Table II. Summary of Model and Calculated Distances
($Cr-O = 2.0$ cm $= 1.99$ Å[20])

Molecule	Model dist, Å	calcd dist, Å	Orientation
Methanol	3.85 (OH)	3.7	Preferential
(OH first)	4.80 (CH_3)	4.7	
DMSO	5.15	5.0	Preferential
(S=O first)			
Benzene	4.6	5.1	Random
(flat and cleft)			
Acetonitrile			Preferential, favors
(N first)	5.28	3.72	CH_3 first
(CH_3 first)	3.09		

$Cr-O = 1.99$ Å $= 2.9$ cm.[20] Several orientations for each molecule were assumed. While the distances should not be taken as absolute values, the good agreement between the calculated distances and distances assuming a given orientation should be indicative of preferential ordering in the outer solvation sphere. For example, methanol is preferentially ordered due to the molecule being oriented along its dipole[2] due to its participation in hydrogen bonding with the acetylacetonate oxygen. The methyl proton distance is very close to that calculated. Agreement for the hydroxyl proton is not as good due to the contribution of the contact term to $1/T_{2m}$ and to the contribution of the additional relaxation mechanism to $1/T_{2p}$. Best agreement for DMSO is obtained by assuming preferential orientation with the oxygen atoms pointed into the octahedral face of the $Cr(acac)_3$. For benzene, a random orientation of the flat and cleft positions best fits the data. The acetonitrile molecule, from the NMR calculations, has a mildly preferred orientation with the methyl group pointing into the octahedral face of the $Cr(acac)_3$. This unexpected orientation is probably stabilized by weak hydrogen bonding between the methyl protons and acetylacetonate oxygens. The methyl protons become capable of hydrogen bonding as a result of the electron-withdrawing nature of the cyano group. The preferential orientation of the methyl group of acetonitrile is further supported by the carbon-13 chemical shift and T_1 data. The methyl carbon is shifted 0.3 ppm downfield [0.1 ppm $Cr(acac)_3$] while the cyano carbon is unshifted. The corrected T_1's for the methyl and cyano carbons are 0.72 and 0.93 s, respectively. Since T_1 is proportional to $1/r^6$ for the electronic–nuclear dipole mechanism,[10] the methyl protons must be closer to the paramagnetic center.

Although the proton chemical shifts for each solvent were small upon addition of 0.1 M $Cr(acac)_3$, the carbon-13 chemical shifts were larger and of the magnitude reported previously.[5] Each of the carbon-13 chemical shifts, except that of the cyano group of the acetonitrile, moves downfield upon addition of the $Cr(acac)_3$, the range being 0.1–0.3 ppm.

Registry No. $Cr(acac)_3$, 13681-82-8; $Cr(en)_3^{3+}$, 15276-13-8; $Cr(DMSO)_6^{3+}$, 19122-76-0.

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Intermediate-Spin ($S = {}^3/_2$) Porphyrinatoiron(III) Complexes

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There is much current interest in the synthesis of new iron porphyrin complexes having unusual electronic states or coordinations. The most common types of iron porphyrins are the pentacoordinate high-spin ($S = {}^5/_2$) iron(III) complexes $Fe(P)X$ (P = porphyrinato dianion, X = anionic group), hexacoordinate low-spin ($S = {}^1/_2$) iron(III) complexes $Fe(P)L_2X$ (L = amine base), and hexacoordinate low-spin ($S = 0$) iron(II) complexes $Fe(P)L_2$. Recently, preparations of a few iron porphyrin derivatives containing high-spin ($S = 2$) and intermediate-spin ($S = 1$) iron(II) have been reported.[1-5] The former are thought[2,3] to be pentacoordinate with the iron atom substantially out of the plane of the porphyrinato nitrogen atoms, while the latter are tetracoordinate with a planar FeN_4 core.[3]

The only apparently unknown ground state for either iron(II) or iron(III) porphyrins is the unusual intermediate-spin ($S = {}^3/_2$) iron(III) state. Although this ground state is not known to occur in natural iron prophyrins, there is evidence for a low-lying $S = {}^3/_2$ state in some heme proteins,[6a] and a new iron–sulfur cluster with $S = {}^3/_2$ has recently been discovered in nitrogenase.[6b] Moreover, the preparation and characterization of $S = {}^3/_2$ tetraaza iron(III) systems has recently been reported.[7]

The criterion for obtaining the $S = {}^3/_2$ state for a d^5 ion is essentially the same as that for obtaining the $S = 1$ state for a d^6 ion: the $d_{x^2-y^2}$ antibonding orbital must lie well above the other d orbitals and be unoccupied, while the remaining four d orbitals must fill by Hund's rules. This requires strong bonding in the equatorial (xy) directions and very weak bonding (or none) in the axial direction so that d_{z^2} remains close in energy to the t_{2g} orbitals. It therefore seemed likely that the $S = {}^3/_2$ state could be stabilized in $Fe(P)X$ type complexes if X were a sufficiently weak-field anion.

Ogoshi et al.[8] have reported the preparation of octaethylporphyrinatoiron(III) perchlorate, $Fe(OEP)ClO_4$, and three of its monoamine adducts. The magnetic moments of all four complexes at 288 K were intermediate between those expected for high-spin and low-spin iron(III). These results, augmented by IR and reflectance spectra, were interpreted in terms of a ${}^6A_1-{}^2T_2$ spin equilibrium.[8] Although the temperature dependence of μ_{eff} for the three adducts appears to support this interpretation, only a single μ_{eff} value at 288 K was reported for $Fe(OEP)ClO_4$. We have now prepared this complex and its bis(ethanol) solvate by a new route and present clear evidence that in both compounds the iron(III)

atom has an intermediate-spin ground state, rather than existing as a mixture of high- and low-spin states.

Experimental Section

All physical measurements were made using equipment and procedures which have been described previously.[4,9]

Preparation of the Complexes. Octaethylporphyrinatoiron(III) chloride,[4,10] Fe(OEP)Cl, was dissolved in dichloromethane and shaken repeatedly with aqueous 2 M sodium hydroxide to give the dimeric μ-oxo-bis[octaethylporphyrinatoiron(III)],[11] which was dried over potassium carbonate. A solution of the dimer in dichloromethane was treated with several different aliquots of 2 M aqueous perchloric acid[12] in a separatory funnel. The aqueous phase was discarded and dichloromethane was gradually replaced by ethanol, using a rotary evaporator at 30 °C. This procedure afforded dark blue crystals of Fe(OEP)ClO$_4$·2EtOH, **1**. Anal. Calcd for C$_{40}$H$_{56}$N$_4$O$_6$ClFe: C, 61.50; H, 7.23; N, 7.17. Found: C, 61.46; H, 7.50; N, 7.23. When **1** was heated in vacuo at 60 °C for 6 h, the unsolvated species Fe(OEP)ClO$_4$, **2**, was obtained. Anal. Calcd for C$_{36}$H$_{44}$N$_4$O$_4$ClFe: C, 62.84; H, 6.45; N, 8.14. Found: C, 62.60; H, 6.48; N, 8.04.

Results and Discussion

Ogoshi et al.[8] prepared **2** by refluxing a benzene solution of Fe(OEP)Cl and AgClO$_4$. The present route is less hazardous in that it avoids both the use of a heavy-metal perchlorate and heating a perchlorate-containing organic solution.

Both **1** and **2** behaved as 1:1 electrolytes in ethanol, with $\Lambda_M \simeq 36$ Ω^{-1} cm^2 mol^{-1} for $\sim 10^{-3}$ M solutions.[13] The electronic spectrum of **2** (CH$_2$Cl$_2$ solution) exhibited a strong Soret band at 380 nm (ϵ_{max} 1.13 × 10^5) and two weaker absorptions at 500 and 633 nm (ϵ_{max} 9.2 × 10^3 and 3.2 × 10^3, respectively), in substantial agreement with Ogoshi et al.[8] The spectrum of **1** showed no important differences.

However, the anion modes in the IR spectra of **1** and **2** were significantly different.[14] For **1** the ν_3 band of the perchlorate ion was split into a doublet separated by 60 cm^{-1} and ν_4 was observed as a singlet. For **2**, on the other hand, the ν_3 splitting was 144 cm^{-1} (somewhat greater than that reported previously[8]) and ν_4 was also split by 7 cm^{-1}. Typical ν_3 splittings in "ionic" perchlorates are ≤60 cm^{-1},[15,16] those in complexes with weakly coordinated monodentate perchlorate groups are usually in the range $\sim$80–150 cm^{-1},[17-19] and in HClO$_4$ the splitting is 280 cm^{-1}.[17] Our results suggest a substantial difference in cation–anion interaction between **1** and **2** and a likelihood of different structures. Ogoshi et al.[8] have assigned a medium-intensity band at about 880 cm^{-1} in the IR spectrum of **2** to ν(Fe–O). We consider this assignment very doubtful since Fe(OEP)Cl also has an absorption at this energy.

The effective magnetic moments at 295 K were 4.5 μ_B (**1**) and 4.8 μ_B (**2**), the latter value agreeing with that given by Ogoshi et al.[8] The moment of **2** was found to decrease as the temperature was lowered, the following values being obtained: 4.4 μ_B (191 K), 4.2 μ_B (127 K), and 4.1 μ_B (84 K). Thus, at low temperature μ_{eff} approaches the spin-only value expected for a spin quartet state (3.9 μ_B) but is significantly larger at room temperature. Since the Mössbauer data (vide infra) rule out the possibility of a temperature-dependent equilibrium between two states of different spin multiplicity, the most likely explanation of the temperature dependence of μ_{eff} is that the ground state of **2** is a *quantum mechanical* admixture of spin quartet and spin sextet states, with the quartet lying lower.[6a] The magnetic moments at 295 K of the recently reported[7] tetraaza iron(III) complexes with $S = {}^3/_2$ ground states lie in the range 3.9–4.2 μ_B, implying less high-spin character of the ground states in these cases. Intermediate-spin porphyrinatoiron(II) complexes also have moments substantially larger than the $S = 1$ spin-only value.[3,4,20] However, it is not known whether these high values result primarily from orbital contributions or from quantum mixed-spin ground states, as only data at room temperature have been published.
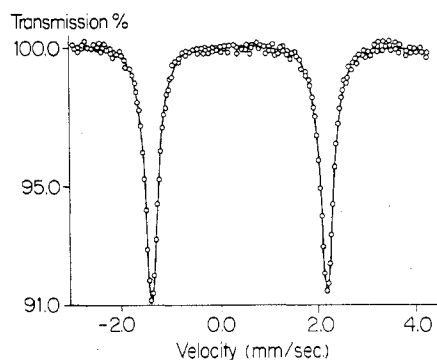

Figure 1. Mössbauer spectrum of [Fe^{III}OEP]$^+$ClO$_4^-$ at 115 K.

Table I. ^{57}Fe Mössbauer Parameters (in mm s^{-1}) for the Complexes[a]

Complex	T, K	δ	ΔE_Q	Γ_1	Γ_2
Fe(OEP)ClO$_4$·	4.2	0.38	3.47	0.31	0.30
2EtOH (1)	115	0.36	3.32	0.33	0.31
	295	0.28	2.97	0.31	0.31
Fe(OEP)ClO$_4$ (2)	4.2	0.37	3.57	0.29	0.31
	115	0.37	3.52	0.30	0.31
	295	0.29	3.16	0.27	0.26

[a] All values are believed accurate to ±0.01 mm s^{-1}. Isomer shifts are given relative to the centroid of the metallic iron spectrum.

^{57}Fe Mössbauer spectra offer convincing evidence for the $S = {}^3/_2$ ground-state assignment and the absence of any thermally induced spin crossover (Figure 1). The spectra of both complexes were characterized by narrow-line symmetric doublets at all temperatures studied between 4.2 and 295 K, with very large quadrupole splittings $|\Delta E_Q|$ (Table I). These splittings are much larger than those found for $S = {}^1/_2$ iron(III) porphyrins ($\sim$1.6–2.3 mm s^{-1})[20-23] and $S = {}^5/_2$ complexes ($\sim$0.6–1.3 mm s^{-1}).[20] $|\Delta E_Q|$ values for other known $S = {}^3/_2$ iron complexes [bis(N,N-dialkyldithiocarbamato)-iron(III)[24,25] and tetraaza iron(III)[7] derivatives] range from 2.3 to 3.0 mm s^{-1}. The present values are among the largest splittings observed for iron(III) compounds.

In every known case of thermal equilibrium between two spin states for either iron(II) or iron(III) complexes, Mössbauer spectra in the transition region show either gross line broadening or two separate quadrupole doublets (depending on the spin relaxation times). Thus, the fact that all the Mössbauer spectra of **1** and **2** recorded in zero magnetic field consisted of two narrow lines is only consistent with the presence of a single spin state. Together, the Mössbauer and magnetic data provide unequivocal evidence that these complexes contain intermediate-spin iron(III) atoms, with the $S = {}^3/_2$ ground state possibly having some high-spin character.

The difference of about 0.2 mm s^{-1} between the quadrupole splittings of **1** and **2** at a given temperature is considerably larger than one would expect if **1** were a simple solvate of **2**. The weaker iron–perchlorate interaction in **1** as shown by IR spectra also produces a smaller electric field gradient (EFG) at iron. This suggests the possibility of a specific interaction between iron and one or both ethanol molecules in this complex. Thus, whereas the iron atom in **2** is presumably pentacoordinate,[26] we think it likely to be hexacoordinate in **1**. Detailed x-ray structural analyses of both compounds are planned.

Mössbauer spectra of **1** and **2** recorded at $\sim$230 K in applied magnetic fields of 5.0 T indicated that in both cases the quadrupole coupling constant e^2qQ was positive, and the asymmetry parameter η of the EFG was nearly or exactly zero.[27] The most likely ground-state configuration for the iron nonbonding electrons is the $^4A_2$ orbital singlet[6a] (d$_{xy}$)^2(d$_{xz}$,

$d_{yz})^2(d_{z^2})^1$, which should not contribute to the EFG. The alternative ^4E orbital doublet configuration $(d_{xz}, d_{yz})^3$-$(d_{xy})^1(d_{z^2})^1$ should produce a large negative contribution to the EFG. Both of these predictions ignore covalency. In iron(II) phthalocyanine, a square-planar $S = 1$ complex, the contribution to ΔE_Q from covalency has been estimated to be +3.8 mm s^{-1}.[28] It would require a slightly smaller covalency correction ($\sim$+3.5 mm s^{-1}) to account for the observed splittings in **1** and **2** if the ground state is the $|xy\rangle$ singlet.[29] The $|xz, yz\rangle$ ground state would seem to require an impossibly large covalency correction to give the observed ΔE_Q values.

Mössbauer spectra of high-spin iron(III) porphyrin complexes invariably show asymmetric line broadening at temperature above 4.2 K owing to slow spin relaxation in higher lying Kramers doublets.[10,20,30] The absence of any relaxation broadening in the zero-field spectra of **1** and **2** suggests fast spin relaxation within both $|\pm^1/_2\rangle$ and $|\pm^3/_2\rangle$ doublets, since it is unlikely that the crystal field splitting parameter D is so large that only the $|\pm^1/_2\rangle$ doublet is occupied at 295 K.[31]

Although the zero-field spectra of **1** and **2** are quite similar, Mössbauer measurements at 4.2 K in applied magnetic fields of 5.0 T revealed pronounced differences. The spectrum of **1** under these conditions approximated to the triplet–doublet pattern typical of diamagnetic complexes, with an effective magnetic field at the ^{57}Fe nucleus of about 3.4 T (estimated from the triplet splitting). This suggests that electronic spin relaxation in **1** is very fast even in the presence of a large applied field. On the other hand, **2** gave a complex but well-resolved hyperfine-split pattern with an effective field, estimated from the total splitting of the spectrum, of about 24 T. (This is similar to the hyperfine field of 27 T found for a tetraaza iron(III) complex with $S = ^3/_2$ ground state.[7]) Thus, although in zero field at 4.2 K spin relaxation in **2** is fast compared to the nuclear precession frequency, it is nevertheless slow enough that an applied field of 5.0 T induces a large magnetization. These results appear to implicate spin–lattice rather than spin–spin relaxation as the dominant relaxation mechanism in these complexes, since the mean Fe–Fe separation in **2** is probably a bit less than in **1** (certainly no greater), and this would tend to make spin–spin relaxation faster in **2** rather than slower. This is another indication of significant structural differences between the two complexes.

Attempts to obtain EPR spectra have thus far been hampered by the very fast electronic relaxation. No signal was observed at 295 K for a polycrystalline sample of **2**, and even at 78 K the signals were extremely broad ($\sim$500–600 G) so that no accurate assignments could be made. However, the signals were centered at g values of approximately 2 and 4, consistent with a quartet ground state. We plan to carry out single-crystal EPR measurements at 4.2 K in an effort to obtain g values for the complexes.

It should be possible to prepare further examples of $S = ^3/_2$ iron porphyrins using other weak anions such as BF_4^-, PF_6^-, etc., and work in this direction is in progress.

Registry No. **1**, 60645-79-6; **2**, 50540-30-2.

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Potassium Hexaisothiocyanatovanadate(II). Preparation and Characterization of a New Vanadium(II) Compound

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Vanadium(II) has been scarcely investigated until now. Further knowledge on its coordination chemistry should be of interest as a counterpart to the well-known chemistry of isoelectronic chromium(III). In particular, a comparison between the two d^3 ions should be revealing under theoretical aspects. Binary complexes are desirable in this connection because their simplicity facilitates interpretation.

Until now no vanadium(II)–hexathiocyanato compound was known. The system V(II)/SCN$^-$ has been subjected to a few