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Spin States in Iron(III) Phthalocyanines Studied by Mössbauer, Magnetic Susceptibility, and ESR Measurements

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Magnetic susceptibility, Mössbauer, and ESR measurements, over a wide temperature range, have been used to determine the ground states and electronic structures of a range of iron(III) phthalocyanine complexes. Anionic six-coordinate species $\mathrm{B^+}$-$[\mathrm{FeL_2(Pc(2-))}]^-$ ($\mathrm{B^+}$ = bulky cation; L = $\mathrm{OH^-}$, $\mathrm{OPh^-}$, $\mathrm{NCO^-}$, $\mathrm{NCS^-}$, $\mathrm{N_3^-}$, $\mathrm{CN^-}$) display low-spin d^5 characteristics. Magnetic moments at 295 K are in the range 2.05–2.49 μ_B and show a Curie–Weiss dependence on temperature between 295 and 4.2 K. Well-resolved ESR spectra were obtained on neat powders of the dihydroxo, diphenoxo, and diazido derivatives. Analysis of the three *g* value line shapes in terms of a simple crystal field model yielded values of the tetragonal and rhombic splitting parameters that were similar in magnitude to those recently reported for anionic iron porphyrins of type $[\mathrm{Fe(OR)_2TPP}]^-$. Mössbauer parameters are in the ranges normally observed for low-spin $\mathrm{Fe^{III}}$–$\mathrm{N_4}$ macrocycles, viz. δ = 0.18–0.29 mm $\mathrm{s^{-1}}$ (relative to Fe) and ΔE_Q = 2.22–2.65 mm $\mathrm{s^{-1}}$, except for L = $\mathrm{CN^-}$ with δ = 0.11 mm $\mathrm{s^{-1}}$ and ΔE_Q = 0.99 mm $\mathrm{s^{-1}}$ (at 4.2 K). The dicyano species generally displays differences in electronic detail from those of the other axially ligated derivatives. In the resonance Raman spectra the cyano, isocyanato, and isothiocyanato complexes display electronic Raman transitions at 525, 490, and 520 $\mathrm{cm^{-1}}$, respectively, arising from transitions within the spin–orbit split sublevels of the $^2T_{2g}$ (O_h) ground state. A wide range of five-coordinate complexes with halide and O-donor axial ligands have been studied of type FeX(Pc(2−)), where X = Cl, Br, I, $\mathrm{RCO_2}$, or $\mathrm{RSO_3}$. These compounds display intermediate-spin ($S = {}^3/_2$) or spin-admixed ($S = {}^3/_2$–$S = {}^5/_2$) behavior as judged by magnetic moments (3.9–4.53 μ_B) and Mössbauer parameters ($\delta \sim$ 0.28 mm $\mathrm{s^{-1}}$; ΔE_Q = 2.94–3.23 mm $\mathrm{s^{-1}}$). Comparisons are made with related FeX(porph) complexes. In contrast to the many examples of high-spin, $S = {}^5/_2$, iron(III) porphyrins, there are very few well-characterized high-spin phthalocyanine analogues. One such example is the binuclear μ-oxo complex $[\mathrm{Fe(Pc(2-))}]_2\mathrm{O}$. Its electronic features are briefly described together with those for the sulfato complex $[\mathrm{Fe(SO_4)(Pc(2-))}]^-$.

Introduction

We describe in this paper a detailed investigation of the magnetic and spectral properties of a range of six- and five-coordinate iron(III) phthalocyanines. The six-coordinate complexes are anionic species of type $[\mathrm{FeL_2(Pc(2-))}]^-$, and the five-coordinate complexes are neutral species of type FeX(Pc(2−)) (Figure 1). Iron(II) phthalocyanines[1-3] and other divalent transition-metal phthalocyanines[4-6] have previously been studied in considerable detail and their electronic structures elucidated. It is only recently that a well-characterized group of $\mathrm{Fe^{III}(Pc(2-))}$ compounds has been made available through newly devised synthetic methods.[7] Comparisons are made where possible with related iron(III) porphyrin complexes whose structural and electronic features have been probed in considerable depth in recent years.[8]

Experimental Section

Preparation of Iron(III) Phthalocyanine Complexes. The method of synthesis of the following complexes has recently been described:[7,9,10] $\mathrm{(PNP)[Fe(OH)_2(Pc(2-))]}$; $\mathrm{(PNP)[Fe(N_3)_2(Pc(2-))]}$; $\mathrm{(PNP)[Fe(CN)_2(Pc(2-))]}$; FeX(Pc(2−)), where X = Cl, Br, or I; $[\mathrm{Fe(Pc(2-))}]_2\mathrm{O}$.

Bis(triphenylphosphine)nitrogen(1+) Diphenoxo(phthalocyaninato)ferrate(III) ((PNP)[Fe(OPh)$_2$(Pc(2−))]). A 114-mg (0.1-mmol) sample of $\mathrm{(PNP)[Fe(OH)_2(Pc(2-))]}$[7] was dissolved in 15 mL of dichloromethane and mixed with a dichloromethane solution containing 27.9 mg (0.3 mmol) of dried phenol. The resulting homogeneous solution yielded crude black crystals on addition of ether. After a single recrystallization from $\mathrm{CH_2CCl_2}$/ether, the complex was isolated as a phenol adduct. When the same amount of the dihydroxo complex was reacted with 0.4 mmol of phenol, products were obtained with nonuniform analytical results. Use of 0.2 mmol of phenol led to $[\mathrm{Fe(Pc(2-))}]_2\mathrm{O}$ complex being mainly produced.

This complex can also be prepared from FeCl(Pc(2−)): 93 mg (1 mmol) of dry phenol dissolved in 5 mL of toluene was mixed with 40 mg (1 mmol) of freshly cut potassium metal and stirred until hydrogen evolution ceased. The white crystals of potassium phenolate that deposited were filtered and suspended in 20 mL of dichloromethane to which 0.64 g of $\mathrm{(PNP)ClO_4}$ was added. $\mathrm{KClO_4}$ was deposited while (PNP)(OPh) remained in solution. The turbid solution was filtered and mixed with 0.3 g (0.5 mmol) of FeCl(Pc(2−)).[7] It was stirred until the chloro complex was mainly dissolved. The dark blue solution was filtered and mixed with ether until crystallization began. The product was recrystallized several times at −25 °C. Anal. Calcd for $\mathrm{C_{80}H_{56}FeN_9O_2P_2}$: C, 74.3; Fe, 4.3. Found: C, 73.5; Fe, 4.3.

Bis(triphenylphosphine)nitrogen(1+) Bis(isocyanato)(phthalocyaninato)ferrate(III) ((PNP)[Fe(NCO)$_2$(Pc(2−))]). This preparation used $\mathrm{Fe(NCO)(Pc(2-))}\cdot x\mathrm{H_2O}$, which was synthesized by acidification with glacial acetic acid of a solution containing 0.73 g (1 mmol) of $\mathrm{Fe(en)_2(Pc(2-))\cdot C_2H_5OH}$ with 0.32 g (4 mmol) of KOCN dissolved in 20 mL of dimethyl sulfoxide. The resulting blue solution was filtered, and a precipitate of the product that deposited was mixed with KOCN-saturated water. $\mathrm{Fe(NCO)(Pc(2-))}\cdot x\mathrm{H_2O}$ was filtered, washed many times with water, and dried under vacuum. Anal. Calcd for $\mathrm{C_{33}H_{18}FeN_9O_2}$: C, 63.1; Fe, 8.9. Found: C, 63.0; Fe, 8.8.

A 0.63-g (1-mmol) sample of $\mathrm{Fe(NCO)(Pc(2-))}\cdot x\mathrm{H_2O}$ was heated to boiling with 2 mmol of (PNP)OCN in dichloromethane for 30 min. During this time the green-blue powder of $\mathrm{Fe(NCO)(Pc(2-))}\cdot x\mathrm{H_2O}$ had transformed to reddish shiny crystals of the desired bis(isocyanato) complex. The crystals were washed with an appropriate solvent and dried under vacuum. They could not be recrystallized from the usual solvents without decomposition. Anal. Calcd for $\mathrm{C_{70}H_{46}FeN_{11}O_2P_2}$: C, 70.6; Fe, 4.7. Found: C, 70.1; Fe 4.7.

Tetra-*n*-butylammonium Bis(isothiocyanato)(phthalocyaninato)ferrate(III) ((TBA)[Fe(NCS)$_2$(Pc(2−))]). A 0.1-mmol sample of a FeX(Pc(2−)) complex (X = halide or carboxylate) was heated to boiling in a 10 mL solution of ethanol containing 39.2 mg (0.4 mmol) of KNCS. The concentrated solution was filtered and the bis(isothiocyanato) complex was deposited as a poorly soluble dark blue solid on addition of (TBA)NCS. The complex was washed with ethanol and water and dried under vacuum. Anal. Calcd for $\mathrm{C_{50}H_{52}FeN_{11}S_2}$: C, 64.8; Fe, 6.0. Found: C, 64.5; Fe, 6.0.

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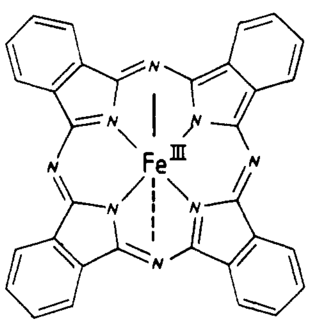

Figure 1. General structure for iron(III) phthalocyanine complexes. The $[FeL_2(Pc(2-))]^-$ complexes contain two L ligands in the axial positions. The FeX(Pc(2−)) complexes contain only one axial ligand.

(Carboxylato)(phthalocyaninato)iron(III) (FeX(Pc(2−)); X = $CF_3CO_2^-$, $CCl_3CO_2^-$, HCO_2^-). Two methods were used. In the first, 73.4 mg (0.1 mmol) of $Fe(en)_2(Pc(2-))$ were suspended in acetone and stirred in air with 0.6 mmol of the appropriate carboxylic acid for 10 min. The product was centrifuged, washed numerous times with anhydrous acetone, and then dried over KOH in a vacuum. The second route used the dihydroxoiron(III) complex. The appropriate acid was added to a solution of 114 mg (0.1 mmol) of $(PNP)[Fe(OH)_2(Pc(2-))]$ in dichloromethane under argon. The resulting precipitate was centrifuged and washed with deoxygenated CH_2Cl_2. As soon as it was acid-free, the complex was stable to oxygen and could be further worked up in air. It was washed again with CH_2Cl_2 and dried under vacuum.

	anal.	
X	% calcd	% found
CF_3CO_2	C, 59.9; Fe, 8.2	C, 61.0; Fe, 8.1
CCl_3CO_2	C, 55.9; Fe, 7.6	C, 55.4; Fe, 7.5
HCO_2	C, 64.6; Fe, 9.1	C, 63.9; Fe, 9.1

(Sulfonato)(phthalocyaninato)iron(III) (FeX(Pc(2−)); X = $CF_3SO_3^-$, *p*-tolSO_3^-). These complexes could be prepared either by the second route described for the carboxylato derivatives or by the following route. FeCl(Pc(2−)) (600 mg) and KOH (200 mg) were stirred at 40 °C for 30 min in methanol (20 mL)/acetone (40 mL). After the resulting blue solution was filtered, the appropriate acid was added to form the product as a precipitate, which was washed repeatedly with acetone and water.

	anal.	
X	% calcd	% found
CF_3SO_3	C, 55.0; Fe, 7.8	C, 57.4; Fe, 7.9
p-tolSO_3	C, 63.3; Fe, 7.5	C, 62.6; Fe, 7.3

Tetra-*n*-butylammonium (Sulfato)(phthalocyaninato)ferrate(III) ((TBA)[Fe(SO_4)(Pc(2−))]). Two methods were used to prepare this complex. In the first, 114 mg (0.1 mmol) of $PNP[Fe(OH)_2(Pc(2-))]$ dissolved in dichloromethane was mixed with 101.4 mg (0.3 mmol) of $(TBA)HSO_4$ dissolved in 5 mL of dichloromethane. After about 20 min, the precipitation of prismatic hexagonal crystals of $(TBA)[Fe(SO_4)(Pc(2-))]$ is complete. The sulfato complex is insoluble in dichloromethane, acetone, or ethanol and could be washed with such solvents. The second method used $Fe(en)_2(Pc(2-))\cdot C_2H_5OH$ as starting material. A 73.4-mg (0.1-mmol) sample in dichloromethane was reacted with 67.8 mg (0.2 mmol) of $(TBA)HSO_4$ in the presence of a few drops of acetic acid. Small crystals of $(TBA)[Fe(SO_4)(Pc(2-))]$ deposited immediately from solution, and these were filtered, dried, washed with water, and dried under vacuum. Anal. Calcd for $C_{48}H_{52}FeN_9O_4S$: C, 63.4; Fe, 6.1. Found: C, 63.6; Fe, 6.1.

Physical Measurements. Details of the methods used for magnetic susceptibility, ESR, Mössbauer, and resonance Raman studies have been given previously.[7,9,11,12]

Results and Discussion

1. Low-Spin ($S = {}^1/_2$) Six-Coordinate Anionic Complexes. A range of six-coordinate anionic complexes of the type $B[FeL_2(Pc(2-))]$ have been synthesized in which B^+ is a bulky cation such as PNP^+ or TBA^+ and L is an anionic ligand such as OH^-, OR^-, NCO^-, NCS^-, N_3^-, or CN^-. The dihydroxo complex[7] has proved to be a particularly useful starting material for obtaining the other compounds by use of substitution reactions. The crystal structure of one of these compounds, $(PNP)[Fe(CN)_2(Pc(2-))]$ has recently been described in detail.[9,13] The geometry is as expected for low-spin Fe(III) and is generally similar to that in the analogous porphyrin complex $K[Fe(CN)_2TPP]$.[8] While dicyano species would be expected to display low-spin behavior, it is surprising that the present dihydroxo and dialkoxo complexes behave likewise since the related iron(III) porphyrin complexes $[FeTPP(H_2O)_2]^+$ and $[FeTPP(ROH)_2]^+$ are high-spin.[8,14] Clearly the OH^- and OR^- groups possess stronger ligand fields than H_2O and ROH, and this has also recently been observed by Sato et al.[15] in ESR studies of $[FeTPP(OMe)_2]^-$.

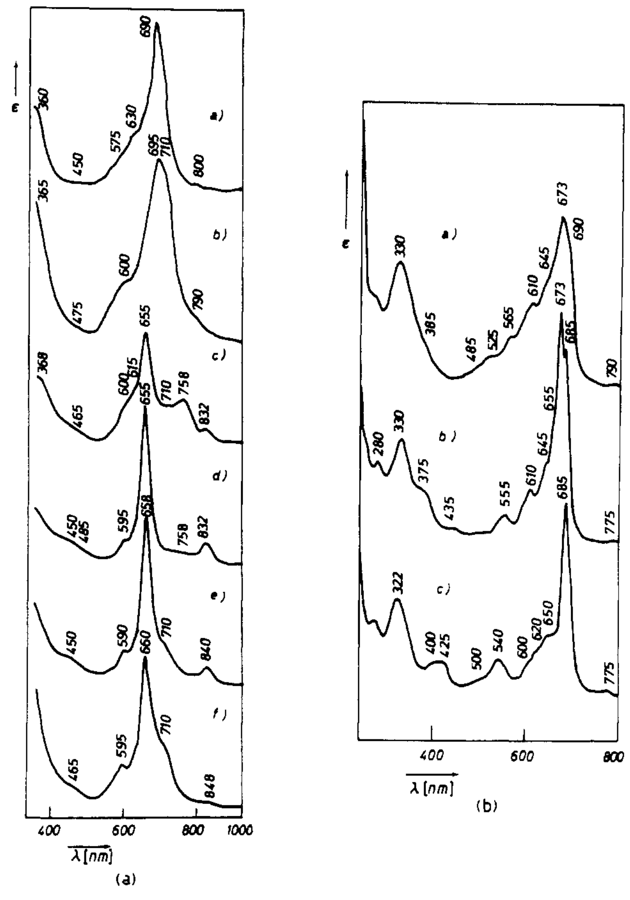

Figure 2. Part a: Electronic spectra of 1-chloronaphthalene solutions of (a) $(PNP)[Fe(OH)_2(Pc(2-))]$, (b) $[Fe(Pc(2-))]_2O$, (c) FeF(Pc(2−)), (d) FeCl(Pc(2−)), (e) FeBr(Pc(2−)), and (f) FeI(Pc(2−)). Part b: Electronic spectra of dichloromethane solutions of (a) $(TBA)[Fe(NCS)_2(Pc(2-))]$, (b) $(PNP)[Fe(NCO)_2(Pc(2-))]$, and (c) $(PNP)[Fe(CN)_2(Pc(2-))]$.

It is possible to qualitatively distinguish the six-coordinate $Fe^{III}(Pc(2-))$ complexes from the five-coordinate complexes by means of UV-visible spectral measurements. This can be seen in parts a and b of Figure 2 where the spectra of three $[FeL_2(Pc(2-))]^-$ and six FeX(Pc(2−)) examples are presented. λ_{max} for the Q-band of the FeX(Pc(2−)) complexes occurs at ~660 nm with shoulders on each side at ~590 and 710 nm. Weak LMCT bands are also observed at 465 and 840 nm. λ_{max} moves to higher wavelengths, ca. 690 nm, in the six-coordinate low-spin species. The latter also display a number of weak bands at lower wavelengths as well as one at 775 nm, some of which are assignable to Pc(2−) → Fe charge-transfer transitions. A more quantitative

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Table I. Mössbauer Effect Parameters for Iron(III) Phthalocyanines (T = 4.2 K; δ Values Relative to α-Fe)

complex	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	spin state
Low-Spin 6-Coordinate			
(PNP)[Fe(OH)$_2$(Pc(2−))][a]	0.18	2.22	$^1/_2$
(PNP)[Fe(OPh)$_2$(Pc(2−))][a]	0.22	2.64	$^1/_2$
(PNP)[Fe(NCO)$_2$(Pc(2−))][a]	0.29	2.25	$^1/_2$
(TBA)[Fe(NCS)$_2$(Pc(2−))]	0.26	2.65	$^1/_2$
(PNP)[Fe(N$_3$)$_2$(pc(2−))]	0.21	2.49	$^1/_2$
(PNP)[Fe(CN)$_2$(pc(2−))]	0.11	0.99	$^1/_2$
Intermediate-Spin or Spin-Admixed 5-Coordinate			
FeCl(Pc(2−))	0.28	2.94	$\underline{^3/_2}$–$^5/_2$
FeBr(Pc(2−))	0.28	3.12	$\underline{^3/_2}$–($^5/_2$)
FeI(Pc(2−))[a]	0.28	3.23	$\underline{^3/_2}$–$^5/_2$
Fe(CF$_3$CO$_2$)(Pc(2−))[a]	0.28	3.08	$\underline{^3/_2}$–$^5/_2$
Fe(CCl$_3$CO$_2$)(Pc(2−))[a]	0.29	3.07	$\underline{^3/_2}$–$^5/_2$
High-Spin 5-Coordinate			
[FePc(2−))]$_2$O[b]	0.37	0.44	$^5/_2$
(TBA)[Fe(SO$_4$)(Pc(2−))][c]	0.55	0.82	$^5/_2$

[a] These Mössbauer spectra show a weak inner doublet due to traces of μ-oxo complex present. [b] A second doublet with 10% of the area is present: δ = 0.24 mm s^{-1}; ΔE_Q = 1.38 mm s^{-1}. [c] The spectral fitting (Figure 9) shows a singlet also present with δ = 0.61 mm s^{-1}.

assignment of the electronic spectra of some of the present species, made by using the models of Gouterman, Lever and co-workers,[16–18] has been presented elsewhere.[7,9]

Mössbauer Spectra. With the exception of the dicyano complex, all of the present complexes display isomer shift and quadrupole splitting values in the 4.2 K Mössbauer spectrum of $\delta = 0.24 \pm 0.06$ mm s^{-1} and $\Delta E_Q = 2.4 \pm 0.2$ mm s^{-1} (Table I). Such values are typical of $S = {}^1/_2$ iron(III) in geometries of the present general type although the ΔE_Q values are at the higher end of the usual range.[19]

There are some interesting features in the shapes of the present spectra. It can be seen in Figure 3 that the sense of the asymmetry in the quadrupole doublet for the O-bonded axial ligand systems such as OH$^-$ and OR$^-$ is opposite to that for the N-bonded systems containing NCO$^-$, NCS$^-$, and N$_3^-$. In the O-bonded systems the line at low velocity is weaker and broader than the line at high velocity, with the reverse situation true for the N-bonded compounds. Whether or not such differences in asymmetry are generally diagnostic of the donor atom in the axial ligands will require studies on further examples. Asymmetry in line shape of the kind displayed in Figure 3 has been observed in a large number of high-spin Fe(III) porphyrin and hemin systems[19] and has also been detected in the small number of available Mössbauer investigations of low-spin hemichromes.[19,20] In the present $S = {}^1/_2$ systems it relates essentially to a slow spin–lattice relaxation rate at low temperature. In the cases in which the high-velocity line is broadened it is probable that the axial component of the electric field gradient, V_{ZZ} is positive, while for cases in which the low-velocity line is broader, V_{ZZ} is negative. Applied-field measurements are necessary, however, to confirm these assignments. In principle, it is possible to deduce the nature of the ligand field ground state from the sign of V_{ZZ}. Thus for $V_{ZZ} > 0$, there is a hole in d$_{xz}$,d$_{yz}$; for $V_{ZZ} < 0$, there is a hole in d$_{xy}$.[19] Interestingly, the ESR spectra of polycrystalline samples (vide infra) show the typical $S = {}^1/_2$ three g values spectra in the cases with L = N$_3^-$, OH$^-$, and OPh$^-$ but only a broad ill-shaped $g \sim 2$ signal for the complexes with L = NCO$^-$ and NCS$^-$. While these ESR differences may relate to a change in ground state or to energy differences between the t$_{2g}$ orbitals, the effects of exchange broadening and/or relaxation can not be ruled out. If intermolecular exchange effects are responsible for the line broadening in the L = NCO$^-$ and NCS$^-$ derivatives, then these must be very weak in magnitude in view of the Curie-like susceptibility behavior.

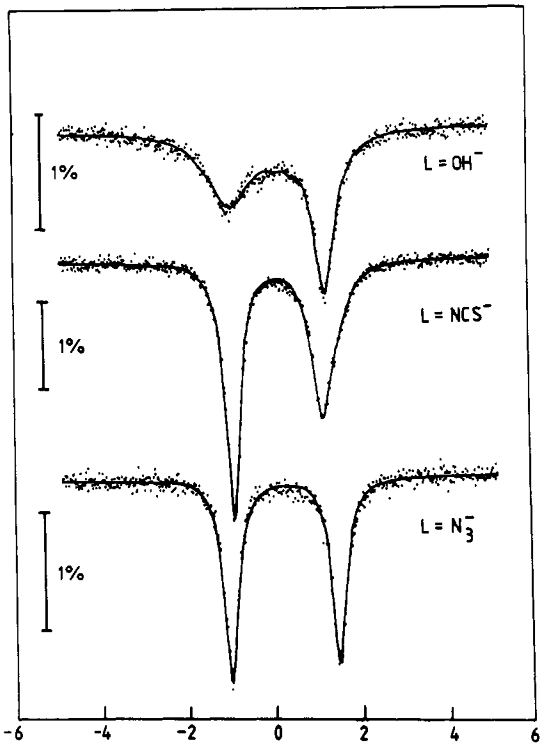

Figure 3. Mössbauer spectra at 4.2 K of [FeL$_2$(Pc(2−))]$^-$ complexes. The weak inner doublet in the spectrum of L = OH$^-$ is due to traces of [Fe(Pc(2−))]$_2$O.

The quadrupole splitting in (PNP)[Fe(CN)$_2$(Pc(2−))] is notably smaller than in the other compounds, and the isomer shift is also reduced. The quadrupole doublet at 4.2 K is almost symmetric in shape. Possible reasons for these differences have been given elsewhere.[9] The decrease in δ probably relates to an increase in covalency due to the CN$^-$ ligand. π-bonding between CN$^-$ orbitals and the out-of-plane iron d$_{xz}$ and d$_{yz}$ orbitals will influence the size of ΔE_Q in comparison to the other axial ligands. Other factors which will also influence the magnitude of ΔE_Q include the symmetry of the ligand field, i.e. tetragonal vs. rhombic contributions, the nature of the ground state and the energies of low-lying excited states. It is noteworthy that dicyanoiron(III) protoporphyrin likewise gives a very small ΔE_Q value in comparison to other axially ligated ferric hemes.[20] A definite reason for this difference has not been given. In contrast, the Schiff-base complex K[Fe(CN)$_2$salen] gives a ΔE_Q value of 2.15 mm s^{-1},[21] which indicates that overall ligand field symmetry and covalency effects resulting from both the in-plane ligand *and* axial CN$^-$ groups are important. Another related system, [Fe(py)$_2$TPP]Cl, has shown an anomalously low ΔE_Q value at 77 K of 1.25 mm s^{-1} in comparison to that of 2.23 mm s^{-1} for [Fe(imH)$_2$TPP]Cl.[19] Sams tentatively suggested that this might be due to a difference in orbital ground state.[19] However, the results of recent ESR studies[22,23] show that the rhombic and tetragonal splittings and their ratio (described below) are much lower for the pyridine adduct than for the imidazole adduct. We suggest that this would explain the lower ΔE_Q value and that a similar situation could

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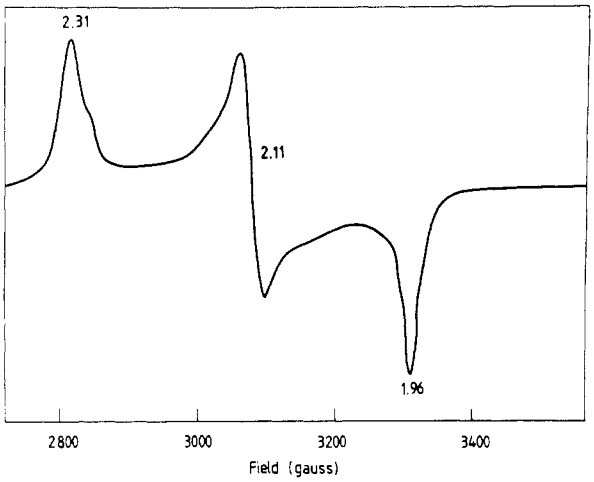

Figure 4. ESR spectrum at X-band frequency of a neat polycrystalline sample of (PNP)[Fe(OH)$_2$(Pc(2-))] (T = 110 K). g_{max}, g_{mid}, and g_{min} are marked.

Table II. Magnetic Moments[a] and ESR g Values[b] for Polycrystalline Iron(III) Phthalocyanines

complex	μ_{Fe}(300 K), μ_B	μ_{Fe}(4.2 K), μ_B	g values[c]
Low-Spin 6-Coordinate			
(PNP)[Fe(OH)$_2$(Pc(2-))]	2.31	2.06	2.31, 2.11, 1.96
(PNP)[Fe(OPh)$_2$(Pc(2-))]	2.30	nd	2.31, 2.12, 1.93
(PNP)[Fe(NCO)$_2$(Pc(2-))]	2.44	1.96	br
(TBA)[Fe(NCS)$_2$(Pc(2-))]	2.40	nd	br
(PNP)[Fe(N$_3$)$_2$(Pc(2-))]	2.05	1.76	2.41, 2.07, 1.79
(PNP)[Fe(CN)$_2$(Pc(2-))]	2.49	1.89	2.00, br
Intermediate-Spin or Spin-Admixed 5-Coordinate			
FeCl(Pc(2-))	4.53	3.25	4.67, 2.0[d]
FeBr(Pc(2-))	4.09	3.20	vbr
FeI(Pc(2-))	3.62	2.32	nd
Fe(CF$_3$CO$_2$)(Pc(2-))	4.08	3.39	ESR silent
Fe(CCl$_3$CO$_2$)(Pc(2-))	3.90	3.06	2.0 radical (vw)
Fe(HCO$_2$)(Pc(2-))	4.09	nd	~6.3, ~4.3
Fe(CF$_3$SO$_3$)(Pc(2-))	4.14	nd	ESR silent
Fe(p-tolSO$_3$)(Pc(2-))	4.17	nd	ESR silent
High-Spin 5-Coordinate			
[Fe(Pc(2-))]$_2$O	2.19	1.17	*e*
(TBA)[Fe(SO$_4$)(Pc(2-))]	5.59	5.08	br, 3.8

[a] μ_{Fe} measured at about 30 temperatures in the range 4.2-300 K. [b] ESR spectra measured on neat powder at 110 K. [c] Key: ND, not determined; br, broad; vw, very weak; vbr, very broad. [d] Some samples of FeCl(Pc(2-)) show a different spectrum with a very broad line (1500 G peak-to-peak) centered at ~1800 G. All other spectral and magnetic properties are identical with those of the sample listed, suggesting that the nature of the polycrystalline structure may influence the line shape. [e] Complex g ~ 2 pattern; g = 6 (monomer impurity).

apply in the case of [Fe(CN)$_2$(Pc(2-))]$^-$.

ESR Spectra and Variable-Temperature Magnetic Susceptibilities. Powdered samples of dihydroxo, diphenoxo, and diazido complexes give well-resolved ESR spectra at 110 K with a three g value pattern typical of low-spin d^5 systems[24,25] (Table II, Figure 4). As indicated above, the bis(isothiocyanato) and bis(isocyanato) complexes give broad, ill-defined spectra, the resolution of which is not improved in frozen solvents (supplementary material). The dicyano complex gives a broad isotropic signal at g ~ 2, which undergoes an increase in line width as the temperature is decreased.[9] As far as we are able to ascertain from the literature, dicyanoiron(III) porphyrins (under similar conditions) give similar line shapes or no observable signal between 300 and 77 K.[26] Thus, apart from similarities in bulk susceptibility behavior, the ESR and Mössbauer features of the dicyano complex would indicate that its electronic structure is in fine detail different from that of the other examples.

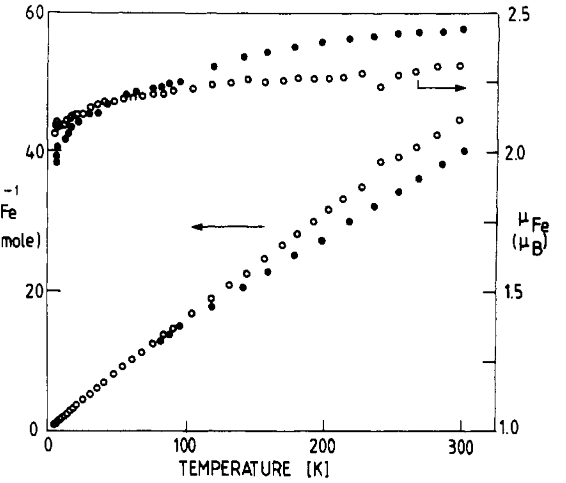

Figure 5. Variable-temperature magnetic moments and reciprocal susceptibilities for (PNP)[Fe(OH)$_2$(Pc(2-))] (○) and (PNP)[Fe(NCO)$_2$(Pc(2-))] (●).

The g values for the hydroxo, phenoxo, and azido species have been analyzed by use of the simple crystal field model applicable to rhombically distorted t$^5_{2g}$ configurations.[24,25] The calculated values of Δ/λ (tetragonal splitting in units of the spin-orbit coupling constant, λ), V/λ (rhombic splitting), and V/Δ (rhombicity) are given in Table III together with the same values for some related Fe(III) porphyrins[15,23,27,28] for comparison. The orbital reduction factor κ has been assumed to be 1.0. Summations of the squares of the coefficients of the d-orbital wave functions, $a^2 + b^2 + c^2$, are very close to 1.0 while a is close to 1.0, thereby confirming the general applicability of the model for a predominantly d$_{yz}$ orbital ground state.[25] The reduction of $\sum g^2$ from 16 in the present compound has also been observed in some related porphyrin systems.[23,27]

A number of points emerge from Tables II and III. The present phthalocyanine complexes and the analogous porphyrin complex [Fe(OMe)$_2$TPP]$^-$ have a low g_z value (~2.4), which combines to yield large values of the tetragonal splitting, Δ/λ, in the range 7.1-12.6. Such splittings, in combination with rhombicity values of 0.5-0.65, occur in the same region of Blumberg and Peisach's[24] "truth" diagrams as do various hydroxo-, alkoxo-, or phenoxo-ligated iron(III) porphyrins and heme proteins.[27,29] The Δ/λ values are much larger than the value of about 3.2 observed in many examples of cationic porphyrin complexes [FeB$_2$(porph)]$^+$, while the value for the anionic porphyrin [Fe(imid)$_2$TPP]$^-$ occurs somewhere in between.[23,27] There are few major differences within the small group of OH$^-$, OPh$^-$, and OMe$^-$-bonded complexes shown in Table III except for a small reduction in rhombicity in changing the equatorial ligand from Pc(2-) to TPP.

The variation of the magnetic susceptibilities with temperature is broadly the same for all the [FeL$_2$(Pc(2-))]$^-$ complexes, each showing Curie-Weiss behavior. There are some differences in the slopes of the χ_{Fe}^{-1}/T plots, especially at higher temperatures, which are reflected in the μ_{Fe} values (Table II). Typical plots are shown in Figure 5 for (PNP)[Fe(OH)$_2$(Pc(2-))] and (PNP)[Fe(NCO)$_2$(Pc(2-))]. This is the behavior expected for

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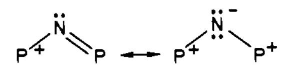
Table III. Crystal Field Parameters for Low-Spin Iron(III) Phthalocyanines and Selected Iron(III) Porphyrins

axial ligation mode	complex	$\sum g^2$	Δ/λ	V/λ	V/Δ	ref
O^-–Fe–O^-	$[Fe(OH)_2(Pc(2-))]^-$	14.5	12.61	6.46	0.51	*a*
	$[Fe(OPh)_2(Pc(2-))]^-$	13.5	9.58	6.01	0.621	*a*
	$[Fe(OMe)_2TPP]^-$	15.0	9.13	4.14	0.45	15
N^-–Fe–N^-	$[Fe(N_3)_2(Pc(2-))]^-$	13.3	7.13	3.74	0.52	10
	$[Fe(imid)_2TPP]^-$	15.7	4.25	2.70	0.63	27, 28
		15.7	3.82	2.41	0.63	23
N–Fe–N	$[Fe(imidH)_2TPP]^+$	15.9	3.24	2.04	0.63	23, 27

[a] This work.

a $^2T_{2g}$ ground state split by a combination of spin–orbit coupling and axial and rhombic components of the ligand field and displaying first- and second-order Zeeman effects. We have recently studied a wide range of low-spin Fe(III) porphyrins of the type $[FeB_2(porph)]^+$, and while these show magnetic behavior related to the that of the phthalocyanines, they give evidence for low-lying high-spin states, which is not evident in the present data. The ESR *g* values for the porphyrin complexes are also in detail different from those of the phthalocyanines.[30]

Another effect that could possibly influence the nature of the Mössbauer and ESR spectra, especially in the solid state, is that due to interactions between large bulky cations, such as PNP^+, and the $[FeL_2(Pc(2-))]^-$ moiety. The PNP^+ cations can exist in a linear conformation with valence-bond representations $P{=}N^+{=}P$, or in a bent conformation with valence-bond representations



While the bent geometry is common, the linear geometry is found[13] in $PNP[Fe(CN)_2(Pc(2-))]$. Spectroscopic data show that it is also linear in the N-bonded NCS^- and NCO^- complexes but bent (to about 145°) in the O-bonded OH^- and OPh^- species. This isomerism in the PNP^+ geometry seems to be independent of the central metal macrocycle and is probably induced in some way by the axial ligand. We are currently trying to obtain crystals of an O-bonded complex suitable for crystal structure determination, which would help us to test out these ideas. In a recent, and somewhat related situation,[15b] it has been observed that solvent methanol can hydrogen bond to the axial OMe^- ligands of $[Fe(OMe)_2TPP]^-$ in solution and thereby modify the ESR spectral parameters. A decrease in the Δ/λ and V/λ parameters accompanied an increase in hydrogen bonding, and this was thought to be due to changes in electron density at the iron brought about by changes in the donor strength of the OMe^- ligands.

Electronic Raman Effect in Resonance Raman Spectra. The complexes with L = CN^-, NCO^-, and NCS^- display Raman bands at 525, 490, and 520 cm^{-1}, respectively, which are much broader than all the other vibrational bands observed in the region 1800–150 cm^{-1}. Associated with each of these broad-band maxima are two or three weaker side bands in the range 510–460 cm^{-1}. As can be seen in the case of $(TBA)[Fe(NCS)_2(Pc(2-))]$ in Figure 6, these bands show intensity and positional changes with changing temperature, while the totally symmetric phthalocyanine vibrations at 760, 685, and 590 cm^{-1} do not change. The intensities of these bands also change as a function of the wavelength of the exciting laser line, being most intense for λ_0 = 514.5 nm, which is the wavelength corresponding to Pc → Fe electronic transitions. All of these data are consistent with these broad bands being assigned to electronic Raman transitions within the crystal field ground state of the low-spin Fe(III) ion. We have recently compared the L = CN^- data to those for $K_3[Fe(CN)_6]$ and $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, which have unequivocally been assigned to electronic Raman transitions.[9] A qualitative explanation has been given in the case of the dicyano complex[9] in terms of a splitting of the $^2T_{2g}$ ground state by spin–orbit couping into a ground $j = {}^1/_2$ level and upper $j = {}^3/_2$ level, the latter being split into two Kramers doublets by a tetragonal (D_{4h}) ligand field component. The 525-cm^{-1} band was assigned to the $j = {}^1/_2 \rightarrow j = {}^3/_2$ transition (i.e., λ = 350 cm^{-1}) with the broadening due to the tetragonal splitting. Similar assignments apply to the 490- (NCO^-) and 520-cm^{-1} (NCS^-) bands.

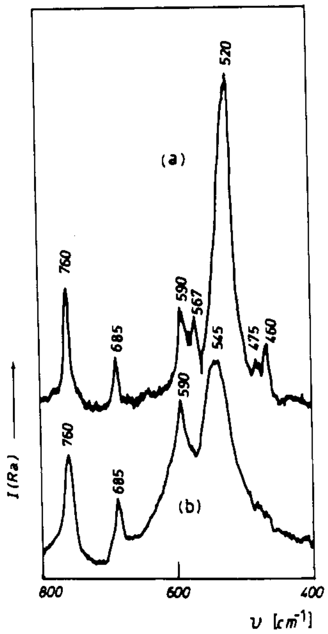


Figure 6. Resonance Raman spectra in the region 800–400 cm^{-1} for $(TBA)[Fe(NCS)_2Pc(2-)]$ at (a) 85 K and (b) 295 K. λ_0 = 514.5 nm.

In the ESR section, above, the related and complementary electronic model has been employed in which the nonoctahedral ligand field components (i.e. tetragonal and rhombic) cause the major splittings of the octahedral ground state with subsequent spin–orbit mixing between the levels. We have suggested that the splitting due to nonoctahedral ligand field components in the dicyano species is probably much reduced compared to that for the L = OH^-, OPh^-, and N_3^- species. The same situation may also apply for the NCO^- and NCS^- complexes although the differences in Mössbauer ΔE_Q parameters indicate that they are not completely analogous to the CN^- complex. These differences might be partly responsible for the lack of electronic Raman bands being observed in the OMe^-, OPh^-, and N_3^- complexes. In the latter case, and in the analogous diazidocobalt(III) complex, the ν(M–N) vibrations at 365 (Fe) and 360 cm^{-1} (Co) are enhanced by using a 514.5-nm excitation line. This enhancement correlates well with the $N_3^-(\pi) \rightarrow a_{1g}(d_{z^2})$ LMCT transition.

2. Intermediate-Spin ($S = {}^3/_2$) or Spin-Admixed ($S = {}^3/_2$–${}^5/_2$) Five-Coordinate Complexes. $FeCl(Pc(2-))$ was the first iron(III) phthalocyanine complex to be reported,[31] and despite a number of subsequent doubts as to its authenticity,[32] its ground state was correctly formulated as $S = {}^3/_2$ from some early Mössbauer measurements.[33] Later studies by Taube et al. showed that

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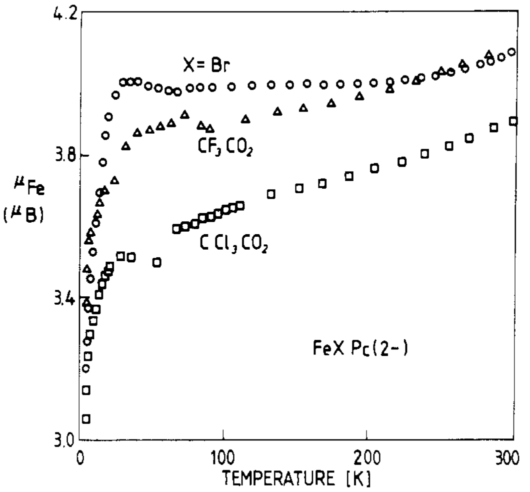

Figure 7. Magnetic moments as a function of temperature for three of the FeX(Pc(2−)) complexes. The data for FeCl(Pc(2−)) are given in ref 35.

FeBr(Pc(2−)) and Fe(p-tolSO_3)(Pc(2−)) also displayed three unpaired electrons.[34] Mössbauer spectroscopy has been particularly useful in distinguishing the spin state since there are dramatic differences in the value of the quadrupole splitting for high-, intermediate-, and low-spin states.

We have extended the range of these five-coordinate compounds to some eight or so derivatives containing halide or oxoanionic ligands. While some of these possess virtually pure $S = {}^3/_2$ ground states, it is clear from the present study that a number of them have low-lying high-spin states admixed into the ground state. FeCl(Pc(2−)) is one such example. As shown in a recent note,[35] the μ_{Fe} value at 300 K of 4.53 μ_B is significantly higher than the spin-only value of 3.87 μ_B, and it decreases to 3.25 μ_B at 4.2 K in a manner similar to that shown by the ${}^3/_2$–${}^5/_2$ iron(III) porphyrin, Fe($OClO_3$)TPP.[14,36] The ESR g values and Mössbauer spectral parameters (Tables I and II) support this electronic description. A good fit of the χ_{Fe}/T data was obtained[35] by using the theoretical model of Maltempo[37] with values of 310 cm^{-1} for the quartet-sextet-state separation and 180 cm^{-1} for the spin-orbit coupling constant being deduced. Limitations of the Maltempo model were pointed out in its application to FeCl(Pc(2−))[35] and to Fe($OClO_3$)TPP.[14,36]

The magnetic data for the bromo complex FeBr(Pc(2−)) (Figure 7) are compatible with a $S = {}^3/_2$ ground state with very little influence of any high-spin admixture. μ_{Fe} remains essentially constant at ca. 4.0 μ_B between 30 and 220 K and then increases gradually to 4.09 μ_B at 300 K. At temperatures below 30 K the moment decreases rapidly due to zero-field splitting of the quartet ground state. The Mössbauer parameters for FeBr(Pc(2−)) are similar to those of the chloro complex although with a slightly larger value of ΔE_Q. The iodide shows a further increase in ΔE_Q, indicating that a change in the axial halide ligand causes small changes in the ligand field. However, the dominant effect on the ligand–field splitting is due to the Pc(2−) group. This is further confirmed by comparison to the spin states of analogous porphyrin systems:[4,8,38] viz. FeCl(TPP), $S = {}^5/_2$; Mn(TPP), $S = {}^5/_2$; Mn(Pc(2−)), $S = {}^3/_2$. The lower observed μ_{Fe} values for FeI(Pc(2−)) compared to those of the chloro and bromo derivatives are probably due to the presence of $[Fe(Pc(2-))]_2O$ in the sample rather than to any inherent electronic differences. Area measurements on an inner quadrupole doublet in the Mössbauer spectrum of FeI(Pc(2−)) shows ca. 13% contamination by the μ-oxo complex. Quantitative fitting of the magnetic data for the bromo and iodo species was not attempted on account of the poor resolution of the ESR spectra not being able to provide g values required for an independent test of the Maltempo model. Nevertheless, the ${}^5/_2$–${}^3/_2$ spin-admixed interpretation is definitely applicable to these halide complexes (and to the O-bonded species described below). Alternative explanations such as weak intermolecular exchange between $S = {}^5/_2$ molecules or a ${}^5/_2 \rightleftharpoons {}^1/_2$ spin equilibrium, with or without residual high-spin component, will neither fit the susceptibility data nor be compatible with the Mössbauer spectral results. The Mössbauer spectra are extremely well resolved and show no evidence for the existence of $S = {}^5/_2$ or $S = {}^1/_2$ molecules (other than the contaminating μ-oxo species pointed out in Table I).

Room-temperature magnetic moments on the carboxylato and sulfonato species Fe(O_2CR)(Pc(2−)) and Fe(O_3SR)(Pc(2−)) are in the range 3.9–4.17 μ_B. These are again indicative of a $S = {}^3/_2$ ground state with only small admixtures of the $S = {}^5/_2$ state. The variations with temperature of μ_{Fe} for the trichloroacetate and trifluoroacetate complexes shown in Figure 7 display similar slopes. The small, but gradual increase at higher temperatures reflects the $S = {}^5/_2$ admixture. Weak exchange effects and/or presence of small amounts of the μ-oxo complex may be responsible for the lower μ_{Fe} values in the $CCl_3CO_2^-$ complex. The Mössbauer parameters for these compounds are similar to those of FeBr(Pc(2−)). Taube, Fluck, et al. have previously reported a larger ΔE_Q value (3.66 mm s^{-1} at 120 K) for Fe(p-tolSO_3)(Pc(2−)) and have used MO calculations in explaining the quadrupole splitting.[39] Except for broad signals at $g \sim 6.3$ and ~ 4.5 for the formate complex, no ESR lines were observed for powdered samples of the other carboxylate and sulfonate complexes under the same conditions as used for the spectrum of FeCl(Pc(2−)). This is probably due to a combination of relaxation rate differences and exchange broadening.

It is interesting to compare the present carboxylate and sulfonate complexes with related Fe(III) porphyrins. The carboxylates, Fe(O_2CR)(porph), are high spin like the halide derivatives.[19] The sulfonates, Fe(O_3SR)(porph), display $S = {}^3/_2$–${}^5/_2$-admixed ground states similar to that of the perchlorate, Fe($OClO_3$)(porph).[36] A complex such as Fe(O_3SCF_3)(TPP) has a μ_{Fe} value of 5.4 μ_B, which signifies that the percentage of the ${}^6A_1$ state is much higher than it is in Fe(O_3SCF_3)(Pc(2−)).

In general we see that the Pc(2−) complex has more $S = {}^3/_2$ character than the porphyrin analogue irrespective of whether the axial ligand is a weakly coordinating O donor or a more strongly coordinating halide. In any attempt to rationalize this equatorial ligand effect, a number of possible contributing factors must be considered. Structural factors will sensitively influence the spin state. The crystal structure of FeCl(Pc(2−)) has, somewhat fortuitously, just become available[40] from studies of the molecule $[FeCl(Pc(2-))]_2I_2$. The Fe–N_p bond length of 1.945 Å is shorter than that of 2.06 Å found in FeCl(TPP), in line with a smaller hole size and a stronger ligand field for Pc(2−). The out-of-plane Fe–N_4 distance, 0.30 Å, is smaller than that in FeCl(TPP), 0.39 Å, but similar to that in Fe($OClO_3$)(TPP), 0.28 Å.[8] These structural manifestations are typical of an intermediate-spin state. The basicity and bonding modes (σ and π) of Pc(2−) will also differ from those of TPP^{2-}. It is generally accepted that Pc(2−) is both a better π-acceptor and σ-donor than is TPP^{2-}.[41] Differences in the equatorial ligand field will affect the relative energies of the highest energy orbital, $d_{x^2-y^2}$ (b_1 in C_{4v}), and of the lowest, d_{xy} (b_2), the former being occupied in the $S = {}^5/_2$ state but not in the $S = {}^3/_2$ state.[8,42] This simple crystal field argument

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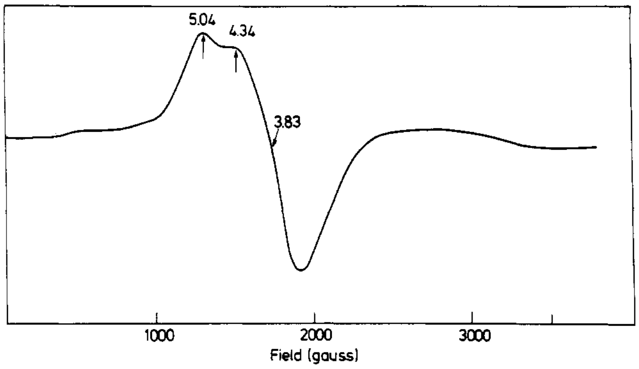

Figure 8. X-Band ESR spectrum of a neat polycrystalline sample of (TBA)[Fe(SO)$_4$(Pc(2−))] at 110 K. Effective g values are marked.

adequately explains the equatorial effects, but it is important to note, in general, that equatorial and axial ligand effects are interdependent in the present kind of molecule.[8,35]

3. High-Spin ($S = {}^5/_2$) Five-Coordinate Complexes. The only well-established high-spin iron(III) phthalocyanine is the μ-oxo binuclear complex [Fe(Pc(2−))]$_2$O[43,44] and some related μ-oxo complexes containing substituted Pc(2−) ligands.[45] Some less well established mononuclear complexes have also recently been described.[46,47] The Mössbauer data for [Fe(Pc(2−))]$_2$O given in Table I have recently been reported by ourselves[44] and others[48] and are clearly compatible with a $S = {}^5/_2$ ground state for Fe(III). The δ and ΔE_Q values are in the normal range observed for many other spin-coupled high-spin Fe(III)–μ-oxo complexes including the porphyrin analogue, (FeTPP)$_2$O.[19,49] The structures of many such μ-oxo complexes show nonlinear Fe–O–Fe bonds and displacement of iron from the equatorial plane.[49] The same structural features probably apply for the present complex. Suggestions[50] that [Fe(Pc(2−))]$_2$O in fact contains Fe(II) in an anionic formulation H$_2$[[Fe(Pc(2−))]$_2$O] is unlikely to be correct in view of both the Mössbauer data and the present method of synthesis using the Fe(III) precursor, [Fe(OH)$_2$)Pc((2−))]$^-$. A second minor doublet with δ 0.24 mm s^{-1} and ΔE_Q 1.38 mm s^{-1} is observed in the Mössbauer spectrum and is due probably to a monomeric $S = {}^5/_2$ impurity.[44]

Fitting of the μ_{Fe}/T data for the μ-oxo complex to a $S = {}^5/_2$ dimer model gave, after correction for the monomer component, a value of −120 cm^{-1} for the exchange coupling constant, J. This is similar to the value for (FeTPP)$_2$O and related μ-oxo porphyrins[49].

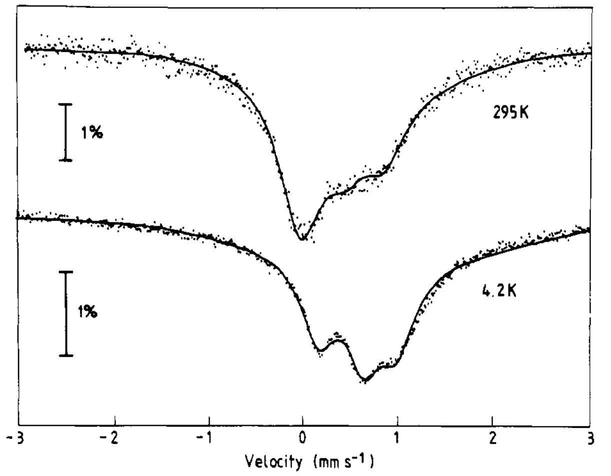

Figure 9. Mössbauer spectra of (TBA)[Fe(SO$_4$)(Pc(2−))]. The best-fit parameter values for the curves shown are as follows. For T = 295 K: δ = 0.18 mm s^{-1}, ΔE_Q = 0.49 mm s^{-1}, half-width = 0.26 mm s^{-1}; δ = 0.40 mm s^{-1}, ΔE_Q = 0.84 mm s^{-1}, half-width = 0.26 mm s^{-1}. For T 4.2 K: δ = 0.55 mm s^{-1}; ΔE_Q = 0.82 mm s^{-1}, half-width = 0.22 mm s^{-1}; δ = 0.62 mm s^{-1}, half-width = 0.21 mm s^{-1}. A broad base curve component was included in the fitting.

The anionic sulfato complex, (TBA)[Fe(SO$_4$)(Pc(2−))] also displays predominantly high-spin magnetic behavior. The magnetic moment, μ_{Fe}, at 295 K of 5.59 μ_B remains constant down to ca. 100 K, and then decreases to 5.08 μ_B at 4.3 K. This behavior is not precisely that expected for a monomeric $S = {}^5/_2$ system but is suggestive either of some lower spinstate character or of magnetic exchange interactions, perhaps between sulfato-bridged Fe(III)Pc centers. The ESR spectrum of a neat polycrystalline sample, shown in Figure 8, displays a broad asymmetric shape centered at g = 3.8, which is not the $g \sim 6$ result expected for an axially distorted d^5 monomer.[14,25] The Mössbauer spectrum further confirms the complexity of the system. Thus, in Figure 9 it can be seen that two electronically distinct Fe(III) sites appear to be present, the line shapes of which change intensity as a function of temperature. The 4.2 K spectrum could be fitted to a singlet with δ = 0.61 mm s^{-1} and a doublet with δ = 0.55 mm s^{-1} and ΔE_Q = 0.82 mm s^{-1}. Both of these δ values are close to the normal range for $S = {}^5/_2$ and are quite different from intermediate- or low-spin iron(III) values. It is possible that the central singlet could be due to some contaminating [Fe(Pc(2−))]$_2$O although the parameters, while close, are not those normally observed. Nevertheless, the data for this sulfato complex are generally indicative of high-spin behavior. It is not immediately obvious why the SO$_4^{2-}$ group should lead to a different spin stte than RSO$_3^-$ groups although the increased negative charge may well be important. We are currently studying other sulfato–iron(III)phthalocyanines obtained from reactions of sulfuric acid and iron(III)–Pc(2−) precursors.

Acknowledgment. This work was supported by the Australian Research Grants Scheme and the Monash University Special Research Fund (K.S.M.). We thank Drs. J. D. Cashion and J. R. Pilbrow for Mössbauer and ESR facilities.

Supplementary Material Available: X-Band ESR spectrum of powdered TBA[Fe(NCS)$_2$(Pc(2−))] at 110 K (1 page). Ordering information is given on any current masthead page.

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