)	1.047 6(3)	0.391 6(7)	0.174 5(4)	C(29)	1.148 1(4)	0.017(1)	0.175 8(7)
C(25)	1.071 1(3)	0.240 7(8)	0.171 9(4)	C(30)	1.109 9(4)	0.008 6(9)	0.174 4(6)
C(26)	1.103 6(3)	0.175 6(9)	0.174 0(5)	C(33)	0.958 8(5)	0.197(1)	0.046 7(5)
N(2A)	0.264 2(2)	0.254 7(6)	0.086 6(3)	C(34)	0.976 9(5)	0.324 8(8)	0.045 4(5)
N(3A)	0.204 0(2)	0.315 8(6)	0.104 4(3)	C(35)	0.964 1(4)	0.306 9(9)	−0.011 6(5)
N(4A)	0.170 6(2)	0.308 1(6)	−0.106 5(3)	C(36)	0.933(1)	0.169(2)	−0.061 8(8)
N(5A)	0.229 8(2)	0.122 6(6)	0.002 5(4)	N(9)	0.974 3(3)	0.257 0(7)	0.082 4(3)
N(6A)	0.199 3(3)	−0.008 7(9)	−0.020 6(5)	N(10)	0.950 5(5)	0.223 7(8)	−0.011 3(5)
C(1A)	0.169 8(3)	0.319 6(7)	−0.049 8(4)	N(1A)	0.199 1(2)	0.299 9(6)	−0.000 4(3)
C(2A)	0.136 5(3)	0.356 3(7)	−0.032 1(4)	C(1S)	0.435	0.424	0.006
C(3A)	0.100 2(3)	0.387 5(8)	−0.065 7(5)	C(2S)	0.391	0.372	−0.006
C(4A)	0.074 1(3)	0.417 6(9)	−0.033 0(5)	C(3S)	0.464	0.362	0.010
C(5A)	0.084 4(3)	0.419 9(9)	0.029 7(5)	O(1S)	0.417	0.497	0.013
C(6A)	0.120 0(3)	0.388 7(8)	0.061 9(5)	C(4S)	0.321	0.168	0.483
C(7A)	0.146 1(3)	0.359 5(7)	0.030 3(4)	C(5S)	0.314	0.236	0.446
C(8A)	0.185 6(3)	0.323 6(7)	0.049 6(4)	O(2S)	0.353	0.132	0.504
C(9A)	0.239 5(3)	0.281 2(7)	0.121 4(4)	C(1I)	0.305	0.013	0.331
C(10A)	0.259 7(3)	0.272 4(7)	0.183 1(4)	C(2I)	0.256	0.031	0.267
C(11A)	0.250 0(3)	0.292 3(7)	0.236 6(4)	C(5I)	0.250	0.052	0.344
C(12A)	0.276 4(3)	0.276 3(9)	0.288 5(4)	C(7I)	0.289	0.232	0.453
C(13A)	0.312 7(3)	0.239(1)	0.290 3(5)	C(8I)	0.332	0.254	0.441
C(14A)	0.322 9(3)	0.216 1(8)	0.237 5(5)	C(9I)	0.314	0.084	0.506

Table 3 Bond distances (Å) for the co-ordination spheres in compound **1**

[{Fe(pc)(mim)}$_2$O]		[Fe(pc)(mim)$_2$]	
Fe(1)–O	1.749(1)	Fe(2)–N(1A)	1.926(6)
Fe(1)–N(1)	1.930(8)	Fe(2)–N(1A)	1.926(6)
Fe(1)–N(2)	1.939(7)	Fe(2)–N(2A)	1.955(7)
Fe(1)–N(3)	1.895(8)	Fe(2)–N(2A)	1.955(7)
Fe(1)–N(4)	1.923(8)	Fe(2)–N(5A)	1.946(7)
Fe(1)–N(9)	2.039(7)	Fe(2)–N(5A)	1.946(7)

Table 4 Bond angles (°) for the co-ordination spheres in compound **1**

[{Fe(pc)(mim)}$_2$O]		[Fe(pc)(mim)$_2$]	
O–Fe(1)–N(1)	89.6(3)	N(1)–Fe(2)–N(1A)	180(1)
O–Fe(1)–N(2)	91.7(2)	N(1A)–Fe(2)–N(2A)	90.4(3)
O–Fe(1)–N(3)	90.9(3)	N(1A)–Fe(2)–N(2A)	89.7(3)
O–Fe(1)–N(4)	90.9(2)	N(1A)–Fe(2)–N(5A)	89.6(3)
O–Fe(1)–N(9)	178.9(4)	N(1A)–Fe(2)–N(5A)	90.4(3)
N(1)–Fe(1)–N(2)	89.0(3)	N(1A)–Fe(2)–N(2A)	89.7(3)
N(1)–Fe(1)–N(3)	179.2(3)	N(1A)–Fe(2)–N(2A)	90.4(3)
N(1)–Fe(1)–N(4)	90.3(4)	N(1A)–Fe(2)–N(5A)	90.4(3)
N(1)–Fe(1)–N(9)	91.5(3)	N(1A)–Fe(2)–N(5A)	89.6(3)
N(2)–Fe(1)–N(3)	91.6(3)	N(2A)–Fe(2)–N(2A)	180.1(8)
N(2)–Fe(1)–N(4)	177.3(4)	N(2A)–Fe(2)–N(5A)	90.4(3)
N(2)–Fe(1)–N(9)	88.1(4)	N(2A)–Fe(2)–N(5A)	89.6(3)
N(3)–Fe(1)–N(4)	89.1(4)	N(2A)–Fe(2)–N(5A)	89.6(3)
N(3)–Fe(1)–N(9)	87.9(3)	N(2A)–Fe(2)–N(5A)	90.4(3)
N(4)–Fe(1)–N(9)	89.2(3)	N(5A)–Fe(2)–N(5A)	180.1(4)

monomeric iron(II) bis adducts [Fe(pc)(mim)$_2$] (present in **1** and **2**) and [Fe(pc)(4Me-py)$_2$].[8]

The compound [Fe(pc)(mim)$_2$] is in both cases (**1** and **2**) six-co-ordinated with the mim molecules at the axial positions. Bond distances and angles are as expected for an iron(II) low-spin (d^6, diamagnetic) species as can be immediately seen by comparison of the Fe–N(pc) and Fe–N(mim) bond distances with those of [Fe(pc)(4Me-py)$_2$] (Table 5).

For [{Fe(pc)(mim)}$_2$O] and the adducts of formula [{Fe(pc)L}$_2$O] (L = py, 4Me-py or pip), as well as for the similar μ-nitrido and μ-carbido series [{Fe(pc)L}$_2$N]$^+$ and [{Fe(pc)L}$_2$C], a low-spin state has been proposed on the basis of chemical and physical information, mainly magnetic susceptibility data, NMR and Mössbauer spectra.[1h,13,18] Analysis of the data reported in Table 5 confirms this assignment. The average Fe–N(pc) bond distances found for [{Fe(pc)(mim)}$_2$O] (1.92 Å), and also for [{Fe(pc)(mim)}$_2$C] (1.95 Å), are practically coincident with those found for the monomeric low-spin iron(II) bis adducts present in both **1** and

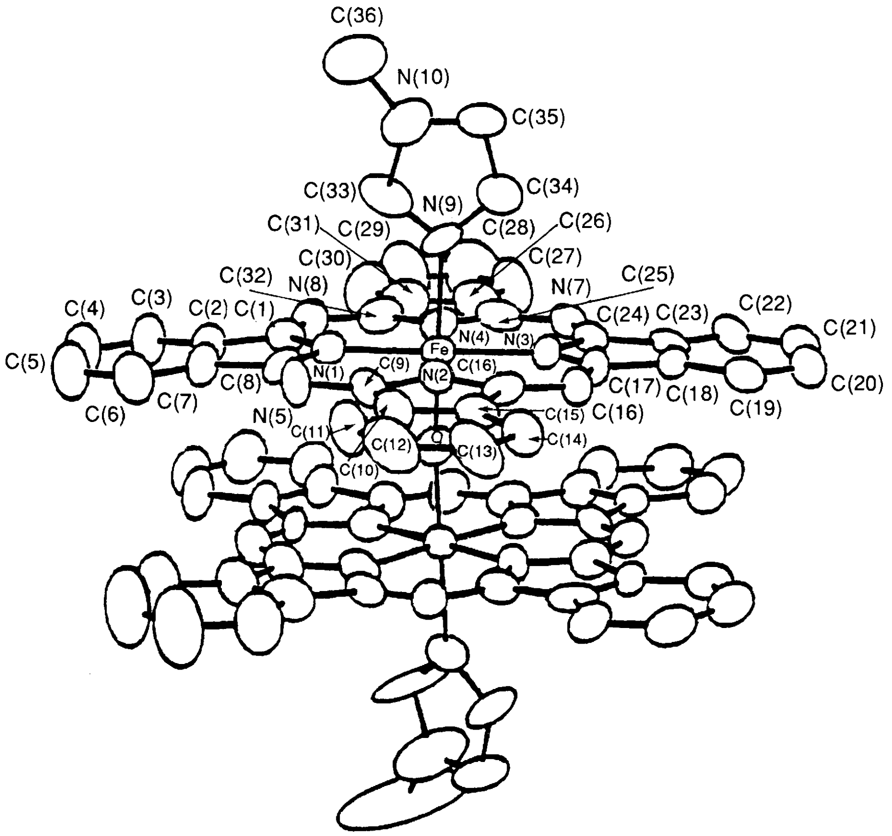

Fig. 1 ORTEP plot, together with the labelling scheme, showing the [{Fe(pc)(mim)}$_2$O] molecule from the side

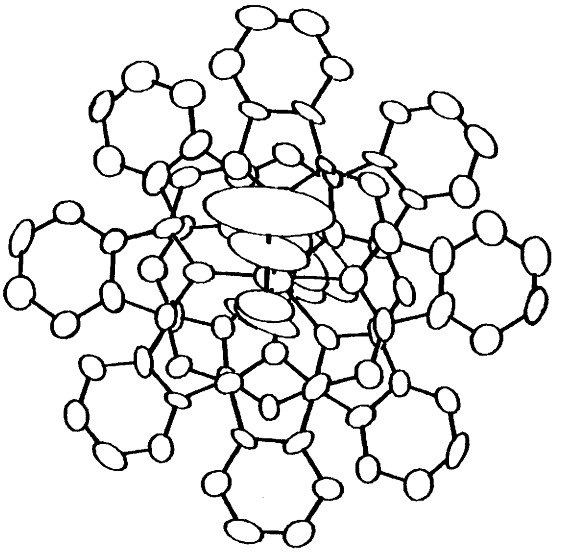

Fig. 2 ORTEP plot of [{Fe(pc)(mim)}$_2$O] as viewed down the Fe–O–Fe bond axis

2 (1.94, 1.93 Å) and for [Fe(pc)(4Me-py)$_2$] (1.93 Å). Significantly different structural features are shown, instead, by the three species [{Fe(tpp)}$_2$O], [{Fe(C$_{22}$H$_{22}$N$_4$)}$_2$O], and [{Fe(salen)}$_2$O] [salen = ethylenebis(salicylideneiminate), C$_{22}$H$_{22}$N$_4$$^{2-}$ = dihydrotetramethyldibenzotetraazacyclotetradecinate] representative of the large class of μ-oxo dimers of macrocyclic porphyrin or porphyrin-like systems which generally contain five-co-ordinate high-spin Fe^{III}, with out-of-plane displacement of Fe from the mean plane of the equatorial ligands and appreciable departure from linearity of the Fe–O–Fe moiety, with implied longer Fe–N bond distances.

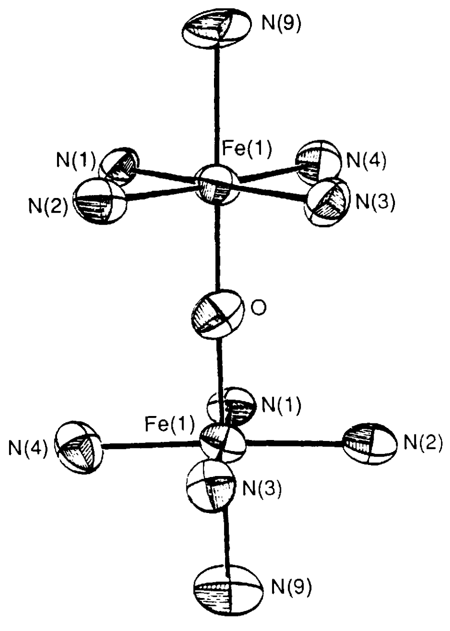

Fig. 3 ORTEP plot of the inner co-ordination sphere of the μ-oxo dimer

The observed Fe–O bond distance in [{Fe(pc)(mim)}$_2$O] (1.75 Å) is longer than the corresponding Fe–C distance in the μ-carbido analogue (1.69 Å) as expected, owing to the higher degree of π bonding in the latter. Accordingly, the corresponding distances in the two parallel species [{Fe(tpp)}$_2$O] and [{Fe(tpp)}$_2$C] are 1.76 and 1.675 Å, respectively. As a consequence of the *trans* effect experienced by mim, the corresponding Fe–N bond is shorter in [{Fe(pc)(mim)}$_2$O] (2.04 Å) than in [{Fe(pc)(mim)}$_2$C] (2.10 Å). The surprisingly

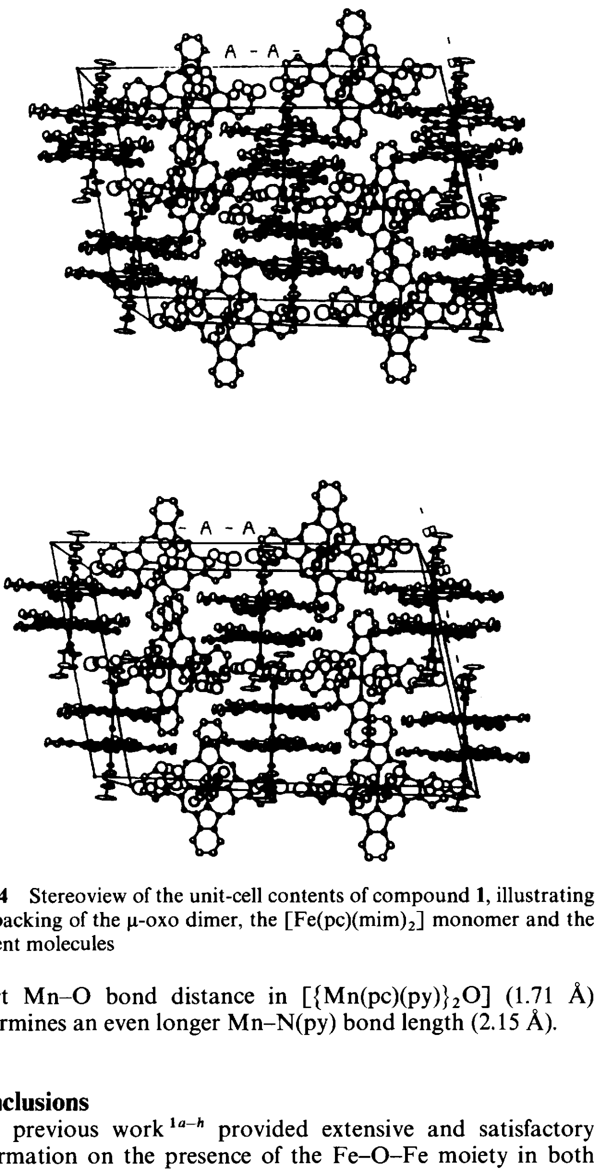

Fig. 4 Stereoview of the unit-cell contents of compound **1**, illustrating the packing of the μ-oxo dimer, the [Fe(pc)(mim)$_2$] monomer and the solvent molecules

short Mn–O bond distance in [{Mn(pc)(py)}$_2$O] (1.71 Å) determines an even longer Mn–N(py) bond length (2.15 Å).

Conclusions

Our previous work[1a–h] provided extensive and satisfactory information on the presence of the Fe–O–Fe moiety in both isomers of [{Fe(pc)}$_2$O] and its adducts [{Fe(pc)L}$_2$O] (L = py, 4Me-py, pip or mim) and the direct co-ordination of the base to the metal ion in the latter series. These results are definitely confirmed by the present X-ray work on compound **1**. Data concerning the synthesis and characterization of [{Fe(pc)}$_2$O] as a μ-oxo dimer [μ-Oxo(1) isomer] in keeping with our findings were published elsewhere.[19] Both μ-Oxo(1) and μ-Oxo(2), as well as an imidazole adduct obtained from μ-Oxo(1), were previously assigned a μ-peroxo structure, Fe–O–O–Fe.[20a–c] This incorrect formulation was already referred to by us[1b,g] and needs no further comment. In reports dealing with the tetra(t-butyl)-substituted iron phthalocyanine, [Fe(tbpc)], and formation of a μ-oxo species therefrom, Luk'yanets and co-workers[21] proposed for the latter and its base derivatives the formulae H$_2$[{Fe(tbpc)}$_2$O] and [HL]$_2$[{Fe(tbpc)}$_2$O], respectively, both suggested to contain Fe^{II}; controversially referring to our work, the rather peculiar acidic formulation for the μ-oxo species and the salt-like structure for its base derivatives were extended to the unsubstituted analogues [{Fe(pc)}$_2$O] and its base adducts.[21] The proposed acidic Fe^{II}-containing structure was previously argued by us[1f] and by other authors.[22] More recently, formation of an oxygen-containing species from [Fe(tbpc)] has been re-examined and the more plausible μ-oxo structure [{Fe(tbpc)}$_2$O] has been considered.[23] The latter, dissolved in pyridine, shows a visible spectrum, and its changes with time, identical to those already observed for [{Fe(pc)}$_2$O].[24] The present data on **1**, as well as the above-mentioned previous and more recent results, definitely indicate that the formulations proposed by Luk'yanets and co-workers should be revised.

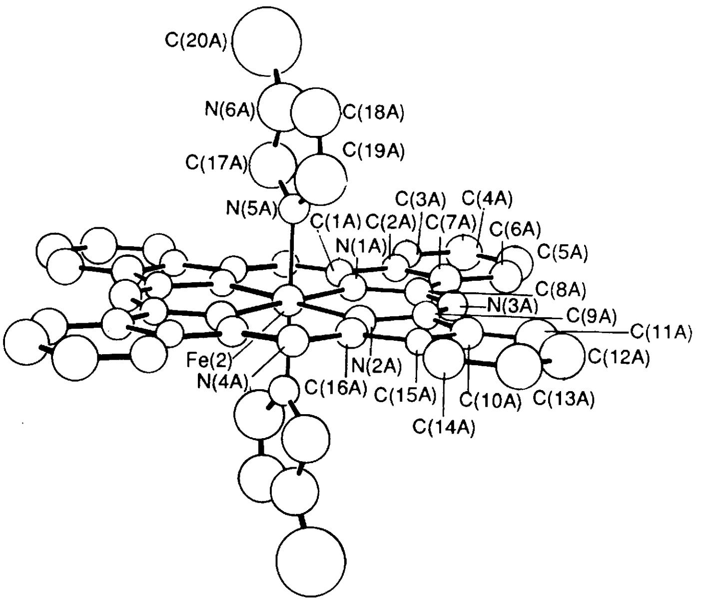

Fig. 5 ORTEP plot of [Fe(pc)(mim)$_2$] together with the labelling scheme

At the very beginning of our work on the interaction of [Fe(pc)] with O$_2$ we carried out a kinetic investigation of this process in concentrated (96%) H$_2$SO$_4$.[25] Examination of the visible spectrum of the reacting system at time intervals showed that the reaction was a two-step process. We associated the first step with the formation of a μ-peroxo species, [(pc)FeO$_2$Fe(pc)], as suggested by the apparent reversibility of the spectral changes {nitrogen bubbling of the oxygenated solution restored the initial spectrum of [Fe(pc)]} and in keeping with the μ-dioxo structure previously assigned to a dioxygen derivative of tetrasulphophthalocyaninatoiron(II) in water solution.[26] In a later kinetic work, carried out in dmso,[1c] we showed that the reaction of [Fe(pc)] with O$_2$ leads to the μ-oxo species [{Fe(pc)}$_2$O], which, being insoluble, eventually separates as a solid material from the reaction medium. Emphasis was given by Collamati[20c] to the different formulations of our proposed oxygen-containing species in H$_2$SO$_4$ and in dmso. Indeed, fairly recently, we could definitely establish that the species [{Fe(pc)}$_2$O] [μ-Oxo(2)] is also obtained from concentrated H$_2$SO$_4$, containing dissolved [Fe(pc)], by bubbling dioxygen under controlled experimental conditions.[1g] On this basis, our previous kinetic data in H$_2$SO$_4$[25] were re-examined and found to be also consistent with the sequence of reactions (1)–(5),

$$[\mathrm{Fe(pc)X_2}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(pc)X}] + \mathrm{X} \qquad (1)$$

$$[\mathrm{Fe(pc)X}] + \mathrm{O_2} \xrightarrow{k_2} [\mathrm{Fe(pc)X(O_2)}] \qquad (2)$$

$$[\mathrm{Fe(pc)X(O_2)}] \xrightarrow[+[\mathrm{Fe(pc)X_2}]]{\text{fast}} 2[\mathrm{Fe(pc)X(O)}] \qquad (3)$$

$$[\mathrm{Fe(pc)X(O)}] + [\mathrm{Fe(pc)X_2}] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{X(pc)FeOFe(pc)X}] \qquad (4)$$

$$[\mathrm{Fe(pc)X(O)}] + \mathrm{R} \xrightarrow[+\mathrm{X}]{k_R} [\mathrm{Fe(pc)X_2}] + \mathrm{RO} \qquad (5)$$

where [{Fe(pc)}$_2$O] is the final key species formed, as occurs in dmso[1c] (X = axial ligand probably HSO$_4^-$, R = unknown reducing impurity).

Table 5 Comparison of structural parameters of $[\{Fe(pc)(mim)\}_2O]$ and $[Fe(pc)(mim)_2]$ with related complexes

Complex	M–O (Å)	M–N_e (Å)	M–N_a (Å)	M–N_4 (Å)[a]	M–O–M (°)	Ref.
$[\{Fe(pc)(mim)\}_2O]$ (in **1**)	1.749(1)	1.92(3)	2.039(7)	0.02	175.1	This work
$[\{Fe(pc)(mim)\}_2C]$ (in **2**)	1.69[b]	1.95(3)	2.102	0.0	178(1)[c]	6
$[\{Mn(pc)(py)\}_2O]$	1.71	1.97	2.15	0.02	178	5
$[\{Fe(pc)Br\}_2N]$	1.639(2)[d]	1.945(6)	2.495(3)[e]	0.0	180[f]	14
$[\{Fe(tpp)\}_2O]$	1.763	2.087(5)		0.50	174.5	15
$[\{Fe(C_{22}H_{22}N_4)\}_2O]$	1.792(1)	2.054(2)		0.698	142.7(1)	16
$[\{Fe(salen)\}_2O]$	1.82	2.10(2)		0.56	139	17
$[Fe(pc)(mim)_2]$ (in **1**)		1.940(15)	1.946(7)	0.0		This work
(in **2**)		1.932(19)	2.012	0.0		6
$[Fe(pc)(4Me\text{-}py)_2]$		1.934(3)	2.040(3)	0.0		8

[a] Distance of M from the centre of the N_4-macrocyclic system. [b] Fe–C. [c] Fe–C–Fe. [d] Fe–N. [e] Fe–Br. [f] Fe–N–Fe.

Under steady-state conditions for both [Fe(pc)X] and

$$-\frac{d[Fe(pc)X_2]}{dt} = \frac{4k_1k_2k_3[Fe(pc)X_2]^2[O_2]}{[k_{-1}[X] + k_2[O_2]]\{k_3[Fe(pc)X_2] + k_R[R]\}} - \frac{2k_{-3}k_R[X(pc)FeOFe(pc)X][R]}{k_3[Fe(pc)X_2] + k_R[R]} \qquad (6)$$

[Fe(pc)X(O)] equation (6) is obtained. If $k_R[R] \ll k_3$ $[Fe(pc)X_2]$, equation (6) reduces to (7). Apart from the coefficient 4 instead of 2, equation (7) is equivalent to equation (7) of ref. 25.

$$\frac{d[Fe(pc)X_2]}{dt} = -\frac{4k_1k_2[Fe(pc)X_2][O_2]}{k_{-1}[X] + k_2[O_2]} \qquad (7)$$

On the other hand, if after a preliminary oxygenation the concentration of dioxygen is brought to zero, equation (6) becomes (8), *i.e.* the spectrum slowly reverts to that of $[Fe(pc)X_2]$ as if the reaction were reversible.

$$\frac{d[Fe(pc)X_2]}{dt} = \frac{2k_{-3}k_R[X(pc)FeOFe(pc)X][R]}{k_3[Fe(pc)X_2]} > 0 \qquad (8)$$

The present reinterpretation of the kinetic results in concentrated H_2SO_4 is also in better agreement with the gas-volumetric measurements carried out in this medium and reported in ref. 25. Under 1 atm (101 325 Pa) pressure of O_2 and 20 °C an O_2 : Fe(pc) mole ratio of 0.60 was measured at the end of the second irreversible step. If it is assumed that the dioxygen-dependent term of the rate equation referring to the second decomposition step [equation (1) of ref. 25] involves the consumption of 1 mol of O_2 per mol of μ-oxo compound, the above ratio can be calculated as 0.59, in excellent agreement with experiment.

Acknowledgements

G. R. is grateful to the Chemistry Department, Florida State University, Tallahassee, for kind hospitality. We thank Mr. S. Alessandrini (ITSE, CNR) for technical assistance. C. E. and F. M. acknowledge financial support by the Minestero della Pubblica Istruzione (60 and 40%).

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Received 31*st July* 1990; *Paper* 0/03497E