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Interaction of (Phthalocyaninato)iron(II) with Molecular Oxygen: Synthesis and Characterization of Two Different Crystalline Forms of (μ-Oxo)bis((phthalocyaninato)iron(III))

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The interaction of (phthalocyaninato)iron(II) with molecular oxygen leads to the formation of two different crystalline forms of a dimeric μ-oxo species containing an Fe-O-Fe system. Infrared and visible (reflectance and solution) spectra, X-ray powder patterns, magnetic measurements, and chemical behavior suggest that the two crystalline forms differ in the Fe-O-Fe bond angles as well as in the relative arrangement of the two phthalocyanine subunits within the dimeric molecule, ultimately resulting in different crystal lattice arrangements. These two μ-oxo forms appear to be the first well-characterized Fe(III) complexes derived from the phthalocyanine molecule. The redox behavior of the Fe(II) and Fe(III) derivatives of phthalocyanine is discussed in terms of the donor basicity of the axially ligated solvent molecules and of the π-bonding properties of the phthalocyanine ring.

Introduction

The interaction of molecular oxygen with the bivalent first-row transition metal ion phthalocyanines of formula $C_{32}H_{16}N_8M$ (M = Cr^{II},[2] Mn^{II},[2a,3] Fe^{II},[4] Co^{II}[5]) (Figure 1a) and their water-soluble tetrasulfonate analogues of formula $(SO_3^-)_4C_{32}H_{12}N_8M$ (M = Mn^{II},[6] Fe^{II},[7] Co^{II}[8]) (Figure 1b) has attracted a great deal of interest owing to the porphyrin-like structure of these molecules. Often, however, some difficulty has been encountered in the exact formulation of the resulting oxygen-containing species, studied either in the solid state or in solution. Examination of the literature indicates that considerable additional chemical and physical work is required for the unambiguous identification of the oxygenated or oxidized species, since their elemental analyses are often inadequate to solve the problem, whereas X-ray crystallographic work can only rarely be carried out because of the difficulty in obtaining suitable single crystals.

Iron(II) phthalocyanine compounds are an important example of this general situation. Iron(II) tetrasulfophthalocyanine (Figure 1b, M = Fe) was reported by Weber and Bush[7a] to act as a reversible carrier of molecular oxygen in the solid state and to be oxidized in aqueous solution. In contrast with these results, Fallab et al.[7b] described iron(II) tetrasulfophthalocyanine as a reversible dioxygen carrier in H_2O. The interaction of this complex with O_2 was more recently reexamined by McLendon and Martell,[7c] who concluded that iron(II) tetrasulfophthalocyanine is irreversibly oxidized by air and that an oxygenated species is not formed, in substantial agreement with the conclusions of Weber and Bush.[7a]

In 1969 Dale[9] reported that solutions of iron(II) phthalocyanine (Figure 1a, M = Fe; hereafter abbreviated as FePc) in dimethyl sulfoxide (Me_2SO) were unstable in contact with air, producing a precipitate that was not investigated further. Later Jones and Twigg[10] observed that 10^{-5} M solutions of FePc were unstable in air or in the presence of pure oxygen. A few years ago we undertook a systematic investigation of the interaction of FePc with dioxygen[4a] and identified the conditions for the reversible interaction between the two species in concentrated H_2SO_4 (96%).[4b] In a short report we have recently described the synthesis and characterization of a solid μ-oxo dimer found by the interaction of FePc with O_2 in dimethylformamide (DMF) and in other solvents.[4c] We present here a complete study of this solid dimer, isolated in two different crystalline forms.

Experimental Section

(Phthalocyaninato)iron(II). The purity of this complex (Eastman Kodak Co.) was checked by elemental analyses; the experimental C, H, and N percentages were usually slightly lower than the calculated values (C about 1%). Oxygen content was found to be between 0.5 and 1.0%. Except for special purposes, the compound was used without further purification. When accurate characterization of our newly synthesized products required a highly purified FePc, the starting material was repeatedly sublimed under vacuum (400 °C, 10^{-2}–10^{-3} mm) before use and its magnetic moment at room temperature was compared to that reported in the literature ($\mu = 3.87\ \mu_B$).[11] Both the commercial and the sublimed FePc samples exhibited the β-crystalline modification (Figure 2A).

(Phthalocyaninato)manganese(II), [MnPc]. This complex was prepared from phthalodinitrile and metallic manganese;[12] it was purified by sublimation under vacuum (400 °C, 10^{-2}–10^{-3} mm).

(μ-Oxo)bis((pyridine)(phthalocyaninato)manganese(III)), $[pyMnPc]_2O$. This compound was prepared according to the literature.[13] Elimination of pyridine from $[pyMnPc]_2O$ to give (μ-oxo)bis((phthalocyaninato)manganese(III)), $[MnPc]_2O$, was obtained by

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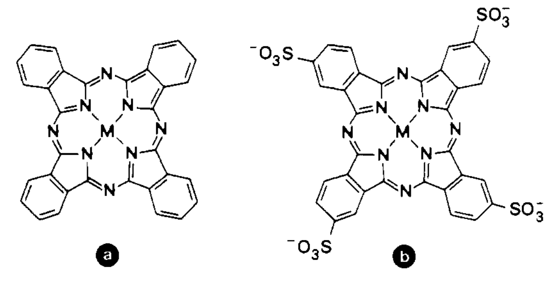

Figure 1.

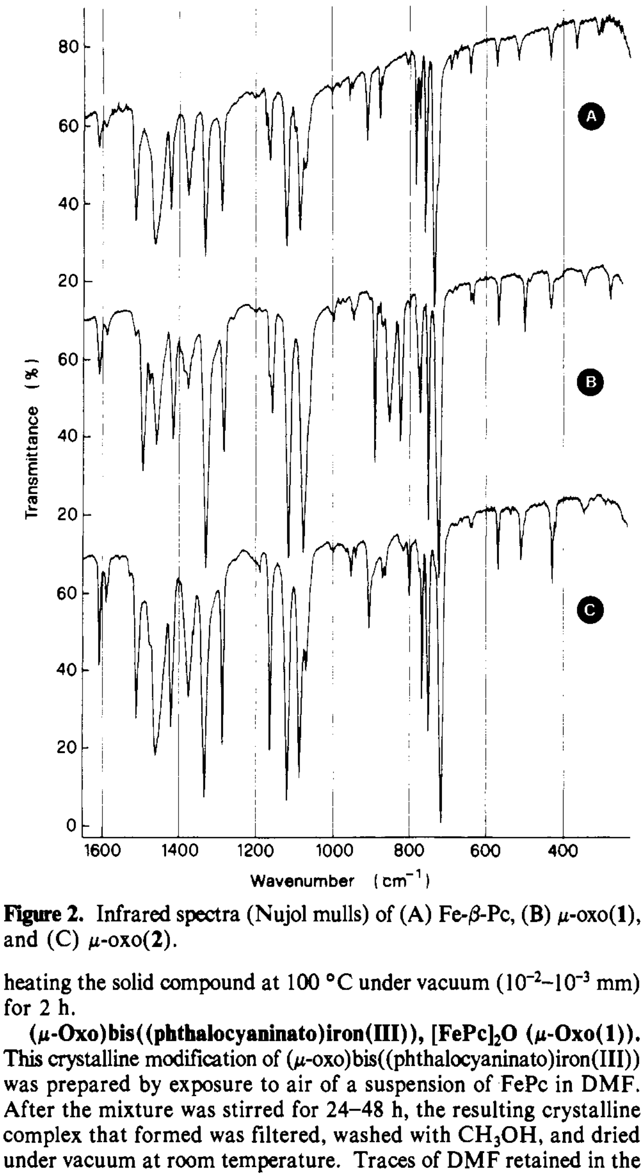

Figure 2. Infrared spectra (Nujol mulls) of (A) Fe-β-Pc, (B) μ-oxo(**1**), and (C) μ-oxo(**2**).

heating the solid compound at 100 °C under vacuum (10^{-2}–10^{-3} mm) for 2 h.

(μ-Oxo)bis((phthalocyaninato)iron(III)), [FePc]$_2$O (μ-Oxo(1)). This crystalline modification of (μ-oxo)bis((phthalocyaninato)iron(III)) was prepared by exposure to air of a suspension of FePc in DMF. After the mixture was stirred for 24–48 h, the resulting crystalline complex that formed was filtered, washed with CH_3OH, and dried under vacuum at room temperature. Traces of DMF retained in the crystal lattice of μ-oxo(**1**) can be eliminated by heating under vacuum (10^{-2}–10^{-3} mm) at 150–160 °C for 2–3 h.

The same species is obtained when DMF is replaced by dimethylacetamide (DMA), tetrahydrofuran (THF), or dioxane. When DMA was used, however, heating under vacuum (10^{-2}–10^{-3} mm, 140–150 °C) was required to eliminate small amounts of occluded solvent. No residual traces of solvent were found after μ-oxo(**1**), obtained from THF or dioxane, was kept for 1–2 h under vacuum (10^{-2}–10^{-3} mm) at room temperature.

In addition to the spectral variations observed in the 900–800-cm^{-1} region (vide infra), other minor IR spectral changes accompany the formation of μ-oxo(**1**) from Fe-β-Pc: (a) new weak bands appear at 1685 (in samples from DMF), 635, and 280 cm^{-1}, (b) some absorptions shift toward lower frequencies by 5–20 cm^{-1}, and (c) the bands characteristic of the β-crystalline modification of FePc (1173, 877, and 780 cm^{-1})[18] disappear. The weak band found at 1685 cm^{-1} in samples obtained from DMF indicates the presence of traces of this solvent (uncoordinated), which can be eliminated as described above. A similar weak solvent band, at 1650 cm^{-1}, is found in the IR spectrum of μ-oxo(**1**) prepared from DMA; no absorptions attributed to the solvent have been found in the IR spectrum of μ-oxo(**1**) obtained from THF or dioxane.

Elemental analyses (C, H, and N) of μ-oxo(**1**) were usually in good agreement with the expected values (Anal. Calcd: C, 66.68; H, 2.80; N, 19.45. Found: C, 66.32; H, 2.92; N, 19.01). However, the oxygen content (2.0–2.5%) was always found to be higher than the calculated value (1.4%). It should be noted that even pure FePc, accurately purified by sublimation, often gave non-zero values for oxygen (usually 0.5–1.0%). Accordingly, elemental analyses alone were not considered reliable in determining the exact iron-to-oxygen ratio and gas-volumetric or other measurements were used. The quantitative uptake of dioxygen by FePc suspended in DMF was followed by performing the experiments in a gas absorption apparatus under an atmosphere of pure O_2, at room temperature and normal pressure. The samples ranged between 0.6 and 3.0 g of FePc and the volumes of gas absorbed varied from ca. 6 to 30 mL, measured with an error of ±0.01 mL (10-mL buret) or ±0.1 mL (50-mL buret). In about 20 experiments the volume of gas absorbed was always between 90 and 100% of the value expected for a 2:1 iron-to-oxygen ratio.

μ-Oxo(**1**) is obtained as a deep blue microcrystalline powder. It is stable to air and can be heated up to ca. 300 °C under vacuum (10^{-2}–10^{-3} mm) without appreciable decomposition. Higher temperatures (330–340 °C) produce partial degradation of the compound and the formation of white sublimed crystals consisting mainly of phthalimide. A thermogravimetric analysis, carried out at a heating rate of 5 °C/min under N_2, revealed no weight loss below 300 °C; the deep blue residual material could be recovered practically unchanged and was shown to be the μ-oxo(**1**) compound by its substantially unmodified IR spectrum.

μ-Oxo(**1**) is completely insoluble in nondonor solvents and also in weakly donating solvents such as DMF or Me_2SO. It dissolves sparingly in pyridine, in which it changes to the bisadduct of FePc, i.e. FePc(py)$_2$. In the presence of volatile N-bases (1-propylamine, 1-*n*-butylamine) μ-oxo(**1**) dissolves in Me_2SO and in chloronaphthalene; evaporation of the N-bases produces a precipitate of either deep blue crystals of μ-oxo(**1**) or, under certain conditions, of μ-oxo(**2**) (see below). Slow evaporation of the volatile N-bases may also result in the formation of bisadducts, e.g. FePc(N-base)$_2$.

Preparation of crystals of μ-oxo(**1**) suitable for an X-ray investigation was attempted from *n*-butylamine; however, the crystals obtained were too small. Furthermore, these crystals probably contain interstitial molecules of solvent, which are readily lost in air, with consequent degradation of the crystalline structure.[14]

(μ-Oxo)bis((phthalocyaninato)iron(III)), [PcFe]$_2$O (μ-Oxo(2)). This compound can be obtained as follows: μ-oxo(**1**) (400 mg) was suspended in chloronaphthalene (ca. 30 mL), to which 2-propylamine (1.5 mL) was added. the solution was rapidly filtered and continuously stirred until all the N-base completely evaporated. The solid that precipitated was washed with methanol and dried under vacuum at room temperature for 1–2 h. Elemental analyses indicated no change in the composition compared to that of the starting material. (Anal. Calcd: C, 66.68; H, 2.80; N, 19.45; O, 1.39. Found: C, 66.43; H, 2.80; N, 19.15; O, 2.15). The compound, however, had different X-ray powder pattern, infrared spectrum, and magnetic properties (vide infra). μ-Oxo(**2**) can also be obtained directly by bubbling O_2 into a solution of FePc in concentrated H_2SO_4 (96%) for the time required for the oxygenation step (ca. 20 min).[4b] Precipitation of μ-oxo(**2**) takes place by carefully pouring the H_2SO_4 solution into cold (5 °C) air-saturated water. However, although this method gives μ-oxo(**2**) reproducibly, the μ-oxo(**1**) $\rightarrow$ μ-oxo(**2**) conversion in chloronaphthalene is to be preferred, since the product precipitated from H_2SO_4 must be repeatedly washed and filtered to remove all traces of acid.

The X-ray powder spectrum of μ-oxo(**2**) is identical with that previously reported for an α-form of FePc (Fe-αII-Pc),[2e] prepared by a very similar procedure.[15] Since the previously prepared sample of Fe-αII-Pc was still available in our laboratory, its X-ray powder

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Table I. Infrared, Magnetic, and X-ray Data on M–O–M Species[a]

compd	ν_3 in the 900–800-cm^{-1} region	μ_{eff}(room temp), μ_B	X-ray data		ref
			M–O–M, deg	M–Ct, Å	
$[Cl_5Ru\text{-}O\text{-}RuCl_5]^{4-}$	888		180		19–22
$[Cl_5Re\text{-}O\text{-}ReCl_5]^{4-}$	855		180		19–21, 23
$[Br_5Ru\text{-}O\text{-}RuBr_5]^{4-}$	860		supposed linear		19–21
$[Cl_5Os\text{-}O\text{-}OsCl_5]^{4-}$	848		supposed linear		19–21
$[MoO_2(C_2O_4)H_2O]_2O$	860		supposed linear		24
$[Fe(HEDTA)]_2O^{2-}$	868 (sh), 838 (s)	1.92	165	0.36	27, 28
$[Fe(EDTA)]_2O^{2-}$	868 (sh), 851 (s)	1.90			27
dimeric haemin	903				36
$[Fe(salen)]_2O\cdot CH_2Cl_2$		1.99	142.2	0.56	25, 26
$[Fe(salen)]_2O\cdot 2py$		1.90	139	0.56	29, 30
$[Fe(TPP)]_2O$	892 (m), 878 (s), 885 (m), 870 (s)	1.8–1.9	174.5	0.50	31–33
$[Fe(TH\text{-}dioxo\text{-}TBTNCTD)]_2O$			157 (1)	0.64	34
$[Fe(C_{22}H_{22}N_4)]_2O\cdot CH_3CN$		1.96	142.8	0.70	35
$[py\cdot PcMn]_2O$	not obsd	diamag (?)	178	0	3a,b
μ-oxo(1)	854 (s)–820 (s)	2.10	departure from 180		this paper
μ-oxo(2)	not obsd	1.4–1.6	close to 180 (?)	close to 0 (?)	this paper

[a] Abbreviations: sh, shoulder; m, medium; s, strong.

spectrum was determined and found to be identical with that previously published[2e] and also with that of μ-oxo(**2**). Also, the visible absorption spectrum of the old sample in concentrated H_2SO_4 (96%) was identical with that of μ-oxo(**2**) in the same medium. The above data indicate unequivocally that the species reported to be an α-polymorph of FePc is instead its corresponding oxidized species, i.e. μ-oxo(**2**). This definitely establishes that FePc cannot be obtained in its α-form by precipitation from air-saturated H_2SO_4.[15]

Formation of μ-oxo(**2**) has been observed also when FePc is dissolved in anhydrous Me_2SO ([FePc] = 10^{-4} or higher) and O_2 is bubbled into the solution. In several experiments of this kind μ-oxo(**2**) precipitated when the volume of solvent was ca. 200 mL (amount of μ-oxo(**2**) formed: 15–20 mg). In one experiment with 400 mg of FePc dissolved in ca. 3 L of Me_2SO at 35 °C, the precipitate formed was essentially μ-oxo(**1**). The solvent recovered from this experiment was then used to dissolve an additional sample of FePc (400 mg). The solution was filtered under N_2, and O_2 was bubbled in for 2 h. The solid, which was separated, washed with CH_3OH, and brought to constant weight under vacuum for 1–2 h, was identified as μ-oxo(**2**). This experiment demonstrates that the formation of either μ-oxo(**1**) or μ-oxo(**2**) in Me_2SO depends upon subtle changes in the experimental conditions used and it is difficult to direct the oxidation process toward the formation of either species.

Preparation of μ-Oxo(1) and μ-Oxo(2) Containing ^{18}O. Isotopically enriched O_2 was purchased from Prochem (London) in 100-mL break-seal flasks. Dioxygen containing 70% or 99% of ^{18}O was used. The following procedure was used for the preparation of μ-oxo(**1**) from FePc and enriched O_2: the 100-mL break-seal flask containing ^{18}O was sealed to a vacuum line having on its left-hand side a bent small arm containing a Teflon-coated iron bar and on its right-hand side a vacuum manifold. In a 100-mL flask connected to the vacuum manifold were introduced first 25 mL of DMF deoxygenated with N_2 and then 500 mg of FePc. The resulting suspension was evacuated for 15–20 min with stirring. The vacuum pump was then disconnected, the capillary tube of the flask containing enriched dioxygen was broken, and the contact between the gas and the suspension was maintained for 48 h (the gas pressure in the reaction vessel was calculated to be ca. 380 mm). The flask was detached from the vacuum line, and the suspended solid was filtered, washed with CH_3OH, and dried under vacuum (10^{-2}–10^{-3} mm) at 150–160 °C.

Oxygen-18-enriched samples of μ-oxo(**2**) were prepared from the corresponding samples of μ-oxo(**1**) by dissolving the latter in chloronaphthalene and 2-propylamine, as described above.

Physical Measurements. IR spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 621 spectrophotometer, with use of Nujol mulls supported between NaCl or CsI windows. Visible transmission spectra of solutions were obtained with a Cary 14 spectrophotometer; diffuse-reflectance spectra were recorded with a Beckman DK 2 instrument equipped with a reflectance accessory. X-ray powder photographs were obtained with a Debye powder camera (114.6 mm in diameter) with Cr Kα radiation (λ = 2.2909 Å). Magnetic susceptibility measurements were carried out on a Gouy balance, having a magnetic field of ca. 7000 G, with a $NiCl_2$ solution as calibrant.[16] The variation of the magnetic moment with the temperature (300–80 K) was measured with an apparatus described previously.[17] Thermogravimetric analyses were performed with a Dupont 950 thermogravimetric analyzer under a stream of N_2 (0.5 L min^{-1}).

Results and Discussion

We have recently given a brief description[4c] of a solid crystalline species formed by the interaction of molecular oxygen with FePc suspended in DMF or in other solvents. On the basis of chemical and physical evidence, the compound was formulated as a dimeric μ-oxo complex, $[FePc]_2O$, containing a bridging iron–oxygen–iron moiety. The complex showed antiferromagnetic behavior, and its IR spectrum had characteristic ν(Fe–O–Fe) absorptions in the 900–800-cm^{-1} region. Two distinct crystalline modifications of such an oligomer are now known and are described here: the species previously reported, indicated as μ-oxo(**1**), and a second form indicated as μ-oxo(**2**), easily distinguishable from the former by its X-ray powder pattern.

The μ-Oxo(1) Crystalline Isomer. The formulation of μ-oxo(**1**) as an oxo-bridged dimer is consistent with all experimental evidence available for this compound. Especially significant are the gas volumetric oxidation experiments described in the Experimental Section, the infrared spectral studies including the isotopic labeling, and the magnetic measurements.

(a) Infrared Spectra. The most significant IR spectral change accompanying the formation of μ-oxo(**1**) from Fe-β-Pc is the appearance of two new strong absorptions at 852 and 824 cm^{-1} (Figure 2A,B) in a region that is uncluttered by the phthalocyanine absorptions.[18] It is well-known that the antisymmetric stretching mode (ν_3) of a linear or quasi-linear M–O–M system (M = Ru, Re, Os, Mo) usually occurs in the 900–800-cm^{-1} region (Table I),[19-21] and an absorption in this region has been observed for a number of Fe–O–Fe systems (Table I). Thus, the 852- and 824-cm^{-1} absorptions of μ-

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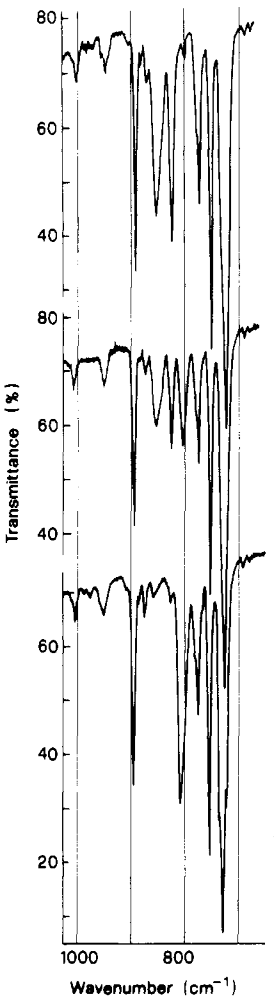

Figure 3. Infrared spectra (Nujol mulls) of μ-oxo(**1**): (A) ^{16}O, (B) 70% ^{18}O, (C) 99% ^{18}O.

oxo(**1**) indicate the existence of an Fe–O–Fe bond system in this compound. This was further supported by previously reported results[4c] on the isotopic substitution of ^{16}O with ^{18}O by using isotopically enriched O_2 (70% in ^{18}O). In the partly ^{18}O-substituted compound, the intensity of both the 852- and the 824-cm^{-1} bands was markedly reduced, while a new absorption of medium intensity appeared at 803 cm^{-1} and all other features of the spectrum remained unchanged (Figure 3A,B). Definitive results have now been obtained by labeling with O_2 99% enriched in ^{18}O. In these experiments, both the 852- and the 824-cm^{-1} bands completely disappeared, while a new strong absorption appeared in the lower energy region, with its maximum centered at 806 cm^{-1} (Figure 3C).

These results clearly show that both the 852- and 824-cm^{-1} bands must be associated with the antisymmetric Fe–O–Fe stretching vibration (ν_3) (the decrease in intensity of the 824-cm^{-1} band had previously been thought[4c] to arise from the fact that this band lies partly on the tail of the 852-cm^{-1} band). The observed isotopic shifts, taken as the difference between 838 cm^{-1} (average of the two components of ν_3 in unlabeled μ-oxo(**1**)) and 806 cm^{-1} (value in ^{18}O-substituted sample) is then calculated to be 32 cm^{-1}. This value agrees well with those found for dimeric haemin[36] (45 cm^{-1}) and for other M–X–M systems (M being a heavy transition metal ion), i.e. 45 cm^{-1} for the complex $K_4[RuOCl_{10}]\cdot H_2O$[26] (Ru–O–Ru bridge) and 37 cm^{-1} for $[Os_2N(NH_3)_8Br_2]Br_3$ (Os–N–Os bridge).[20] The occurrence in the unlabeled μ-oxo(**1**) of two conjugated bands associated with ν_3 most likely arises from Fermi resonance[37] of this vibration with the second overtone of the 433-cm^{-1} band assigned to a symmetry-adapted out-of-plane vibration of the phthalocyanine ring. The shift undergone by ν_3 as a result of ^{18}O isotopic substitution breaks down the resonance, so that only one band appears at 806 cm^{-1} in the labeled compound. In the low-energy region below 600 cm^{-1}, no appreciable shifts are observed in going from μ-oxo(**1**) to its corresponding ^{18}O-enriched sample. Even the weak band at 280 cm^{-1}, absent in Fe-β-Pc, remains unshifted; hence, it cannot be assigned as the symmetric counterpart (ν_1) of the Fe–O–Fe mode. In a linear system ν_1 should be IR inactive, but it might be activated by the loss of the center of symmetry due to a slightly bent Fe–O–Fe moiety or even by crystal effects. We are aware of only one similar case, i.e. $[TPPFe]_2O$,[38] in which the symmetric stretching mode ν_1 has been identified (363 cm^{-1}) by Raman spectroscopy.

The complete disappearance of the 852- and 824-cm^{-1} bands and the simultaneous appearance of the 806-cm^{-1} band upon ^{18}O substitution also points out that the Fe–^{16}O–Fe system must transform into Fe–^{18}O–Fe by a mechanism involving oxygen atoms provided exclusively by dioxygen. Thus, the solvent or any impurity present in the solvent may be ruled out as the source of bridging oxygen atoms, a conclusion which is especially important because most gas volumetric measurements, as well as isotopic substitution reactions, were carried out in oxygen-containing solvents such as DMF.

In an evaluation of the evidence just discussed, it should be kept in mind that the compound we formulate as μ-oxo(**1**) in the present paper has been previously assigned,[39] on the basis of elemental analyses alone, a μ-dioxo structure of the type Fe–O_2–Fe. Species containing Fe–O_2–Fe bridges are rare in the literature. We are aware of (a) a synthetic compound of formula $[(SCN)_2(bt)_2Fe–O_2–Fe(bt)_2(NCS)_2]$ (bt = 2,2′-bi-2-thiazoline),[40] which has yet to receive confirmation, (b) the compounds of formula (P)Fe–O_2–Fe(P) (P = a porphyrin dianion),[41] which are stable only at very low temperatures and change to the corresponding μ-oxo compounds when brought to room temperature, and (c) oxyhemerythrin, which has been studied by Raman spectra[42] and by isotopic O_2 substitution (58% in ^{18}O).

For a Fe–O_2–Fe dioxo species, three IR absorptions should appear[42] in the 860–800-cm^{-1} region upon isotopic labeling with O_2 70% enriched in ^{18}O: one at highest energy due to –^{16}O–^{16}O–, one due to –^{16}O–^{18}O– (–^{18}O–^{16}O–) (medium en-

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Table II. Magnetic Susceptibility Data on μ-oxo(**1**) and μ-oxo(**2**)[a]

μ-oxo(**1**)			μ-oxo(**2**)		
T, K	$10^6\chi_{\mathrm{Fe}}$	μ_{eff}, μ_{B}[b]	T, K	$10^6\chi_{\mathrm{Fe}}$	μ_{eff}, μ_{B}[b]
297.5	1834	2.09	292	919	1.47
279.5	1909	2.06	280	551	1.11
258.5	1909	1.99	260	459	0.98
244.5	1942	1.95	226.5	367	0.81
227.5	1845	1.83	211	367	0.78
210	1909	1.79	195	184	0.42
194	1942	1.73	179.5	91	0.32
177	1942	1.65	142	92	0.32
160.5	1942	1.57	123	183	0.42
140	1942	1.47			
123.5	1877	1.36			
101.5	1845	1.22			

[a] The diamagnetic correction per phthalocyanine molecule was assumed to be 4.35×10^{-6} cgsu. The magnetic moments are calculated per iron. [b] Calculated from the formula $\mu_{\mathrm{eff}} = 2.84(\chi_{\mathrm{a}}T)^{1/2}$.

ergy absorption expected to appear at ca. 820 $\mathrm{cm^{-1}}$), and one arising from $-^{18}\mathrm{O}-^{18}\mathrm{O}-$ (lowest energy absorption). These absorptions should furthermore appear with area ratios $(1-\alpha)^2:2\alpha(1-\alpha):\alpha^2$ (where α is the atom fraction of $^{18}\mathrm{O}$), i.e. 0.09:0.42:0.49. For the labeled sample the higher energy 852- and 824-$\mathrm{cm^{-1}}$ bands should be extremely weak, while an intermediate absorption of area comparable to that of the lowest energy band at 803 $\mathrm{cm^{-1}}$ should appear at ca. 820 $\mathrm{cm^{-1}}$. These expected features are in obvious contrast with the observed spectral pattern. In conclusion, the hypothesis of a dioxo structure[39] is not only in striking contrast with our gas volumetric measurements but is also totally incompatible with IR spectral observations and the chemical behavior discussed below.

(b) Magnetic Susceptibility Measurements. The magnetic behavior of solid μ-oxo(**1**) was investigated in the temperature range 300–100 K; the data are summarized in Table II. μ-Oxo(**1**) exhibits a room-temperature magnetic moment of 2.10 μ_{B}, which is markedly quenched by lowering the temperature. This is indicative of antiferromagnetic interactions between the iron atoms of the dimer. The magnetic behavior of μ-oxo(**1**) is thus very similar to that of other $\mathrm{Fe^{III}}$ μ-oxo dimers.[26,27,30] For some of these dimers, X-ray studies (Table I) have shown the Fe–O–Fe moieties to be nonlinear, with the Fe atoms located out of the planes of the respective tetracoordinating ligands. Similar features might be present in the structure of μ-oxo(**1**), although the large variations in the Fe–O–Fe angles and Fe–O distances observed in other Fe–μ-oxo species (Table I) show that departure from linearity of the Fe–O–Fe system as well as out-of-plane displacement of the Fe atoms from the phthalocyanine ring cannot be easily correlated to either IR or magnetic data. An X-ray investigation has been undertaken on single crystals of μ-oxo(**1**) obtained from *n*-butylamine.[14] Data so far available are as follows: $a = 19.171$ (9), $b = 44.907$ (21), $c = 25.668$ (5) Å; $\alpha = \beta = \gamma = 90°$; space group C_{cc2}. Attempts are in progress to isolate larger crystals suitable for a complete solution of the structure, which is made difficult by the larger cell dimensions and the many independent atoms present in the asymmetric unit.

The μ-Oxo(2) Crystalline Isomer. The formulation of this stable solid species is based on analytical, spectroscopic, and chemical evidence. First, the analytical composition is identical with that of μ-oxo(**1**). Second, the visible reflectance spectra of powdered samples of μ-oxo(**1**) and μ-oxo(**2**) (Figure 4) are practically superimposable, consisting of an intense maximum at 695 nm and a lower intensity absorption at 365 nm. This absorption pattern is similar to, but not identical with, that of solid Fe-β-Pc. The two μ-oxo species give also the same spectrum when dissolved in 96% H_2SO_4; this spectrum coincides with that obtained when FePc is allowed to react with O_2 for the time required for the first reversible oxygenation process.[4a,b] As previously reported,[4b] this first oxygenation in H_2SO_4 is followed by the irreversible oxidation of the phthalocyanine molecule;[4b] solutions of μ-oxo(**1**) and μ-oxo(**2**) in this medium follow the same behavior: i.e., both are irreversibly oxidized by bubbling in O_2. Conversely, the spectrum of FePc is restored by bubbling in N_2 as expected.[4b]

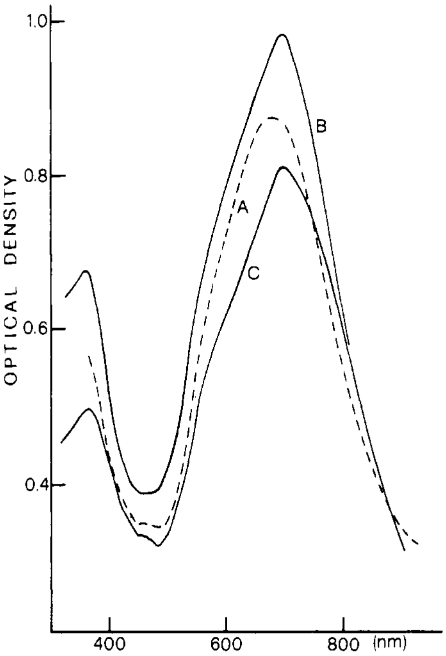
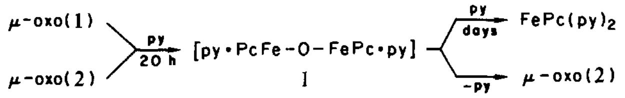


Figure 4. Visible (diffuse-reflectance) spectra of (A) Fe-β-Pc, (B) μ-oxo(**1**), and (C) μ-oxo(**2**).

The close relationship between μ-oxo(**1**) and μ-oxo(**2**) is further shown by their behavior toward pyridine. Both isomers give the same spectrum when dissolved in pyridine, with the most intense visible absorption located at 620 nm; this spectrum changes gradually with time, finally giving the typical absorption pattern of $\mathrm{FePc(py)_2}$.[9] Interaction with pyridine is also observed when solid μ-oxo(**1**) or μ-oxo(**2**) are exposed to vapors of this N-base. When μ-oxo(**1**) is left in air saturated with pyridine for several days, it changes to $\mathrm{FePc(py)_2}$ (identified by visible and infrared spectra and X-ray powder pattern). However, if contact with pyridine vapors is maintained for only 20 h, a well-defined new pyridine adduct, I, is formed. Exactly the same pyridine adduct I is produced under the same experimental conditions from μ-oxo(**2**). The visible spectrum of I in pyridine is identical with that obtained immediately after dissolution of either μ-oxo(**1**) or μ-oxo(**2**) in the same solvent and shows the same changes with time. This indicates that I still has a μ-oxo structure and may therefore be tentatively formulated as a bis(pyridine)adduct of the type [py·PcFe–O–FePc·py]. This formulation is further supported by the fact that I can be desolvated by heating under vacuum (10^{-2} mm, 100 °C) with loss of the two pyridine molecules. Thus, the species obtained, PcFe–O–FePc, is always μ-oxo(**2**). The overall process can be summarized as



A manganese analogue of I, i.e. $[\mathrm{py{\cdot}PcMn}]_2\mathrm{O}$, has been described elsewhere.[13] We prepared this compound by bubbling in O_2 through a pyridine solution of MnPc until the solvent had completely evaporated; the residual solid was then kept under a stream of O_2 for several hours at room temperature. The complex obtained gave the expected visible spectrum in pyridine solution[13] with a maximum at 620 nm characteristic of the μ-oxo species. When heated under vacuum (10^{-2} mm, 100 °C) for 2 h, [py·PcMn]$_2$O gives the corresponding μ-oxo compound, i.e. PcMn–O–MnPc. Comparison of the X-ray powder spectrum of this species with that of μ-oxo(**2**) shows that they are isomorphous, giving additional support to the structure assigned to μ-oxo(**2**).

The two isomers, μ-oxo(**1**) and μ-oxo(**2**), are easily interchangeable; μ-oxo(**1**) can be transformed into μ-oxo(**2**) in chloronaphthalene in the presence of 2-propylamine (see Experimental Section). Conversely, μ-oxo(**2**) may be changed in part to μ-oxo(**1**) by dissolving it in *n*-butylamine and then rapidly evaporating off the solvent. The ease of interconversion of the two forms by slightly varying the experimental conditions, together with the observation that under certain circumstances either form may separate in a rather unpredictable manner, suggests that the difference between the two forms arises from different internal frameworks within the same dimeric molecular structure.

The isomorphism of μ-oxo(**2**) with PcMn–O–MnPc, in which the Mn–O–Mn system is very nearly linear (Mn–O–Mn angle 178°,[3a] Table I), may reasonably be considered to indicate that a linear or quasi-linear Fe–O–Fe bond system is also present in μ-oxo(**2**), if it is assumed that elimination of pyridine leaves substantially unchanged the geometry of the Mn–O–Mn moiety of [py·PcMn]$_2$O. A linear geometry of the Fe–O–Fe bridge in μ-oxo(**2**), expected to favor π-bonding between the Fe and O atoms, would account for the significant magnetic exchange displayed by the two antiferromagnetically coupled iron atoms of the dimer (Table II).

The infrared spectrum of μ-oxo(**2**) shows slight differences from that of the parent Fe-β-Pc, with only a new weak band appearing at 801 cm^{-1} (Figure 2C). Isotopic labeling with O_2 containing either 70% or 99% ^{18}O does not cause appreciable shifts for any of the bands of μ-oxo(**2**), suggesting that the antisymmetric stretching frequency, ν_3, is not observed. This is surprising, for this band would be expected to be still IR active as the metal–oxygen–metal system becomes more closely linear.[43] It should be noted, however, that a similar absence of absorptions unequivocally attributable to the Mn–O–Mn antisymmetric vibration has been also reported for the closely related species of formula [L·PcMn]$_2$O (L = *N*-methylimidazole, 3-picoline, and piperidine),[3d] including [py·PcMn]$_2$O,[3b] and also for [PcMn]$_2$O.

Relative Stabilities of Fe(II) and Fe(III) Phthalocyanine Complexes. Iron phthalocyanine complexes are much more stable as Fe^{II} species than are the corresponding porphyrin analogues, and characterization of well-defined Fe^{III} derivatives has so far been generally unsuccessful. An exception are the species FePcX$_2$ (X = Cl, Br),[44] which, however, contain the phthalocyaninato radical anion Pc(1–). The compound FePcCl, prepared for the first time by Linstead et al. in concentrated HCl,[45] has been repeatedly investigated[46] with contrasting conclusions. First formulated as an Fe^{III} chloride species,[45] this compound was then proposed to be a hydrochloric acid derivative of FePc, i.e. FePc·HCl.[47] Later, the hypothesis was advanced[44] that it might be a mixture of Fe^{II} and Fe^{III} products, with composition depending upon the experimental conditions used for the preparation. More recently the earlier formulation of a Fe^{III} species[45] has again been given support by voltammetric studies in Me$_2$SO and in DMF solution.[46] Therefore, it appears that the μ-oxo species described in the present paper are among the first, if not unique, well-authenticated solid Fe^{III} derivatives of the phthalocyaninato dianion.[49]

It has been shown electrochemically[50] that the tendency of FePc to form Fe^{III} species can be strongly dependent upon the nature of the solvent and the supporting electrolyte used and that the following sequence of solvents can be given for the ability of FePc to give Fe^{III} compounds: DMF $\approx$ DMA $>$ Me$_2$SO $>$ py. We observed that the interaction of FePc with O_2, which also results in the formation of Fe^{III} species, depends on the nature of the solvent as well. In this respect, it is difficult to differentiate between DMF and Me$_2$SO because of the heterogeneity of the systems used and precipitation of the oxidized species. In fact, FePc suspended in either solvent is quantitatively converted into the corresponding μ-oxo species. In pyridine, no reaction at all has been observed, a fact which is in agreement with the highest redox potential found in this solvent.[50] The high redox potential in pyridine also explains why no reaction could be observed for FePc dissolved in Me$_2$SO containing an excess of pyridine or for the complex FePc(py)$_2$ dissolved in toluene. In the solvent sequence given above the stabilization of FePc and Fe^{II} species seems to increase with an increase of the σ-donor basicity of the axially ligated solvent. This is apparently allowed by a shift of the excess of electronic charge density from the Fe^{II} onto the phthalocyaninato ring through a π mechanism, thus evidencing the π-acceptor properties of the tetradentate planar chromophore.[50,51]

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Registry No. I, 86308-25-0; **1**, 74353-48-3; **1**, ^{18}O enriched, 86308-24-9; FePc, 132-16-1; MnPc, 14325-24-7; [py·PcMn]$_2$O, 39368-58-6.

Supplementary Material Available: Listings of X-ray powder and IR spectra for μ-oxo(**1**), μ-oxo(**2**), and their py adducts (4 pages). Ordering information is given on any current masthead page.

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