

Figure 1. Boron NMR spectra (28.9 MHz): (A) B_2Cl_4 , 20% weight in CCl_4 , after 75 h at 100 °C (the resonances at -65, -62, and -47 ppm are due to B_8Cl_8 , B_2Cl_4 , and BCl_3 , respectively); (B) after ca. 14 days at 100 °C; (C) after removal of all very volatile material from the reaction (the resonance at -58 ppm is due to B_9Cl_9).

addition of pentane, no reaction is observed at ambient temperature. However, the formation of pentene commences upon raising the temperature to 100 °C.

In all of these reactions dihydrogen (material not condensable at -196 °C) is unobserved. The identity of all of the boron-containing products has not, as yet, been unequivocally proven; however, mass spectrometric and NMR evidence is consistent with the presence of partially hydrogenated nonaboron chlorides, e.g., $B_9H_4Cl_5$. Boron trichloride and HCl are also formed.

In conclusion, the chemistry of the polyhedral boron halides has been selected for study because these clusters lack the requisite or "magic" numbers of electrons ($2n + 2$) associated with the frameworks of many of the most stable deltahedral compounds,^{1,2} and it seemed most likely that unusual reactivity patterns might emerge.

We believe that some of the reactions above do illustrate that the polyhedral boron halides may well prove to have a most interesting and diverse chemistry. In particular they illustrate that at 100 °C B_8Cl_8 can accept hydrogen from pentane, liberating pentene in the process. The activation of CH bonds¹⁸ in this system is under further study.

Acknowledgment. The financial assistance of the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

Registry No. B_8Cl_8 , 32915-80-3; B_2Cl_4 , 13701-67-2; BCl_3 , 10294-34-5; $B_9(t-Bu)_9$, 83416-55-1; $CH_3B_9Cl_8$, 83416-56-2; $(CH_3)_2B_9Cl_7$, 83416-57-3; $(CH_3)_3B_9Cl_6$, 83416-58-4; B_9Cl_9 , 31304-34-4; $(CH_3)_4B_9Cl_5$, 83416-59-5; *n*-pentane, 109-66-0; 1-pentene, 109-67-1; 2-pentene, 109-68-2.

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Magnetic Interactions in Metalloporphyrin π -Radical Cations of Copper and Iron

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Received June 4, 1982

When a paramagnetic metalloporphyrin complex is oxidized to a π -radical cation, the opportunity exists for magnetic interactions between the unpaired electrons of the metal and the ligand. There is little understanding of the nature of this phenomenon, and also, there is conflict in the literature over the characterization of species that display it. For example, $[Cu^{II}(TPP)]^+$ (TPP = tetraphenylporphyrinate) and related copper porphyrins have been variously described as $S = 0$ or $S = 1$ systems.¹⁻⁴ Experimentally, three different states can be distinguished: (a) the diamagnetic $S = 0$ antiferromagnetic state, (b) the $S = 1$ ferromagnetic state having a spin-only magnetic moment $\mu_s = 2.83 \mu_B$, and (c) the independent spin $S = 1/2, S = 1/2$ state having $\mu_s = 2.45 \mu_B$.⁵ The distinction between b and c does not appear to have been considered previously. Unexpectedly, the present work reveals that a noninteracting $S = 1/2, S = 1/2$ state should be considered for the solution phase but that a strongly antiferromagnetically coupled $S = 0$ state exists in crystalline $[Cu(TPP\cdot)][SbCl_6]$. A further intriguing case is provided by the pair of closely related complexes $Fe^{III}(OCIO_3)_2(TPP\cdot)$ and $[Fe^{III}Cl(TPP\cdot)][SbCl_6]$.^{6,7} Although the latter was previously taken to be an iron(IV) complex,⁸ both are high-spin iron(III) radical cations, bringing together an $S = 5/2$ metal and an $S = 1/2$ ligand. The interesting observation is that the perchlorate complex behaves like an independent spin $S = 5/2, S = 1/2$ system, whereas the chloride complex is a strongly coupled overall $S = 2$ system. Moreover, the magnetic behavior of both complexes differs from that of compound I of horseradish peroxidase (HRP I), an $S = 1$ iron(IV)/ $S = 1/2$ porphyrin radical, which has been interpreted in terms of a weak antiferromagnet ($-J \sim 1.5 \text{ cm}^{-1}$).⁹

Synthetically, we are finding that selected organic radicals allow metalloporphyrin radical cations to be isolated in analytically pure crystalline form, many for the first time. Treatment of $Cu(TPP)$ or $Cu(TTP)$ (TTP = tetra-*p*-tolylporphyrinate) with tris(*p*-bromophenyl)ammonium hexachloroantimonate¹⁰ or thianthremium perchlorate,¹¹ respectively, in dichloromethane gives good yields of purple crystalline $[Cu(TPP\cdot)][SbCl_6]$ and $[Cu(TTP\cdot)][ClO_4]$.¹²

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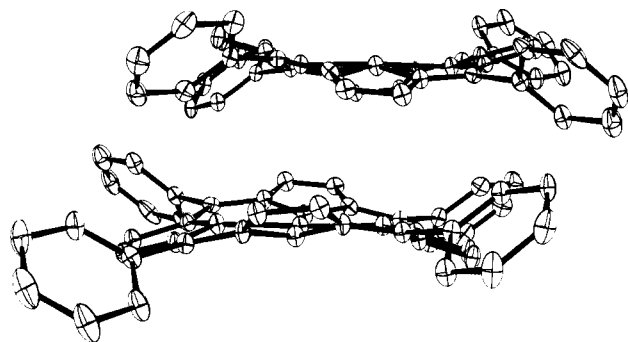


Figure 1. Edge-on view of the centrosymmetric $[\text{Cu}(\text{TPP}\cdot)]^+$ dimer. The Cu...Cu separation is 5.434 (3) Å. The extreme ruffling of the core allows interatomic contacts as short as 3.28 Å; however, the separation between the mean planes of the two cores is 3.84 Å. The closest approach of the copper atom to an atom of the other core is 3.57 Å. The average Cu-N distance is 1.988 (4) Å.

UV-vis spectra (λ_{max} for $[\text{Cu}(\text{TPP}\cdot)]^+$ in CH_2Cl_2 : 408 nm (Soret), 475, 630) concur with previous solution studies² and solid-state IR spectra, which show the diagnostic π -radical cation band⁷ at 1295 cm^{-1} , affirm porphyrin ring oxidation rather than copper oxidation. Repeated magnetic susceptibility measurements in dichloromethane- d_2 (^1H NMR shift method) give $\mu_{\text{corr}}^{300} = 2.4\ \mu_{\text{B}}$, suggestive of an $S = 1/2, S = 1/2$ state. Previous measurements ($\mu = 2.8\ \mu_{\text{B}}$) have been taken to indicate an $S = 1$ state, but uncertainty in the concentration may have led to an overestimate.² The lack of an EPR signal under normal conditions has also been interpreted in terms of an $S = 1$ state, although a new study on the octaethylporphyrin (OEP) analogue¹³ suggests that signals may become visible under different conditions. In contrast with this solution paramagnetism, $[\text{Cu}(\text{TPP}\cdot)][\text{SbCl}_6]$ is diamagnetic in the solid state (Faraday method). The X-ray crystal structure, shown in Figure 1, suggests a rationale for this. The cations consist of tightly associated pairs with unusually large ruffling of the porphyrin cores. Although dimers of octaethylporphyrin π cations are common,^{3,14,15} the existence of TPP \cdot dimers has previously been dismissed on the basis of phenyl group steric repulsion. The face-to-face π - π attraction lacks any recognizable specific orientation such as a HOMO-LUMO interaction or the popular, but unproven intermolecular metal-nitrogen interaction.^{16,17} Our first impulse was to ascribe diamagnetism to intermolecular π - π and d-d interactions arising in the dimer. However, while intermolecular π - π spin coupling in π radicals is very common, there is no evidence for more than trivial d-d coupling between cofacial $d_{x^2-y^2}$ orbitals. Indeed, tight dimers of $[\text{Cu}(\text{OEC}\cdot)]^+$ (OEC = octaethylchlorinate) whose copper atoms are ~ 4 Å apart show trivial d-d coupling ($-J \sim 2\text{ cm}^{-1}$)³ and the present structure has a much larger Cu-Cu separation (5.43 Å). For similar reasons intermolecular d- π coupling is considered unlikely. This leaves intramolecular d- π coupling within each $[\text{Cu}(\text{TPP}\cdot)]^+$ molecule as the likely source of complete diamagnetism. Apparently, the loss of D_{4h} symmetry in the ruffled porphyrin destroys the orthogonality of the ligand a_u and the metal $d_{x^2-y^2}$ magnetic orbitals thereby providing an overlap pathway for antiferromagnetic exchange. In solution, however, we assume that monomeric $[\text{Cu}(\text{TPP}\cdot)]^+$ is planar and that strict orthogonality of the magnetic orbitals gives rise to the paramagnetic state.

The same principles can be applied to the pair of high-spin iron(III) complexes, $\text{Fe}(\text{OCIO}_3)_2(\text{TPP}\cdot)$ and $[\text{FeCl}(\text{TPP}\cdot)][\text{SbCl}_6]$. The former can readily accommodate a centrosymmetric iron atom

and preserve strict magnetic orbital orthogonality, but the latter cannot. Crystalline $\text{Fe}(\text{OCIO}_3)_2(\text{TPP}\cdot)$ was prepared from $\text{Fe}(\text{OCIO}_3)(\text{TPP})$ ¹⁸ and thianthrenium perchlorate.¹² Its formulation as a porphyrin π radical rather than an iron(IV) complex is based on the collective evidence from UV-vis, IR, and Mössbauer spectroscopies. The Soret maximum (394 nm in dichloromethane) is blue-shifted and significantly lowered in intensity relative to $\text{Fe}(\text{OCIO}_3)(\text{TPP})$, and the α, β region is broad (λ_{max} 516 nm, 600, 672). The IR spectrum (KBr) shows the diagnostic π -radical band at 1285 cm^{-1} and is otherwise very similar to $\text{Fe}(\text{OCIO}_3)(\text{TPP})$ except that the perchlorate modes ($1150, 1115, 860, 615$ (br) cm^{-1}) have doubled intensities. This is indicative of bis-monodentate coordination. The crystal structure confirms symmetrical hexa-coordination and in addition shows that the porphyrin core is planar.¹⁹ The zero-field Mössbauer spectrum at 4.2 K is a quadrupole pair with δ 0.44 and $\Delta E = 1.65\text{ mm s}^{-1}$, these parameters being typical of high-spin ferric porphyrin complexes.²⁰ Application of a 6-T field over the range 4.2–300 K also produces spectra typical of axial high-spin complexes. Detailed simulation is achieved by assuming $D = 13\text{ cm}^{-1}$ and $A^* = 1.46\text{ mm s}^{-1}$ (21.5 T). For comparison we note that $[\text{Fe}(\text{Me}_2\text{SO})_2(\text{TPP})][\text{ClO}_4]$ ²⁰ has the same hyperfine coupling constant, A^* , and $D = 12.5\text{ cm}^{-1}$. The spectra at 6 T show no detectable sign of spin coupling, consistent with an $S = 5/2, S = 1/2$ independent spin state for the complex. Magnetic susceptibility measurements (Squid method) on the crystalline material show normal paramagnetism with a strictly linear Curie plot over the temperature range 4–300 K. The magnetic moment at 300 K is $6.1\ \mu_{\text{B}}$, and the same value was obtained in dichloromethane solution by NMR methods. Again, these results are suggestive of an independent $S = 5/2, S = 1/2$ spin state ($\mu_s = 6.17\ \mu_{\text{B}}$)⁵ rather than an $S = 3$ state ($\mu_s = 6.9\ \mu_{\text{B}}$).

By contrast, $[\text{FeCl}(\text{TPP}\cdot)]^+$ is an $S = 2$ system with $\mu_{\text{corr}}^{300} = 5.1\ \mu_{\text{B}}$ in the solid state⁶ and in dichloromethane solution (NMR methods). Mössbauer spectra show zero-field parameters typical of high-spin ferric complexes ($\delta = 0.39, \Delta E = 0.58\text{ mm s}^{-1}$ at 4.2 K), but high-field measurements are clearly not typical of a simple $S = 5/2$ system. In a 6-T applied field at 4.2 K the spectra are characteristic of an axially symmetric site with positive ΔE and a large transverse susceptibility. Preliminary fitting and spin coupling calculations with an $S = 2$ Hamiltonian have been interpreted to yield the parameters for the central iron complex $D = 16\text{ cm}^{-1}$ and $A^* = 1.46\text{ mm s}^{-1}$, both relative to an $S = 5/2$ Hamiltonian. These are in the range observed for high-spin ferric complexes.²⁰ Notably, the effective field H_{eff} is abnormally low (220 kG), consistent with strong antiferromagnetic coupling of high-spin iron(III) to an $S = 1/2$ radical. The manifest differences in magnetic properties of $\text{Fe}(\text{OCIO}_3)_2(\text{TPP}\cdot)$ and $[\text{FeCl}(\text{TPP}\cdot)]^+$ can be understood in terms of molecular symmetry. The D_{4h} $\text{Fe}(\text{OCIO}_3)_2(\text{TPP}\cdot)$ preserves strict orthogonality of its six magnetic orbitals, apparently giving rise to the uncoupled state, whereas the five-coordinate $[\text{FeCl}(\text{TPP}\cdot)]^+$ with its out-of-plane iron atom⁶ (and ruffled porphyrin core in the solid state)¹⁹ cannot. The result is an overlap pathway for strong antiferromagnetic exchange giving rise to an $S = 2$ state.

We have purposefully avoided discussion of a_{1u} vs. a_{2u} π -radical type since, even though all of the present species appear to be of the a_{2u} type by the modestly reliable criterion of solution UV-vis spectroscopy,⁴ there is no unambiguous criterion for the solid state. Besides, the orbital orthogonality arguments are unaffected by the radical type. It is likely, however, that the magnitude of spin coupling will be affected by the radical type. The magnitude will also be affected by the metal d orbital occupation and the extent of departure from D_{4h} symmetry. We note that HRP I, believed to be an iron(IV) a_{2u} radical, is a very weakly interacting system

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($-J \sim 1.5 \text{ cm}^{-1}$),⁹ suggesting that the heme group does not have a highly distorted structure.

The concept of orthogonal magnetic orbitals is currently enjoying considerable success in rationalizing ferromagnetic interactions.²¹ What is surprising about the present results is the lack of experimental evidence for ferromagnetic interactions in symmetrical systems, despite the close proximity of spins. And yet, upon distortion, very strong antiferromagnetic interactions can result. Continuing synthetic and structural investigations will test the generality of our observations. In particular, we are investigating Co(TPP)(SbCl₆), whose properties (broad, low intensity, blue-shifted Soret (405 nm) relative to Co(TPP) and broad α, β bands (544 nm, 605, 645); diagnostic IR band at 1290 cm⁻¹) identify it as a cobalt(II) radical rather than a cobalt(III) complex as previously reported.²² Like [Cu(TPP)]⁺, it is paramagnetic in solution ($\mu_{\text{corr}}^{300} = 2.5 \mu_B$) but diamagnetic in the solid state.

Acknowledgment. We are pleased to acknowledge and thank Dr. Jean-Claude Marchon for discussion of results prior to publication. This work was supported by The National Science Foundation (CHE 80-26812 to C.A.R.) and The National Institutes of Health (HL 15627 to W.R.S. and HL 16860 to G.L.).

Registry No. [Cu^{II}(TPP)]⁺, 28206-02-2; [Cu(TPP)](SbCl₆), 83435-78-3; Fe^{III}(OCIO₃)₂(TPP), 83435-87-4; [Fe^{III}Cl(TPP)](SbCl₆), 78023-40-2; Cu(TPP), 14172-91-9; Cu(TTP), 19414-66-5; [Cu(TTP)](ClO₄), 83435-80-7; tris(*p*-bromophenyl)ammonium hexachloroantimonate, 40927-19-3; thianthrenium perchlorate, 35787-71-4.

Supplementary Material Available: Table I, a summary of crystal data and intensity collection parameters for [Cu(TPP)](SbCl₆); Table II, fractional atomic coordinates in the unit cell; Table III, anisotropic thermal parameters, and structure factor tables (20 pages). Ordering information is given on any current masthead page.

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Iron(III)-Porphyrin π -Cation Radical Complexes. Molecular Structures and Magnetic Properties

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Received June 28, 1982

Interest in the synthesis and structure of high-valent iron porphyrin complexes stems from the demonstrated or proposed involvement of species of this type in various biological processes mediated by peroxidases,¹ catalases,² or cytochromes P-450³ and

in model systems.⁴ In this communication, we report on the full magnetic and structural characterization of two iron(III)-porphyrin cation radical complexes, and we suggest a qualitative explanation of the magnetic interactions observed in these compounds.

It was first reported a decade ago⁵ that five-coordinate (tetraphenylporphyrinato)iron(III) complexes FeX(TPP) can be oxidized electrochemically to reversible one-electron oxidation products FeX(TPP)⁺, but the latter have not been isolated, and their full characterization had to await the development of a better synthetic procedure. Recent work in these laboratories⁶ showed that the hexachloroantimonate salt of phenoxathiin cation radical is a convenient stoichiometric one-electron oxidant which cleanly yields FeCl(TPP)(SbCl₆), **1**, from FeCl(TPP). This product is isolable as black crystals. It has a magnetic moment of 4.9 μ_B , which is indicative of four unpaired electrons. Its Mössbauer spectral parameters ($\delta = 0.41 \text{ mm/s}$, $\Delta E_Q = 0.56 \text{ mm/s}$ at 4.2 K) are in the range of those observed for high-spin iron(III) porphyrins,⁶ and its ¹H NMR spectrum strongly suggests a singly occupied d_{x²-y²} orbital and a large spin density on a porphyrin orbital of a_{2u} symmetry.^{6,7} These data provide good evidence for a high-spin iron(III)-porphyrin cation radical configuration where the $S = 5/2$ iron is spin-coupled to the $S = 1/2$ porphyrin radical to give an overall $S = 2$ state. Further support to this assignment was brought recently by the detection of an infrared absorption band characteristic of porphyrin-centered oxidation.⁸ It is therefore likely that the alternative high-spin iron(IV) formulation, previously proposed on the basis of some solution spectroscopic data,^{5b,c} is erroneous.

An X-ray crystal structure of this complex was desirable to make a final decision on its electronic structure. Spin state-stereochemical relationships are well established for iron(II) and iron(III) porphyrins,⁹ and it was expected that high-spin iron(III), having an occupied d_{x²-y²} orbital, would show long Fe-N distances (ca. 2.05 Å). On the other hand, high-spin iron(IV), if present, would have an unoccupied d_{x²-y²} orbital and therefore shorter Fe-N distances (<2.00 Å). Crystals of **1** suitable for X-ray studies were grown from 1,1,2,2-tetrachloroethane/*n*-hexane, but crystallographic difficulties forced us to abandon them. An analogous tetra-*p*-tolylporphyrin complex, **2**, was prepared in a similar way and gave large black crystals of a 1,1,2,2-tetrachloroethane solvate of moderate quality, which were subjected to crystal structure analysis.¹⁰ The crystal lattice consists of discrete FeCl(TTP)⁺

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