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# Four-Coordinate Iron(II) Porphyrinates: Electronic Configuration Change by Intermolecular Interaction

**Chuanjiang Hu,† Bruce C. Noll,† Charles E. Schulz,*,‡ and W. Robert Scheidt*,†**

*Department of Chemistry and Biochemistry, University of Notre Dame,*
*Notre Dame, Indiana 46556, and Department of Physics, Knox College, Galesburg, Illinois 61401*

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The syntheses and structures of three four-coordinate iron(II) porphyrinates are reported. The three derivatives are tetraarylporphyrin species, where the aryl is either phenyl, *p*-methylphenyl, or *p*-methoxyphenyl. One of these derivatives, that of tetraphenylporphyrin, Fe(TPP), is a new crystalline phase that is distinct from the earlier reported phase (Collman, J. P.; et al. *J. Am. Chem. Soc.* **1975**, *97*, 2676). This new phase of Fe(TPP) has a very saddled porphyrin core; the prior phase was ruffled. The iron atom has close interactions (∼3.10 Å) with two pyrrole $C_b$–$C_b$ bonds above and below the porphyrin plane. Mössbauer spectra and magnetic susceptibility measurements, different for the two phases, provide strong evidence that the two phases of Fe(TPP) have distinct electronic structures that originate from intermolecular interactions.

We report that solid-state effects have a significant influence on the electronic structure of square-planar iron(II) porphyrinates. Although the electronic states of iron(II) porphyrinates have been intensively investigated both experimentally and theoretically, they are yet far from being determined (or understood) with certainty. Four-coordinate iron(II) porphyrinates or phthalocyanines are constrained by the macrocyclic ligand to square-planar coordination.

In an early theoretical investigation of $d^6$ iron(II) with $D_4$ symmetry, Griffith[1] noted that the orbital pattern always requires that the $d_{x^2-y^2}$ orbital be of higher energy than the other orbitals, and thus the species will always be intermediate spin ($S = 1$). Subsequently, the ground states of the intermediate-spin four-coordinate iron(II) porphyrins and phthalocyanines have been studied primarily by Mössbauer and magnetic susceptibility. The two most thoroughly investigated species are Fe(TPP)[2,3] and Fe(Pc). Despite their expected similarities, these two species have significant differences in their Mössbauer properties and magnetic susceptibilities.[4–8] Fe(TPP)($I\bar{4}2d$) has a much smaller quadrupole splitting value and a larger magnetic moment, which indicates that it has a different ground state than Fe(Pc). Most studies have assigned ${}^3E_gA$ $[(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1]$ as the ground state for $Fe^{II}$(Pc)[9–12] and ${}^3A_{2g}$ $[(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^2]$ for Fe(TPP)($I\bar{4}2d$).[9,13]

As part of our investigation of iron(II) porphyrinates, we have recently isolated and structurally characterized three four-coordinate $Fe^{II}$(Porph) complexes. These derivatives (Porph = TPP, TTP, T-*p*-$OCH_3$PP) were synthesized by reduction of the corresponding $[Fe(Porph)]_2O$ complex.[14] ORTEP diagrams for all three crystalline derivatives are shown in Figure 1; packing diagrams are given in the Supporting Information. Solvent interactions are minimal. Fe(TTP) has crystallographically imposed inversion sym-

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* To whom correspondence should be addressed. E-mail: cschulz@knox.edu (C.E.S.), Scheidt.1@nd.edu (W.R.S.).

† University of Notre Dame.

‡ Knox College.

(1) Griffith, J. S. *The Theory of Transition-Metal Ions*; Cambridge University Press: London, 1961; pp 370−373.

(2) Abbreviations: Porph, a generalized porphyrin dianion; TPP, dianion of *meso*-tetraphenylporphyrin; TTP, dianion of *meso*-tetratolylporphyrin; T-*p*-$OCH_3$PP, dianion of *meso*-tetra-*p*-methoxyphenylporphyrin; Pc, phthalocyanine; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEC, *trans*-7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato(octaethylchlorinato) dianion; $F_8$TPP, dianion of *meso*-tetra(2,6-difluorophenyl)porphyrin; $TF_5$PP, dianion of *meso*-tetra-(pentafluorophenyl)porphyrin; TPrPc, 2,7,12,17-tetrapropylporphycene; $N_p$, porphyrinato nitrogens; THF, tetrahydrofuran.

(3) The original preparation of crystalline Fe(TPP), a crystalline phase reported by Collman et al.[4] in 1975, crystallizes in the tetragonal system and appears to be the generally studied phase. We denote this phase as Fe(TPP)($I\bar{4}2d$).

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(14) The four-coordinate species $Fe^{II}$(Porph) was prepared by reduction of $[Fe(Porph)]_2O$ in different solvents with excess ethanethiol (>200 fold) according to Stolzenberg et al.[15] More detail is given in the Supporting Information.

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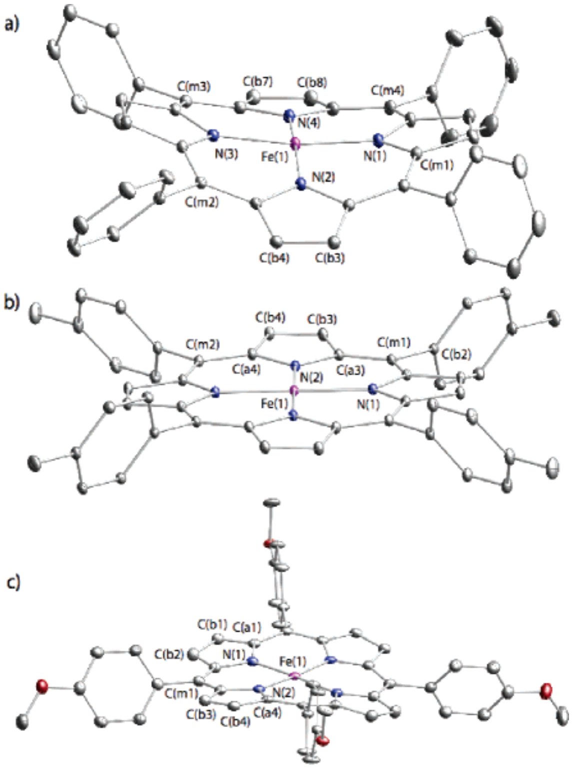

**Figure 1.** ORTEP diagrams for three Fe(Porph) complexes: (a) Fe(TPP)($P\bar{1}$); (b) Fe(TTP); (c) Fe(T-*p*-$OCH_3$PP). The hydrogen atoms of the porphyrin ligands have been omitted for clarity. 50% probability ellipsoids are depicted.

**Table 1.** Selected Structural Data for Fe(Porph) and Related Species

| compound | conf[a] | Fe−$N_p$[b] | closest intermolecular distance to iron[b] | ref |
|---|---|---|---|---|
| Fe(TTP) | pla | 1.986(1) | >4.0 | tw |
| Fe(T-*p*-$OCH_3$PP) | ruf | 1.976(1) | >3.95 | tw |
| Fe(TPP)($P\bar{1}$) | sad | 1.966(2) | 3.10 (Fe⋯$C_\beta$) | tw |
| Fe(TPP)($I\bar{4}2d$) | ruf | 1.972(4) | >3.9 | 12 |
| Fe(OEP) | pla | 1.996(16) | >3.47 (Fe⋯$C_\alpha$) | 23 |
| Fe(OEC) | ruf | 1.982(16) | 3.12 (Fe⋯$C_m$) | 23 |
| Fe(Pc) | pla | 1.926(1) | 3.24 (Fe⋯$N_m$) | 20 |
| Fe($F_8$TPP) | pla | 2.002(2) | 3.11 (Fe⋯$C_s$[c]) | 24a |
| Fe($TF_5$PP) | pla | 1.994(6) | 3.06 (Fe⋯$C_s$[c]) | 24b |
| Fe(TPrPc) | pla | 1.915(24) | 3.32 (Fe⋯C5A) | 24c |

[a] Predominant core conformation contribution: pla, planar; ruf, ruffled; sad, saddled. [b] In angstroms. [c] $C_s$, carbon atom of the solvate molecule.

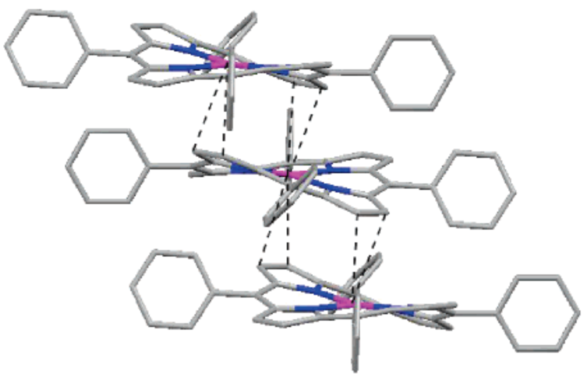

**Figure 2.** Intermolecular interactions for Fe(TPP)($P\bar{1}$). Dashed lines link atoms with closest intermolecular distances.

metry and Fe(T-*p*-$OCH_3$PP) twofold symmetry, whereas a new phase of Fe(TPP)($P\bar{1}$) has no required symmetry. This complex also has a distinctly saddled core conformation, very different from those previously observed for Fe(Porph) species, all of which were either planar or ruffled. Selected structural data are listed in Table 1. Observed Fe−$N_p$ distances in these four-coordinate complexes are much shorter than those in high-spin species, 2.057(4) Å in [Fe(TPP)$(THF)_2$],[16] 2.067(7) Å in [Fe(TTP)(THF)$)_2$],[17] and 2.080 Å in five-coordinate imidazole-ligated species,[18] consistent with the expected intermediate-spin state for iron. Formal core diagrams along with averaged bond distances and angles for the porphyrin cores are given in Figure S1 in the Supporting Information. As is commonly observed, the saddled and ruffled Fe(TPP) complexes have shorter Fe−$N_p$ distances than planar Fe(T-*p*-$OCH_3$PP) and Fe(OEP).[19]

The new Fe(TPP)($P\bar{1}$) structure is a toluene solvate,[20] quite different from the previously reported unsolvated form. The crystal packing is significantly different between the two. There are no close contacts in Fe(TPP)($I\bar{4}2d$), with the closest intermolecular approach to iron greater than 3.9 Å. However, for Fe(TPP)($P\bar{1}$), there are $\pi-\pi$ interactions between adjacent porphyrin molecules as shown in Figure 2. In this packing arrangement, adjacent porphyrin rings have individual pyrrole rings nesting into each other to form a one-dimensional ABAB chain. The two $\beta$-carbon atoms of adjacent pyrrole rings interact with the iron atom of the molecule above and the molecule below, yielding very short intermolecular distances (3.098, 3.239 Å and 3.142, 3.266 Å). The arrangement of the two $C_b-C_b$ "double"-bond interactions around the iron atom is approximately orthogonal. These ethylenic interactions and other close contacts are associated with the saddled core conformation. Similar packing arrangement, core conformation, and explanation were noted for isomorphous Co(TPP) some time ago.[21]

We note that the differences in iron environments are similar to those found between Fe(Pc) and Fe(TPP)($I\bar{4}2d$). The crystalline environment in Fe(TPP)($P\bar{1}$) leads to iron becoming pseudo-six-coordinate (Table 1). Similarly, *meso*-nitrogen atoms of adjacent Pc rings in centrosymmetric Fe(Pc) are 3.24 Å away, generating a pseudo-six-coordinate environment for iron.[22] Such axial interactions should lead to an increase in the energy of the $d_{z^2}$ orbital, which could cause a change in the relative d-orbital energy levels. Most theoretical calculations[11,25,26] agree that the $^3A_{2g}$ and $^3E_gA$

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**Table 2.** Mössbauer and Magnetic Data for Fe(TPP)($P\bar{1}$) and Related Species

| | Mössbauer data | | | magnetic data | | | |
|---|---|---|---|---|---|---|---|
| compound | temp, K | $\Delta E_\text{Q}$, mm/s | $\delta$, mm/s | temp, K | $\mu_{\text{eff},}$[a] $\mu_\text{B}$ | $D$, cm$^{-1}$ | $g_\text{iso}$ |
| Fe(TPP)($I\bar{4}2d$) | 4.2 | 1.51[b] | 0.52 | 5−300 | 4.2,[b] 4.4[c] | 70 | 2.94 |
| Fe(Pc) | 4 | 2.70[d] | 0.49 | 1.6−300 | 3.9 | 64 | 2.74 |
| Fe(TPP)($P\bar{1}$)[e] | 20 | 2.21 | 0.57 | 1.8−300 | 4.0 | 108 | 2.77 |
| Fe(OEC) | 4.2 | 2.55[f] | 0.63 | 296 | 3.5[f] | | |
| Fe(OEP) | 4.2 | 1.71[f] | 0.62 | 296 | 4.6[f] | | |

[a] Room temperature. [b] Reference 7. [c] Reference 4. [d] Reference 6. [e] This work. [f] Reference 23.

states are low-lying and separated by an energy ranging from several hundred to two thousand reciprocal centimeters. Mispelter's calculations[27] further suggest that a small axial perturbation can induce a reverse of these two-electron configurations. So the energy levels in iron(II) porphyrin could be affected by differences in the crystal packing,[7,27] which could lead to different electronic configurations.

Accordingly, we have further investigated properties that could provide insight into the similarities and differences in the electronic structures between the two forms of Fe(TPP). The Fe(Pc) versus Fe(TPP)($I\bar{4}2d$) dichotomy suggests that the Mössbauer quadrupole splitting values observed for Fe(TPP)($P\bar{1}$) would be higher than that seen for the other crystalline form of Fe(TPP). As shown in Table 2, that is indeed the case (2.21 vs 1.51 mm/s). This quadrupole splitting value difference is consistent with a shift from a $^3A_{2g}$ state for Fe(TPP)($I\bar{4}2d$) to a $^3E_gA$ state for Fe(TPP)($P\bar{1}$). (The similar Fe−$N_p$ distances in these two phases rule out covalency effects as the factor of the $\Delta E_\text{Q}$ change.) The use of these simple assignments must be tempered by the recognition that all $S = 1$ states are quite close in energy.[11,25,26] Values of $\Delta E_\text{Q}$ for related species are also given in Table 2. It is seen that Fe(OEP) has a smaller $\Delta E_\text{Q}$ than Fe(OEC) does, consistent with differences in iron environments that are similar to those of Fe(TPP).

These results suggest that the magnetic susceptibilities of the two Fe(TPP) phases should also display differences with Fe(TPP)($P\bar{1}$) having lower values of magnetic moment over the entire range of measurements. Magnetic moments for Fe(TPP)($P\bar{1}$) over the temperature range 1.8−300 K are shown in Figure 3. For comparison, the results of Boyd et al.[7] for Fe(TPP)($I\bar{4}2d$) have also been plotted in Figure 3 (top curve). Both data sets have been fit as described in the figure caption. A characteristic feature of all of the magnetic susceptibility fits of four-coordinate species has been a very large value of the zero-field-splitting parameter, $D$.

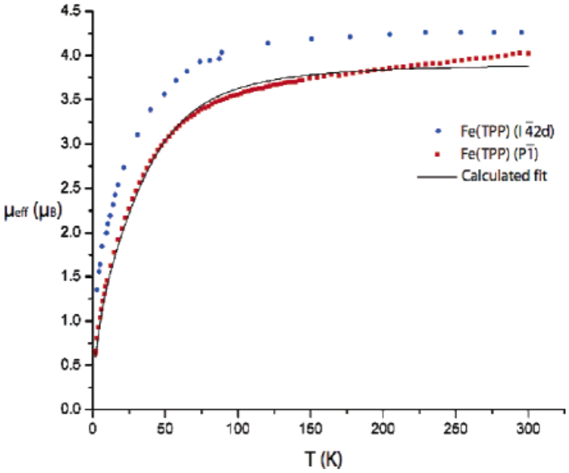

**Figure 3.** Temperature dependence of the magnetic moment of the polycrystalline samples. Top curve: Fe(TPP)($I\bar{4}2d$). Bottom curve: Fe(TPP)($P\bar{1}$). The diagram $\mu_\text{eff}$ vs $T$ was fitted by the equation $\mu_\text{eff} = 2.83(\chi T)^{1/2}$, where $\chi = 1/3(2\chi_\perp + \chi_{||}) = 1/3\{2Ng_{||}^2\mu_\text{B}^2/\kappa T[\exp(-D/\kappa T)]/[1 + 2\exp(-D/\kappa T)] + 4Ng_\perp^2\mu_\text{B}^2/D[1 - \exp(-D/\kappa T)]/[1 + 2\exp(-D/\kappa \text{T})]\}$ as in ref 28 and $g_{||} = g_\perp = g_\text{iso}$.

In summary, the syntheses and structures of three new four-coordinate iron(II) porphyrinate derivatives are reported. Most significantly, the synthesis and characterization of a second crystalline form of Fe(TPP) has shown that weak axial interactions in the solid state are sufficient to lead to a change in the electronic character of the intermediate-spin complex, with the state $^3E_gA$ becoming more favorable than the $^3A_{2g}$ state. This conclusion is supported by Mössbauer and magnetic susceptibility measurements that have been made on both crystalline forms.

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**Supporting Information Available:** Experimental details, Table S1 listing variable-temperature Mössbauer parameters, Tables S2−S19 giving complete crystallographic details, atomic coordinates, bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions, Figure S1 giving diagrams with displacement of each core atom from the 24-atom core, Figures S2−S4 giving packing diagrams, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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