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^1H and ^{13}C NMR Study of the Effects of Meso Substituents on the $S = 3/2, 5/2$ Spin State Admixture of (Perchlorato)(tetraarylporphinato)iron(III) Complexes

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The relative proportion of $S = 3/2$ and $S = 5/2$ states in the $S = 3/2, 5/2$ spin state admixture of (perchlorato)(tetraarylporphinato)iron(III) complexes can be altered by phenyl para substituents of varying electron-releasing or -withdrawing ability. ^1H and ^{13}C NMR spectra of 4-methoxy, 4-H, 4-chloro, and 4-trifluoromethyl derivatives indicate increasing $S = 5/2$ admixture with increasing substituent electron-withdrawing ability as measured by the Hammett σ constant ($p\text{-OMe} < p\text{-H} < p\text{-Cl} < p\text{-CF}_3$). The observed effects of spin state can be explained in terms of stabilization and increased population of the iron $d_{x^2-y^2}$ atomic orbital as electron density of the porphyrin ring is decreased. Consistent with this suggestion, (TPP(2,4,6-OCH₃))FeClO₄, which is substituted with highly electron-releasing groups, appears to exist in a nearly pure $S = 3/2$ state at ambient temperature. Comparison of NMR shifts of the pyrrole protons and carbons in the paramagnetic complexes supports a π -delocalization mechanism for unpaired spin density in the $S = 3/2$ spin state of iron(III). The shift insensitivity of the porphyrin meso carbons is consistent with delocalization from the porphyrin $3e(\pi)$ molecular orbital into the iron atomic orbitals of e symmetry (d_{xz}, d_{yz}).

Introduction

Quantum mechanically admixed $S = 3/2, 5/2$ (porphinato)iron(III) complexes have evoked considerable interest because of suggestions that the biologically important hemins cytochrome c' peroxidase¹⁻³ and (by inference) P-450^{4,5} may under certain conditions exist in this spin state admixture. ^1H and ^{13}C NMR has proven to be a particularly useful and sensitive technique for characterizing changes in spin state admixture, with the shifts of the pyrrole β -proton and α - and β -carbons serving as diagnostic indicators. The relative weight of each component in $S = 3/2, 5/2$ admixed (porphinato)iron(III) has been shown to be in part a function of the axial counterion ligand.⁶⁻⁹ We report results of ^1H and ^{13}C NMR studies on a series of (perchlorato)(*meso*-tetraarylporphinato)iron(III) complexes that indicate the admixture can also be modulated by changes in electron density distribution on the porphyrin ring resulting from meso aryl substituents of varying electron-withdrawing or -releasing capabilities.

A change from $S = 5/2$ to $S = 3/2$ results from interactions that raise the energy of the singly occupied iron $d_{x^2-y^2}$ orbital to a point where demotion of the electron to d_{xy} is favored.¹⁰ One mechanism involves contraction of the porphyrin core, brought about by axial coordination of the weak-field perchlorato ligand, which destabilizes the $d_{x^2-y^2}$ orbital through repulsive interactions with electron density centered on the pyrrole nitrogens.^{8,11} Another possible mechanism is suggested by MO calculations and ^1H NMR studies on *meso*-tetraarylporphyrin free bases¹² and ferric complexes¹³ in which porphyrin-protein interactions of heme-containing enzymes are modeled by varying the electron-withdrawing or -releasing capability of porphyrin-ring substituents. Corresponding changes in electron density occur in the porphyrin $3e(\pi)$ molecular orbital, which has a large component on the pyrrole nitrogens. The changes in electron density at the pyrrole nitrogens might be expected to modulate the $d_{x^2-y^2}$ energy level and consequently the proportion of $S = 3/2$ in the $S = 3/2, 5/2$ admixture, in accord with our observations.

Experimental Section

The porphyrin free bases were obtained by condensation of pyrrole with appropriately substituted benzaldehydes according to published methods.^{14,15} The benzaldehydes employed were commercially available and were used as received. The free bases were metalated

by refluxing with excess freshly prepared anhydrous ferrous chloride in dimethylformamide,¹⁶ and the crude chloro complexes were purified by chromatography on dry-packed alumina columns¹⁷ with chloroform eluant. The bands containing the chloro complexes and μ -oxo dimers (hydroxy complex for the 2,4,6-trimethoxy-substituted compound) were combined and treated with dry HCl to generate pure chloro complexes. The perchlorates were obtained initially as bis(tetrahydrofuran) adducts by treating the chloro complexes with 15% stoichiometric excess of anhydrous silver perchlorate in refluxing tetrahydrofuran (THF).⁸ Except for the highly hindered 2,4,6-trimethoxy complex, the coordinated THF could not be removed by heating under vacuum.⁷ The perchlorato complexes of the 4-phenyl-substituted compounds were obtained from the THF adducts by recrystallization from toluene followed by redissolution in chloroform or methylene chloride and precipitation by addition of heptane. Several of the complexes retained chlorocarbon solvent despite heating under reduced pressure (70 °C, 0.02 torr). The stoichiometry of included solvents was confirmed by integration of the solvate resonance in ^1H NMR spectra. Assignments of both ^1H and ^{13}C resonances are based upon published results for other mixed-spin (tetraarylporphinato)iron(III) complexes.^{6,7,18}

NMR spectra were recorded in chloroform-*d* on a Bruker WM250 spectrometer at 250 MHz for proton spectra and 62.8 MHz for carbon-13 spectra. Magnetic moments were determined from magnetic susceptibilities measured in the solid state at ambient temperature (22 °C) by using a Faraday balance. Calculated molecular weights included solvent of crystallization, and diamagnetic corrections were

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Table I. ^{13}C Resonances of Para-Substituted (Tetraphenylporphinato)iron Perchlorates

compd	^{13}C shifts, ppm ^a							
	pyrrole			phenyl				substituent
	β	α	meso	m	o	p	q	
(TPP(2,4,6-OCH ₃))FeClO ₄	91	60	238	95	218	166	30	58, 57.4
(TPP(4-OCH ₃))FeClO ₄	580	363	363	123	299	171	12	57
(TPP)FeClO ₄	634	438	368	143	301	140	21	
(TPP(4-Cl))FeClO ₄	680	508	352	140	299	147	21	
(TPP(4-CF ₃))FeClO ₄	790	661	346	139	301	141	25	122 ^b
(TPP(4-OCH ₃))FeClO ₄ ·2THF	615	448	327	123	277	169	32	58

^a Shifts given downfield from Me₄Si. ^b Quartet; $J = 269$ Hz.

applied by using Pascal's constants.

(Perchlorato)(tetraphenylporphinato)iron(III) ((TPP(4-OCH₃))-FeClO₄): IR (KBr) ν_{ClO_4} 1170, 1150, 1120, 840, 610 cm⁻¹; $\mu_{\text{eff}} = 5.2$ μ_{B} . Anal. Calcd for FeC₄₄H₂₈N₄ClO₄·2H₂CCl₂ (mol wt 938): C, 58.91; H, 3.44; N, 5.97. Found: C, 58.82; H, 3.34; N, 6.10.

(Perchlorato)(tetrakis(4-methoxyphenyl)porphinato)iron(III) ((TPP(4-OCH₃))FeClO₄): IR (KBr) ν_{ClO_4} 1170, 1100, 845, 600 cm⁻¹; $\mu_{\text{eff}} = 4.2$ μ_{B} . Anal. Calcd for FeC₄₈H₃₆N₄ClO₈·H₂CCl₂ (mol wt 973): C, 60.48; H, 3.94; N, 5.76. Found: C, 60.74; H, 4.38; N, 5.90.

(Perchlorato)(tetrakis(4-chlorophenyl)porphinato)iron(III) ((TPP(4-Cl))FeClO₄): IR (KBr) ν_{ClO_4} 1170, 845, 610 cm⁻¹; $\mu_{\text{eff}} = 4.7$ μ_{B} . Anal. Calcd for FeC₄₄H₂₄N₄Cl₅O₄·³/₂HCCl₃ (mol wt 1085): C, 50.80; H, 2.71; N, 4.98. Found: C, 50.80; H, 2.71; N, 4.98.

(Perchlorato)(tetrakis(4-(trifluoromethyl)phenyl)porphinato)iron(III) ((TPP(4-CF₃))FeClO₄): IR (KBr) ν_{ClO_4} 1165, 1125, 1105, 860, 625 cm⁻¹; $\mu_{\text{eff}} = 4.8$ μ_{B} . Anal. Calcd for FeC₄₈H₂₄N₄F₁₂ClO₄ (mol wt 1040): C, 55.43; H, 2.32; N, 5.39. Found: C, 55.64; H, 2.40; N, 5.16.

(Perchlorato)(tetrakis(2,4,6-trimethoxyphenyl)porphinato)iron(III) ((TPP(2,4,6-OCH₃))FeClO₄): IR (KBr) ν_{ClO_4} 1155, 1125, 835, 625 cm⁻¹; $\mu_{\text{eff}} = 4.6$ μ_{B} . Anal. Calcd for FeC₅₆H₅₂N₄ClO₁₆·HCCl₃ (mol wt 1247): C, 54.87; H, 4.28; N, 4.49; Fe, 4.48. Found: C, 54.9; H, 5.15; N, 4.44; Fe, 4.37.

Results

The ^1H NMR spectra of the perchlorato complexes of the series (tetrakis(4-methoxyphenyl)- (Ia), (tetraphenyl)- (Ib), (tetrakis(4-chlorophenyl)- (Ic), and (tetrakis(4-(trifluoromethyl)phenyl)porphinato)iron(III) (Id) show a marked downfield shift of the pyrrole β -proton resonance toward the high-spin value with increasing electron-withdrawing capability of the phenyl 4-substituents ordered according to the Hammett σ constants (4-OCH₃ < 4-H < 4-Cl < 4-CF₃; Figure 1). IR (KBr) bands of Ia-e are present in regions typical of the coordinated perchlorato anion, 1170-1100, ~850, and 640-600 cm⁻¹, as reported for other $S = 3/2$, $5/2$ spin-allowed (perchlorato)(tetraarylporphinato)iron(III) complexes.⁸ Coordination of THF has the effect of shifting the pyrrole proton resonance to lower field; in bis(tetrahydrofuran) Ia, "free perchlorate" bands at 1090 and 630 cm⁻¹ indicate displacement of the anion from the iron center. The pyrrole resonances of Ia-d exhibit the same degree of nonlinear dependence of upfield shift with decreasing temperature reported for other mixed-spin-state (tetraarylporphinato)iron(III) derivatives.^{7,8} Although the Hammett σ correlation cannot be applied to (TPP(2,4,6-OCH₃))FeClO₄ (Ie), the upfield shift of the pyrrole proton resonance of this highly basic (porphinato)iron complex at ambient temperature is striking (Figure 2) when compared to those of Ia-d or the high-spin value (~80 ppm). The range of shifts over the series Ia-e is also noteworthy, covering 57 ppm.

The shifts of both α and β pyrrole carbons of the mixed-spin-state perchlorates Ia-d are much smaller than for the corresponding high-spin iron complexes.^{6,18,19} As is the case for the pyrrole β -proton resonances, the carbons shift pro-

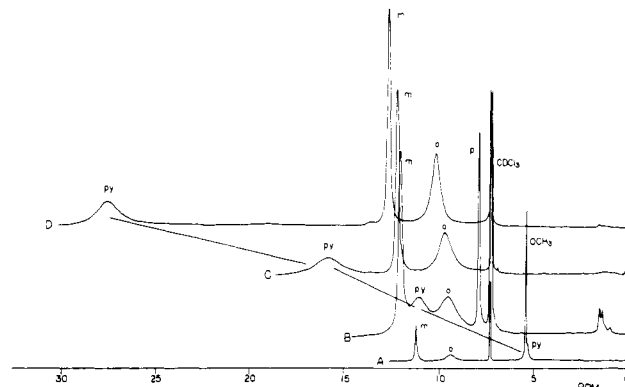


Figure 1. ^1H NMR (250 MHz, chloroform-*d*, 29 °C) of 4-substituted phenyl perchlorato complexes: (A) 4-methoxyphenyl; (B) unsubstituted tetraphenyl; (C) 4-chlorophenyl; (D) 4-(trifluoromethyl)phenyl. Proton designations: o, ortho H; m, meta H; p, para H; OCH₃, 4-methoxy H; py, pyrrole β -H. Solutions are ~2 mM in complex.

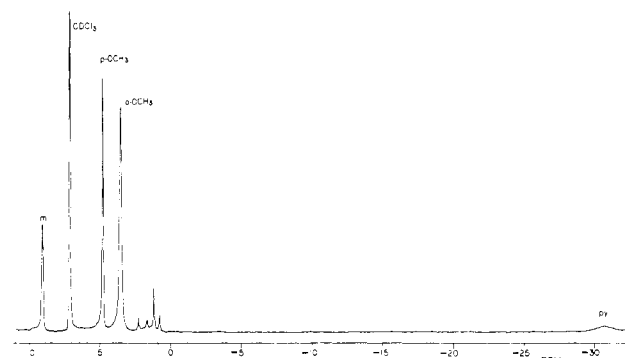


Figure 2. ^1H NMR (250 MHz, chloroform-*d*, 29 °C) of (perchlorato)(tetrakis(2,4,6-trimethoxyphenyl)porphinato)iron(III), ~0.8 mM. Proton designations: m, meta H; o-OCH₃, ortho-methoxy H; p-OCH₃, para-methoxy H; py, pyrrole β -H.

gressively downfield toward the high-spin positions as the electron-withdrawing character of the phenyl 4-substituent increases (Table I). The pyrrole carbon resonances of the bis(tetrahydrofuran) adduct of Ia reflect the slight shift toward high-spin values observed for the proton NMR. The meso ^{13}C resonances appear upfield from the high-spin range. Electron-withdrawing substituents cause a relatively slight upfield shift away from high-spin positions, with coordination of THF resulting in the largest upfield shift. The resonance of quaternary phenyl carbon (q) bonded to the meso position moves downfield in the perchlorates and, as for the meso carbon, the range of shifts is narrow.

For Ia, the meso and pyrrole carbon resonances experience a substantial upfield shift compared to those of Ia-d. Broadened signals at ~60 and ~30 ppm are tentatively assigned to the pyrrole β -carbon and quaternary phenyl carbon bonded to the meso position. As is the case for the proton data, the most striking feature of the carbon NMR spectra is the

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large range of shifts for the pyrrole resonances within the series Ia-e.

Discussion

The ^1H and ^{13}C NMR data present a self-consistent picture that appears to be in agreement with the current qualitative molecular orbital description⁷ of the intermediate-spin (porphinato)iron(III) compounds. Quantum-mechanical admixture involves partial depopulation of the iron $d_{x^2-y^2}$ atomic orbital and π -type unpaired spin delocalization by ligand-to-iron electron transfer from the porphyrin $3e(\pi)$ molecular orbital. The large changes we have induced in the proton and carbon shifts of the perchlorato complexes by varying the phenyl substituents are consistent with changes in occupancy of the $d_{x^2-y^2}$ iron orbital. Much smaller differences are reported (2-3 ppm) for substituent effects on the proton and carbon resonances of low-spin bis(imidazole)(porphinato)iron(III) complexes¹³ in which the same $3e(\pi) \rightarrow \text{Fe}$ spin-delocalization mechanism is operative but no change in iron orbital occupancy is involved. Therefore, changes in unpaired spin density distribution do not per se produce effects of the magnitude observed for Ia-e. The possibility that the pyrrole proton or carbon shifts result from an equilibrium phenomenon is discounted (for Ia-d) by the upfield progression of the pyrrole β -H resonance with decreasing temperature, which is typical of spin-admixed perchlorato complexes.^{7,8}

Upfield proton and carbon shifts are characteristic of $d_{x^2-y^2}$ vacancy²⁰ and are predicted for an increasing $S = 3/2$ component as $d_{x^2-y^2}$ becomes depopulated. The large upfield shift of the pyrrole proton of (TPP(2,4,6-OCH₃))FeClO₄ suggests that the $d_{x^2-y^2}$ orbital is vacant or nearly so in this complex,^{7,20} and hence the complex appears to approach the $S = 3/2$ spin state even at ambient temperature. In addition to the electronic effects of the strongly electron-releasing methoxy substituents, steric hinderance may weaken axial interaction between iron and the perchlorato ligand, causing a further increase in $d_{x^2-y^2}$ orbital energy by producing additional core contraction of the porphyrin.⁷

The observed movement of pyrrole ^1H resonances (Figure 1) toward high-spin shifts with increasingly electron-withdrawing phenyl substituents would result as the decreased repulsive interactions between the $d_{x^2-y^2}$ orbital and the attenuated spin density on the pyrrole nitrogens lower the $d_{x^2-y^2}$ orbital energy and the $d_{x^2-y^2}$ orbital is repopulated. The concomitant downfield shift of the pyrrole carbons is also consistent with behavior expected on repopulating the iron $d_{x^2-y^2}$ orbital with consequent enhancement of unpaired spin delocalization through σ interaction characteristic of the high-spin configuration.^{20,21} The relatively constant shift of the meso carbon resonance with changing spin-state admixture reflects small changes in the amount of delocalized unpaired spin density at the meso positions despite variation in spin-state admixture. Changes in unpaired spin density contributed by the high-spin component may be inefficiently transmitted through the σ -framework because of the E-geometric relationship of the meso position to the paramagnetic iron center. The π -delocalization mechanism postulated^{7,8} for the intermediate-spin component would be insensitive to the weight of the $S = 3/2$ component in the admixture if the $3e(\pi)$ porphyrin MO, which has a node at the meso carbons, is involved and contact shift makes the predominant contribution to the isotropic shift of the meso carbons. The effect of THF coordination is consistent with stabilization of the $d_{x^2-y^2}$ orbital through axial ligand interaction with iron and the ensuing expansion of the porphyrin core.

Because of crystallite orientation, included solvate, and single-ion anisotropy effects, solid-state magnetic moments cannot be accurately predicted⁸ and the values of μ_{eff} determined for the complexes serve primarily to confirm that the properties of Ia-e are consistent with an $S = 3/2, 5/2$ spin state admixture.

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Registry No. Ia, 91128-43-7; Ib, 57715-43-2; Ic, 92186-38-4; Id, 92186-39-5; Ie, 90764-29-7; (TPP(4-OCH₃))FeClO₄·2THF, 92219-73-3.

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Infrared Study of Ambient-Temperature Chloroaluminates as a Function of Melt Acidity

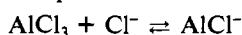
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The infrared spectra of butylpyridinium chloride/aluminum chloride and 1-methyl-3-ethylimidazolium chloride/aluminum chloride room-temperature molten salts have been examined over a range of mole ratios (acidities). Bands observed in the 4000-630-cm⁻¹ range have been assigned and spectral changes attributed to the formation of ion pairs, which may involve distortion of the aromatic ring since there is an accompanying loss of aromatic character. This effect is more pronounced in the imidazolium melts where more highly basic melts can be studied due to the greater liquidus range. Several isobestic points are reported. Addition of H₂O/D₂O to imidazolium melts gave rise to distinct new features in the spectra. In an acidic melt a new spectrum emerged after spectral subtraction, which is believed to be due to the formation of either AlO(OH) or, more likely, AlOHCl₂. Addition of H₂O/D₂O to a basic melt gave a complex spectrum.

Introduction

Until recently it has been accepted that melt equilibria in *N*-(1-butyl)pyridinium chloride (BuPyCl)/aluminum chloride (AlCl₃) and the 1-methyl-3-ethylimidazolium chloride (ImCl)/aluminum chloride room-temperature melts can be described by the two equilibria¹



The former is dominant in basic melts, i.e. where the AlCl₃:BupyCl mole ratio is less than 1, and the latter in acid melts, where the ratio is greater than 1. The role of the cation had been ignored until Wilkes et al.² and Popov³ undertook

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