property whereas changes on O/S substitution are essentially constant.

The UV/visible spectra of **1** and **2** in MeCN solution are shown in Figure 4. Pertinent values of λ_{max} (nm) and ϵ_M (L mol^{-1} cm^{-1}) are 312 (sh) (3.6×10^3) and 622 (74) for **1** and 417 (5.4×10^3) and 900 (82) for **2**. The intense, high-energy absorptions are reasonably attributable to charge-transfer transitions and the weaker, low-energy absorptions to essentially metal-based d–d transitions. The major effect of O/S substitution is thus to shift all transitions to lower energy, a behavior also observed in VE(acen) and VE(salen) spectra.[15]

Acknowledgment. We thank the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this work and the Bloomington Academic Computing Service for a gift of computer time.

Registry No. **1**, 97689-51-5; **2**, 97689-53-7; VO(acac)$_2$, 3153-26-2.

Supplementary Material Available: Complete listings of atom coordinates, isotropic and anisotropic thermal parameters, interatomic distances and angles, and calculated and observed structure factors for $(NMe_4)Na[VO(edt)_2]\cdot 2EtOH$ and $(PPh_4)Na[VS(edt)_2]\cdot xEt_2O$ (50 pages). Ordering information is given on any current masthead page.

Notes

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(μ-Oxo)iron(III) Phthalocyanine. Electronic Structure of the Solid Form Obtained from a Dihydroxo-Iron(III) Precursor

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Heinrich Homborg,[*‡] and Winfried Kalz[‡]

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The chemistry of iron(III) porphyrins has proved to be of great interest over recent years, both in relation to the biological importance of the heme proteins and because of the large and varied behavior of such systems.[1] The chemistry of the closely related iron(III) phthalocyanines is poorly understood in comparison, partly because it appears that the stable oxidation state of iron phthalocyanines is +2 and partly because the method usually employed to obtain such complexes (the oxidation of Fe^{II}(Pc(2−)) under various conditions) often gives rise to a mixture of products.[2]

It has only been in the last few years that any of the products of oxidation of Fe^{II}(Pc(2−)) have been properly characterized, although as yet a crystal structure is available only on (PNP)[Fe^{III}(Pc(2−))$(CN)_2$].[3] Recently, Ercolani and co-workers[4] have shown that under suitable conditions the μ-oxo dimer $[Fe(Pc(2-))]_2O$ (I) can be isolated. An earlier μ-superoxo formulation for this complex, $[Fe(Pc(2-))O_2Fe(Pc(2-))]$ seems to be incorrect.[5] Ercolani et al.[4] reported that, depending on the exact reaction conditions used, two crystalline forms of I could be isolated, each displaying different IR spectral bands and magnetic susceptibilities. The published magnetic data for these forms of I, while suggestive of strong antiferromagnetic coupling between the two iron centers, offered no firm evidence as to the exact size of the coupling. The spin states of the iron centers were likewise not delineated.

Recently, we[6] have reported alternative syntheses of I based on the condensation of the dihydroxo iron(III) complex PNP[$Fe(OH)_2$(Pc(2−))]. The UV–visible and IR spectral data of the samples prepared by these methods correspond exactly to those reported by Ercolani et al. for their sample, μ-oxo I. Owing to the unusual reactivity toward molecules such as pyridine and PPh_3 displayed[7] by μ-oxo I, together with the observation[8] that a monomer such as Fe(Pc(2−))Cl has the relatively rare $S = {}^5/_2 - {}^3/_2$ admixed ground state, it seemed desirable to us to fully characterize the spin-state and electronic properties of $[Fe(Pc(2-))]_2O$.

While the present paper was being reviewed, a study of the Mössbauer spectroscopy of three samples of $[Fe(Pc(2-))]_2O$, prepared by the methods of Ercolani et al., has been reported.[9] There are some remarkable similarities to the results presented here, which is intriguing in view of the different methods of synthesis used. The authors do not report any ESR, magnetic or synthetic details on their samples, and this leads them into assignments of minor peaks with which we do not agree. However, this study and the present one both show the existence of only one form of $[Fe(Pc(2-))]_2O$, viz. μ-oxo I.

Experimental Section

Abbreviations: PNP = bis(triphenylphosphine)nitrogen(1+); Pc(2−) = phthalocyaninato dianion.

Synthesis. $[Fe(Pc(2-))]_2O$ was prepared and characterized as described previously.[6] This involved dissolving 0.57 g (0.5 mmol) of PNP[$Fe(OH)_2$(Pc(2−))] in dichloromethane, chloroform, or acetone. Within 1 day at room temperature a fine blue crystalline precipitate of $[Fe(Pc(2-))]_2O$ was quantitatively deposited from these solutions. Alternatively, acidification of a saturated solution of PNP[$Fe(OH)_2$(Pc(2−))] in dichloromethane with acetic acid precipitated the μ-oxo complex immediately. It was also possible to add iodine or water to the dichloromethane solution and obtain the μ-oxo complex. Products were washed with dichloromethane. All attempts to grow single crystals from solution have been unsuccessful. The various samples displayed identical UV–visible and IR spectra.[6] The IR spectra were also identical with those reported by Ercolani et al.[4] and by Frampton and Silver[9] for samples that they label μ-oxo I.

Analyses. Microanalytical data were obtained at Kiel University (sample B) and at the Australian Mineral Development Laboratories, Melbourne (sample A (1 year old), sample C). In our experience, there are difficulties in obtaining consistent and reproducible microanalytical data for metal phthalocyanines and metal porphyrins so the results should be treated with some caution. Anal. Calcd for $[Fe(Pc(2-))]_2O$ ($C_{64}H_{36}Fe_2N_{16}O$): C, 66.7; H, 2.8. Found, sample A: C, 64.9; H, 2.8; Cl, <0.5. Found, sample B: C, 66.1. Found, sample C: C, 66.6; H, 3.0; Cl, <0.5. All these samples showed the presence of Cl by scanning electron microprobe analysis, presumably due to traces of dichloromethane of solvation being present.

Instrumentation. Mössbauer, ESR and magnetic susceptibility measurements were made as described elsewhere.[10] Double integration of the ESR spectra were carried out with the kind assistance of Dr. J. R. Pilbrow (Department of Physics, Monash University). Electron microprobe analyses were carried out on powdered samples with a Cambridge S410 scanning electron microscope linked via a Nuclear Equipment Corp.

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(1) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 583.
(2) Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461.
(3) (a) Küppers, H.; Homborg, H.; Kalz, W. *Acta Crystallogr.* in press. (b) Kalz, W.; Homborg, H.; Küppers, H.; Kennedy, B. J.; Murray, K. S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1478.
(4) Ercolani, C.; Gardini, M.; Monacelli, F.; Pennesi, G.; Rossi, G. *Inorg. Chem.* **1983**, *22*, 2584.
(5) Collamati, I. *Inorg. Chim. Acta* **1979**, *35*, L303.
(6) Kalz, W.; Homborg, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 470.
(7) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G. *J. Chem. Soc., Chem. Commun.* **1983**, 549.
(8) Kennedy, B. J.; Brain, G.; Murray, K. S. *Inorg. Chim. Acta* **1984**, *81*, L29.
(9) Frampton, C. S.; Silver, J. *Inorg. Chim. Acta* **1985**, *96*, 187.
(10) Mitchell, A. J.; Murray, K. S.; Newman, P. J.; Clark, P. E. *Aust. J. Chem.* **1977**, *30*, 2439.

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Table I. Comparison of Properties of Three Samples of $[Fe(Pc(2-))]_2O$

property	sample A	sample B	sample C
method of synthesis[a]	i	i	ii
ν(Fe–O–Fe), cm^{-1}	851, 822	851, 822	851, 822
μ_{Fe}(295 K), μ_B	2.19	2.23	2.23
μ_{Fe}(4.2 K), μ_B	1.17	1.13	0.95
Mössbauer doublets (at 4.2 K), mm s^{-1}: δ; ΔE_Q			
main	0.37; 0.44 (87.3%)	0.36; 0.45 (80.1%)	0.37; 0.43 (88.1%)
minor	0.24; 1.38 (12.7%)	0.24; 1.34 (19.9%)	0.24; 1.34 (11.9%)
ESR of powder, 77 K	as in Figure 1	as in Figure 1, weaker $g \sim 6$ than A	as in figure 1, weaker $g \sim 6$ than A or B

[a] Method i: PNP$[Fe(OH)_2(Pc(2-))]$ in dichloromethane + acetic acid, 5 h in air, at Kiel University. Method ii: PNP$[Fe(OH)_2(Pc(2-))]$ in dichloromethane, 24 h in air, at Monash University.

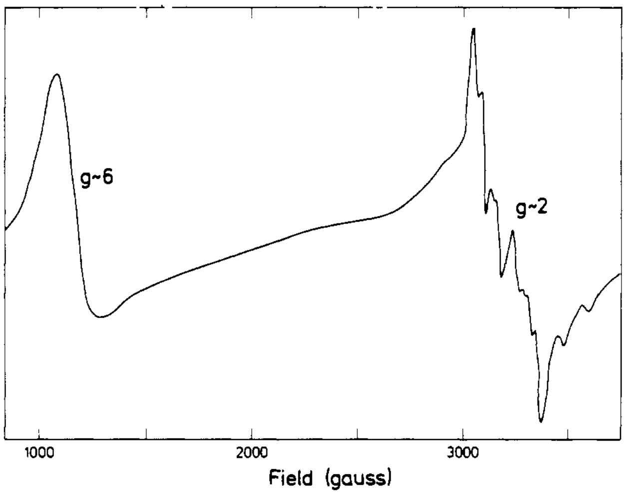

Figure 1. ESR spectrum of powdered sample of $[Fe(Pc(2-))]_2O$, sample A, measured at 77 K with microwave frequency of 9.297 GHz.

X-ray detector and X-ray pulse processing system to a Hewlett-Packard multichannel analyzer. The results were plotted on a pen recorder, and the signal to noise characteristics suggested a detection limit of approximately 1% relative to the main Fe Kα line at 6.4 keV. However, as indicated above, Cl is detectable even when present in <0.5% concentration according to conventional microanalytical techniques.

Results and Discussion

The room-temperature magnetic moments of a number of samples of I prepared from PNP$[Fe(OH)_2(Pc(2-))]$ under various conditions (described in the Experimental Section) all lie in the range 2.2–2.3 μ_B (per Fe). The samples all show identical infrared spectra[6] with characteristic Fe–O–Fe stretching frequencies at 851 and 822 cm^{-1}. These data compare well with the results of Ercolani et al.[4] and show that the samples consist predominantly of μ-oxo I. Three such samples have been studied in detail over a wide range of temperatures, and a summary of their spectroscopic and magnetic data is given in Table I.

ESR Spectra. While aware of the general problems in obtaining good resolution from neat powders due to exchange broadening, etc., we have been encouraged by the resolution obtained in the spectra of mononuclear Fe^{III} phthalocyanines.[8] Spectra of the three samples of I, recorded at 77 K, are generally very similar and quite unusual. It can be seen in Figure 1 that the spectra consist of a signal at $g \sim 6$ together with a well-resolved set of signals near $g \sim 2$, which appear to be superimposed on a very broad line. The $g \sim 6$ signal varies in intensity relative to the $g \sim 2$ signal from sample to sample. It is also possible in the spectra of some of the samples to detect a weak signal at $g \sim 4.3$, which is either due to Fe^{III} in trigonal-type symmetry or to "half-field" transitions arising from pairwise interactions. Although the $g \sim 6$ signal is typical of $S = {}^5/_2$ Fe(III) complexes, the $g \sim 2$ signal is not. Normally the $g \sim 2$ signal in axially distorted high-spin d^5 systems is much weaker than the $g \sim 6$ line and does not display any fine structure of the type shown in Figure 1. There are a number of possible explanations for the structure observed in the $g \sim 2$ region.

(i) The samples are contaminated with small amounts of ions such as Co^{II} or Mn^{II}, which could give rise to hyperfine splitting. This appears unlikely in view of the clean spectrum exhibited by samples of PNP$[Fe(OH)_2(Pc(2-))]$, which were used to prepare the μ-oxo complex. The uneven splitting between component lines would also militate against this possibility. Furthermore, scanning electron microprobe analyses of samples A, B, and C did not show evidence for any metal ion other than Fe being present, although it is possible that ESR is a more sensitive probe. Interestingly, the electron microprobe analysis revealed the presence of trace quantities of chlorine in the samples, which we presume is due to the presence of solvated dichloromethane in the lattice. Previous work has shown that $[Fe(Pc(2-))]_2O$ has a tendency to occlude solvate molecules.[4]

(ii) The compound contains a small amount of an oxidized species containing the radical cation Pc(1–), which may give rise to hyperfine splitting. Spectral data do not support the presence of such a species; the IR spectrum does not show characteristic bands at ca. 1350 and 1450 cm^{-1} nor does the UV–visible spectrum[6] display bands due to Pc(1–).

(iii) The $g \sim 2$ signals arise from the antiferromagnetically coupled Fe(III)–O–Fe(III) moiety. Unfortunately, the ESR spectra of μ-oxo iron(III) dimers are still poorly understood. They are generally regarded to be ESR silent even at temperatures above 77 K although complexes such as $[Fe(Salen)]_2O$ do give broad signals.[11] We note also that similar line shapes in the $g \sim 2$ region have been observed in μ-oxo Fe(III) "lacunar" complexes prepared by Busch and co-workers.[12]

Of the three possibilities, we favor (iii) even though a full assignment of the line shape is not yet possible. The $g \sim 6$ signal arises from a minor high-spin monomeric Fe(III) component, further evidence for which has been obtained from Mössbauer and magnetic susceptibility data (vide infra). In order to eliminate the possibility that the $g \sim 2$ and $g \sim 6$ signals all arise from "impurities" in ESR-silent $[Fe(Pc(2-))]_2O$ samples, we have estimated the intensities of the signals by double integration and have compared the results with those for Fe(TPP)Cl, an $S = {}^5/_2$ complex with a well-characterized $g_\perp = 6$, $g_\parallel = 2$ spectrum. Integration of all signals in the field-range 500–4500 G clearly shows, by comparison with Fe(TPP)Cl, that the line shape shown in Figure 1 represents the bulk sample of $[Fe(Pc(2-))]_2O$ and not just a small percentage of paramagnetic impurity. Attempts to compare the intensity of the $g \sim 6$ line relative to the intensity of the $g \sim 2$ lines in the spectra of the various samples were less precise because of the approximations inherent in integrating only part of a total resonance as well as deficiencies in the current understanding of integrations in coupled systems. Nethertheless, the results were broadly in agreement with the variable-temperature susceptibility data. Sample C, for instance, shows a weaker $g \sim 6$ signal than that for sample A and a correspondingly lower μ_{Fe} value at 4.2 K, compatible with a smaller percentage of a high-spin component being present.

The ESR spectrum of a freshly prepared solution of I in pyridine at 77 K showed only a very weak broad line at $g \sim 2$, which

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(11) Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1.

(12) Herron, N., private communication. Herron, N.; Cameron, J. H.; Neer, G. L.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298.

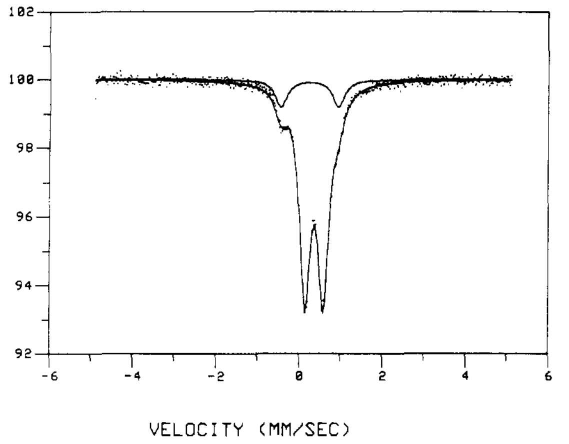

Figure 2. Mössbauer spectrum of $[Fe(Pc(2-))]_2O$, sample A, at 4.2 K. The origin of the weaker second doublet is discussed in the text.

Table II. Mössbauer Parameters for $[Fe(Pc(2-))]_2O$, Sample A

T, K	ΔE, mm s^{-1}	δ,[a] mm s^{-1}	Γ,[b] mm s^{-1}	% area of total spectrum
		Major Component (μ-oxo I)		
4.2	0.44	0.37	0.17	87.3
77	0.44	0.36	0.16	90.8
295	0.42	0.25	0.22	100
		Minor Component		
4.2	1.38	0.24	0.18	12.7
77	1.35	0.25	0.12	9.2

[a] Relative to α-Fe. [b] Half-width at half-height.

displayed hyperfine splitting with a separation of ca. 50 G. This resonance is due to axially ligated $[pyFe(Pc(2-))]_2O$ formed in the sequence[4,6,7]

$$[Fe(Pc(2-))]_2O + py \rightarrow [pyFe(Pc(2-))]_2O \rightarrow (py)_2Fe(Pc(2-))$$

the final Fe^{II} product of which is diamagnetic. This suggests that the complexity of the $g \sim 2$ region in the spectra of neat polycrystalline samples may originate partly through solid-state effects. Such effects have recently been observed in other Fe^{III} systems.[13]

Mössbauer Spectra. While the interpretation of the ESR spectrum remains tentative, that of the Mössbauer spectrum is more straightforward. The spectrum of sample A recorded at 4.2 K shows two distinct doublets (Figure 2). Warming to 77 K causes very little change in the appearance of the spectrum, although further warming to 295 K results in a poorly resolved spectrum showing only a single quadrupole-split doublet. Unfortunately only a very low effect was observed at 295 K, so it is difficult to determine if the second weaker doublet is still present. Spectra recorded for samples B and C at 4.2 K showed identical results except for small changes in the area ratios for the major and minor doublets (Table I). The detailed isomer shifts and quadrupole splittings for sample A are summarized in Table II.

As indicated previously, the IR spectral and room-temperature susceptibility measurements indicate that the major species in the sample is μ-oxo I, and there is no doubt that the main Mössbauer peaks are due to this species. The observed isomer shifts and quadrupole splittings of this inner doublet are characteristic[1,14] of high-spin Fe(III) complexes and quite different from low-spin or intermediate-spin iron(III) phthalocyanine values.[15] In addition the observed temperature dependence of the Mössbauer spectra of this species, which is very similar to that observed[14] in the analogous iron porphyrin complexes $[Fe(por)]_2O$, (por = TPP, OEP) is indicative of strong antiferromagnetic coupling between adjacent $S = {}^5/_2$ centers. This coupling results in a nonmagnetic ground state. The recent study by Frampton and Silver on μ-oxo I prepared from Fe(Pc(2−)) gave similar results and interpretation.[9]

The Mössbauer parameters for the second outer doublet also fall within the range of values observed for high-spin Fe(III) complexes, although the relatively large quadrupole splitting found here, ca. 1.4 mm s^{-1} is much larger than that typically observed in five-coordinate square-pyramidal species, viz. ΔE = 0.3–0.9 mm s^{-1}, but rather falls in the range observed[16] in some octahedrally coordinated high-spin Fe(III) species (ΔE = 0.6–1.5 mm s^{-1}). The possibility that this signal arises from some unreacted $PNP[Fe(Pc(2-))(OH)_2]$ can be discounted as this hydroxy species displays a Mössbauer spectrum at 4.2 K typical of low-spin Fe(III); δ = 0.18 mm s^{-1} and ΔE = 2.22 mm s^{-1}.[15] Similarly, it is thought unlikely that this second species is a five-coordinate hydroxy species, as all complexes of the type Fe(Pc)X so far studied[8,15] have a predominantly $S = {}^3/_2$ ground state with a characteristically large quadrupole splitting of ΔE = 3.0–3.5 mm s^{-1}.

It is very interesting to note that the parameters for the present outer doublet are virtually identical with those observed by Frampton and Silver[9] for a sample of $[Fe(Pc(2-))]_2O$ prepared by bubbling O_2 through a solution of Fe(Pc(2−)) in 96% H_2SO_4. These samples also gave a second doublet due to μ-oxo I, which appeared to be present in about 50% concentration according to the area ratios of the two doublets. It is possible that the outer doublet arises from the same chemical species in both studies. If this is so, we do not believe that it is due to a low-spin sulfonated phthalocyanine–iron(II) complex as proposed by Frampton and Silver. We say this not only because sulfuric acid was not present in our syntheses but also because the published IR data showed no evidence for SO_3^- groups not were any analytical data provided. Furthermore, the $g \sim 6$ ESR signal observed here, together with susceptibility values greater than those predicted for a pure μ-oxo complex (described further below), strongly implicate a high-spin compound. We believe that an equilibrium of the type

$$[Fe(Pc(2-))]_2O \rightleftharpoons Fe(Pc(2-))(OH) \rightleftharpoons Fe(Pc(2-))(OH_2)(OH)$$

or something similar, is probably occurring in these preparations. Indeed, it is possible to isolate a solid compound directly from the solution from which $PNP[Fe(OH)_2(Pc(2-))]$ is prepared, which displays microanalytical, spectral, and magnetic data compatible with a high-spin complex of formulation $Fe(Pc(2-))(OH_2)(OH)$.[17] Related hydroxo species have been postulated to occur in oxidized iron phthalocyanine species that were supported on carbon electrodes.[18] We note also that a number of substituted-phthalocyanine–iron(III) complexes have recently been described that display $g \sim 6$ signals and Mössbauer quadrupole doublets not unlike those shown by the present minor component.[19] While these were not the only lines displayed by such samples, it appears likely that they do contain monomeric $S = {}^5/_2$ (or[8] admixed ${}^5/_2$–${}^3/_2$) components. The axial ligands were not identified.

Magnetic Susceptibilities. In an attempt to better understand the nature of the minor species, and partly because of the limited susceptibility data reported by Ercolani,[4] the susceptibilities of

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(13) Kennedy, B. J.; Brain, G.; Horn, E.; Murray, K. S.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 1647.

(14) Sams, J. R. In "The Porphyrins" Dolphin, D., Ed.; Academic Press: NY, 1979; Vol. IV, Chapter 9.

(15) Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W., manuscript in preparation.

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

(17) The ESR spectrum of this product shows strong $g \sim 6$ lines and weak lines at $g \sim 2$. The μ_{Fe} value at 295 K of 5.0 μ_B is lower than the pure high-spin value but shows a dependence on temperature typical of a monomer displaying zero-field splitting. Mössbauer data at 4.2 K show that the proposed monomer is present with δ = 0.29 and ΔE = 1.37 mm s^{-1}, as well as some low-spin $[Fe(Pc(2-))(OH)_2]^-$ with δ = 0.25 and ΔE = 2.62 mm s^{-1}, and another high-spin component with δ = 0.36 and ΔE = 0.53 mm s^{-1} (μ-oxo I or Fe(Pc(2−))OH?). The IR spectrum is very similar to that of μ-oxo I except for ν(FeOFe) bands being very weak.

(18) Melendres, C. A. *J. Phys. Chem.* **1980**, *84*, 1936.

(19) (a) Kobayashi, N.; Koshiyama, N.; Funayama, K.; Osa, T.; Shirai, H.; Hanabusa, K. *J. Chem. Soc., Chem. Commun.* **1983**, 913. (b) Kobayashi, N.; Shirai, H.; Hoju, N. *J. Chem. Soc., Dalton Trans.* **1984**, 2107.

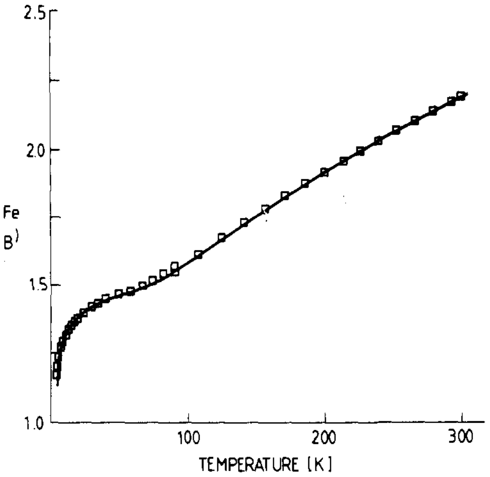

Figure 3. Temperature dependence of the magnetic moment, per Fe, for $[Fe(Pc(2-))]_2O$, sample A. The solid line is the curve computed by using the parameters given in the text, assuming a $^5/_2$–$^5/_2$ dimer and a small percentage of $^5/_2$ monomer.

three samples of I between 4.2 and 300 K were determined. The results for sample A are shown in Figure 3. The plots for samples B and C are very similar in shape but the μ_{Fe} values are a little different in magnitude due, we think, to differing quantities of the high-spin minor species.

These data cannot be explained solely in terms of a simple $^5/_2$–$^5/_2$ coupled system, although the rapid decrease in μ_{eff} between 300 and 70 K shows that such interactions are important. Below 70 K μ_{eff} appears to go through a slight plateau before decreasing very rapidly below 30 K, reaching a value of 1.17 μ_B at 4.2 K. The χ_{Fe}^{-1}/T plot in this low-temperature region is linear with a Curie constant of ca. 4 as expected for a $S = {}^5/_2$ monomer contribution. Given that the Mössbauer spectra also suggest two high-spin Fe(III) complexes are present, one of which is a strongly coupled $S = {}^5/_2$ dimer, the data were analyzed in terms of a mixture of species, viz.

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

with χ_1 given by the usual $^5/_2$–$^5/_2$ dimer expression[11] and χ_2 by a monomeric high-spin Fe(III) expression. In order to reproduce the observed decrease in μ_{eff} at a very low temperature the effect of zero-field splitting on the monomeric species was considered. Susceptibilities for such a species were calculated by solving the Hamiltonian

$$\mathcal{H} = g\beta\hat{H}\cdot\hat{S} + D[\hat{S}_{z^2} - {}^1\!/_3S(S + 1)]$$

By careful variation of the three parameters D, J, and ρ a good fit was obtained with $J = -120 \pm 5$ cm^{-1}, $\rho = 0.063 \pm 0.002$, and $D = 15 \pm 5$ cm^{-1}.

As seen from Figure 3, these parameters successfully reproduce the observed temperature dependence of μ_{eff} over the entire temperature range. The percent monomer impurity calculated from the susceptibility measurements, 6.3%, is significantly lower than that estimated from peak areas in the Mössbauer spectra, ca. 10%. This probably is due to differing Debye–Waller factors in the two complexes.[20] The percent monomer deduced from the $g \sim 6$ ESR line intensity is broadly in agreement with the susceptibility analysis.

Summary

The following points can be made.

(i) Samples of $[Fe(Pc(2-))]_2O$ prepared from PNP[Fe$(OH)_2(Pc(2-))$] consist predominantly of μ-oxo I but invariably contain a small amount of monomeric $S = {}^5/_2$ phthalocyanine iron(III)hydroxo species. Alternative syntheses by Frampton and Silver,[9] using the methods of Ercolani et al.,[4] produce either pure μ-oxo I or mixtures of μ-oxo I plus what appears to be the same monomeric species as obtained here, albeit in higher concentration.[24]

(ii) $[Fe(Pc(2-))]_2O$ is a strongly coupled $^5/_2$–$^5/_2$ complex with a J value of -120 cm^{-1}, similar in magnitude to those of other μ-oxo complexes.[11] It provides the best characterized example of the few known high-spin iron(III) phthalocyanines. The Mössbauer parameters, $\delta = 0.37$ mm s^{-1} and $\Delta E = 0.44$ mm s^{-1}, are clearly indicative of $S = {}^5/_2$ Fe^{III} and are quite different from those of $S = {}^1/_2$ and $S = {}^3/_2$ derivatives.[15] Other recently reported μ-oxo complexes of substituted phthalocyanines[21] appear to have the same electronic structure as found here for $[Fe(Pc(2-))]_2O$. The spectral and magnetic properties of μ-oxo I are only compatible with the oxidation state +3 on each Fe. Formulations of the type $H_2[(Fe(Pc(2-)))_2O]$, which involve Fe^{II}, have been suggested by Lukyanets et al.[22] to apply to *tert*-butyl-substituted Pc(2–) μ-oxo species. These compounds have recently been discussed by Hanack et al.[23] A study, of the present type would quickly confirm or deny such proposals.

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Registry No. I, 74353-48-3; Fe^{3+}, 20074-52-6.

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(20) Haddad, M. S.; Lynch, M. W.; Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 123 and references therein.

(21) Lever, A. B. P.; Licoccia, S.; Ramaswany, B. S. *Inorg. Chim. Acta* **1982**, *64*, L87. These authors reported IR and UV–visible spectra and some magnetic data for two long-chain alkanesulfonamide PcFe^{III} μ-oxo complexes. The results are compatible with $S = {}^5/_2$ Fe(III) centers.

(22) Mekhryakova, N. G.; Bundina, N. I.; Gulina, T. Y.; Kaliya, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1984**, *54*, 1656.

(23) Metz, J.; Schneider, O.; Hanack, M. *Inorg. Chem.* **1984**, *23*, 1065.

(24) Ercolani et al. are able to consistently obtain a second crystalline form, μ-oxo II, by oxidizing Fe(Pc(2–)) in a solution of isopropylamine and chloronaphthalene. This form has Mössbauer properties different from those of the minor product in this work and from those of μ-oxo 2(b) of Frampton and Silver[9] (Ercolani, C., private communication, June 1985).

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The Novel Displacement of a η^6-Arene by η^5-Cyclopentadienide. Synthesis and Structure of $[(\eta^5\text{-}C_5H_5)Ni(C_6F_5)_2][(C_2H_5)_4N]$

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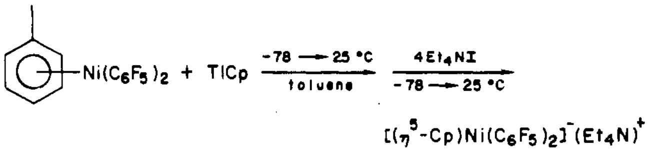
In the course of our continuing investigation of (η^6-arene)MR$_2$ systems,[1] we have discovered a very unusual reaction that has led to the isolation of a new type of organonickel complex. Treatment of (η^6-toluene)bis(pentafluorophenyl)nickel(II) with thallium cyclopentadienide (TlCp) followed by cation exchange with Et$_4$NI resulted in the overall replacement of the η^6-arene by η^5-Cp$^-$:



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