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Nature of Iron(I) and Iron(0) Tetrphenylporphyrin Complexes. Synthesis and Molecular Structure of (Dibenzo-18-crown-6)bis(tetrahydrofuran)sodium (*meso*-Tetrphenylporphinato)ferrate and Bis[tris(tetrahydrofuran)sodium] (*meso*-Tetrphenylporphinato)ferrate

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A synthetic and structural investigation of the so-called iron(I) and iron(0) tetrphenylporphyrin complexes, $[\text{Fe}(\text{TPP})]^-$ and $[\text{Fe}(\text{TPP})]^{2-}$, resolves a number of the existing ambiguities about their identity. $[\text{Fe}(\text{TPP})]^-$ has a low-spin $S = 1/2$ state and is devoid of axial ligation at least in the solid state where it crystallizes as the purple, air-sensitive $[\text{Na}(\text{dibenzo-18-crown-6})(\text{THF})_2]^+$ salt. Crystal data: $\text{C}_{72}\text{H}_{68}\text{O}_8\text{N}_4\text{FeNa}$, monoclinic, space group $P2_1/m$, $a = 12.796$ (2) Å, $b = 21.861$ (4) Å, $c = 12.108$ (2) Å, $\beta = 103.47$ (1)°, $Z = 2$; $\text{Fe}-\text{N}_p(\text{av}) = 1.980$ (6) Å. Analysis of the structural data requires inclusion of substantial iron(II) π -radical anion character in the previously favored iron(I) formulation. The green dianion $[\text{Fe}(\text{TPP})]^{2-}$ has been isolated for the first time. It is diamagnetic and crystallizes in a tightly ion-paired structure where two $[\text{Na}(\text{tetrahydrofuran})_3]^+$ cations interact with a pair of porphinato nitrogen atoms ($\text{Na}\cdots\text{N} = 2.784$ (4), 2.825 (4) Å) above and below the porphyrin plane. The porphinato core bond lengths reveal considerable π -radical anion character. Crystal data: $\text{C}_{68}\text{H}_{76}\text{O}_6\text{N}_4\text{FeNa}_2$, triclinic, space group $P\bar{1}$, $a = 11.877$ (3) Å, $b = 13.242$ (3) Å, $c = 11.242$ (2) Å, $\alpha = 113.69$ (2)°, $\beta = 110.01$ (2)°, $\gamma = 77.55$ (2)°, $Z = 1$; $\text{Fe}-\text{N}_p(\text{av}) = 1.968$ (1) Å.

The precise nature of species referred to as iron(I) porphyrins has never been particularly clear. Their existence, as discrete species that are reduced by one or more electrons below the iron(II) oxidation level, was first established in the early solution studies of Cohen et al.³ and Lexa et al.^{4,5} Renewed attention was given to these reduction products once it was recognized that they might be useful for investigating certain aspects of cytochrome P-450 chemistry.⁶⁻⁹ However, each successive study revealed inconsistencies with a prior one. The issue of spin state was particularly confusing as was the nature of axial ligation chemistry, if any. There was also the fundamental question of the appropriateness of the iron(I) formulation and the d configuration of the ground state. A critical review¹⁰ published in 1982 identified these problems and suggested a consistent interpretation for the conflicting data in the primary literature. In this paper we provide the full experimental details that substantiate this interpretation. In particular, we report the syntheses and crystal structures of materials containing the ions $[\text{Fe}(\text{TPP})]^-$ and $[\text{Fe}(\text{TPP})]^{2-}$ (TPP = tetrphenylporphyrinate).¹¹ The important conclusions are that these anions are unambiguously low spin, they have no apparent axial ligation chemistry, and since they have manifest radical anion character, the iron(I) and iron(0) labels must be used quite guardedly.

Experimental Section

All manipulations were carried out in an inert-atmosphere glovebox as previously described.¹²

Table I. Summary of Crystal Data and Intensity Collection Parameters

	$[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2][\text{Fe}(\text{TPP})]$	$[\text{Na}(\text{THF})_3]_2[\text{Fe}(\text{TPP})]$
empirical formula	$\text{NaFeO}_9\text{N}_4\text{C}_{76}\text{H}_{76}$	$\text{Na}_2\text{FeN}_4\text{O}_6\text{C}_{68}\text{H}_{76}$
cryst dimens, mm	$0.2 \times 0.3 \times 0.7$	$0.18 \times 0.75 \times 1.1$
temp, °C	20 ± 1	20 ± 1
a, Å	12.796 (2)	11.877 (3)
b, Å	21.861 (4)	13.242 (3)
c, Å	12.108 (2)	11.242 (3)
α , deg	90.0	113.69 (2)
β , deg	103.47 (1)	110.01 (2)
γ , deg	90.0	77.55 (2)
V, Å ³	3293.8	1515.2
space group	$P2_1/m$	$P\bar{1}$
d_{caled} , g/cm ³	1.28	1.26
Z	2	1
radiation	graphite monochromated Mo K α ($\bar{\lambda} = 0.71073$ Å)	
μ , mm ⁻¹	0.292	0.314
scan technique	$\theta-2\theta$	$\theta-2\theta$
scan range, deg	$2\theta_{\text{K}\alpha_1} - 0.6$ $2\theta_{\text{K}\alpha_2} + 0.6$	$2\theta_{\text{K}\alpha_1} - 0.7$ $2\theta_{\text{K}\alpha_2} + 0.7$
scan rate, deg/min	4.0-24.0	2.0-24.0
bkgd/peak time ratio	1.0	0.5
2θ limits, deg	3.5-54.9	3.5-54.9
($\sin \theta$)/ λ_{max}	0.648	0.648
criteria for observn	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
no. of unique data	7549	6945
obsd	4160	4904
R_1	0.068	0.091
R_2	0.081	0.101
GOF	2.25	2.18
data/parameters	9.7	13.3

$[\text{Na}(\text{THF})_3][\text{Fe}(\text{TPP})]$ and $[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2][\text{Fe}(\text{TPP})]$. A THF solution (3 mL, 0.2 M, 0.6 mmol) of sodium anthracene was added to a stirred solution of $\text{FeCl}(\text{TPP})$ (176 mg, 0.25 mmol) in THF (20 mL). After 30 min the solution was filtered and heptane (80 mL) added, and the solution was set aside for crystallization. Purple leaflets were collected and washed with heptane; yield 210 mg (93%). $\mu_{\text{eff}}(24^\circ\text{C}) = 2.3 \mu_{\text{B}}$. EPR (THF, 77 K): $g_{\perp} 2.28$, $g_{\parallel} 1.92$. UV-Vis (THF): λ_{max} 390 nm, 423, 510, 575, 605 (see Figure 1 of ref 10). Mössbauer (4.2 K, paraffin wax suspension, relative to Fe):

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- (2) University of Notre Dame.
- (3) Cohen, I. A.; Ostfeld, D.; Lichtenstein, B. *J. Am. Chem. Soc.* **1972**, *94*, 4522-4525.
- (4) Lexa, D.; Momenteau, M.; Mispelter, J. *Biochim. Biophys. Acta* **1974**, *338*, 151-163.
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- (7) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Haller, K. 1st International Symposium on O₂ Activation and Selective Oxidations Catalyzed by Transition Metals, Bendor, France, 1979; Poster Abstract.
- (8) Welborn, C. H.; Dolphin, D.; James, B. R. *J. Am. Chem. Soc.* **1981**, *103*, 2869-2871.
- (9) Lexa, D.; Saveant, J.-M. *J. Am. Chem. Soc.* **1982**, *104*, 3503-3504.
- (10) Reed, C. A. *Adv. Chem. Ser.* **1982**, No. 201, 333-356.
- (11) Abbreviations: TPP, tetrphenylporphyrinate; THF, tetrahydrofuran; DB-18-crown-6, dibenzo-18-crown-6.

- (12) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948-2958. Reed, C. A.; Kouba, J. K.; Grimes, C. J.; Cheung, S. K. *Inorg. Chem.* **1978**, *17*, 2666-2670.

δ 0.65, ΔE_q 2.23 mm \cdot s $^{-1}$; minor component (\sim 10%) with δ 0.66 and ΔE_q 2.04 also observed. For analytical data see ref 10.

Crystals suitable for X-ray analysis were obtained by dissolving the above product (220 mg, 0.24 mmol) and dibenzo-18-crown-6 (110 mg, 0.30 mmol) in pyridine (35 mL) and THF (70 mL). After the mixture was allowed to stand for several days, long purple needles of [Na(dibenzo-18-crown-6)(THF) $_2$][Fe(TPP)] were collected; yield 180 mg (62%). μ_{eff} (29 °C) = 2.9 μ_B .

[Na(THF) $_3$] $_2$ [Fe(TPP)]. This compound was isolated as dark green crystals by a similar procedure to the above except that 0.85 mmol of sodium anthracene was used: yield 220 mg (77%); diamagnetic. UV-Vis (THF): λ_{max} 358 nm, 448, 515, 710, 778 (see Figure 1 of ref 10). Mössbauer (4.2 K, paraffin wax suspension): δ 0.48, ΔE_q 1.29 mm \cdot s $^{-1}$. For analytical data see ref 10.

X-ray Data Collection. Single crystals were mounted in thin-walled glass capillaries in a N $_2$ -filled drybox; both complexes are exceedingly air sensitive. Preliminary examination of both [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)] and [Na(THF) $_3$] $_2$ [Fe(TPP)] and were carried out on a Nicolet P1 diffractometer. Unit cell parameters were obtained from least-square refinements based on the setting angles of 60 reflections, collected at $\pm 2\theta$ at the ambient laboratory temperature of 20 ± 1 °C. The dimensions of the crystals, the unit cell parameters, and other crystal data are listed in Table I. Delauney reductions did not reveal any hidden symmetry. Intensity data were collected with the crystals used for the preliminary examinations. Details of the intensity measurements are given in Table I. Four standard reflections from diverse regions of reciprocal space were measured every 50 reflections throughout data collection to monitor the long-term stability. [Na(THF) $_3$] $_2$ [Fe(TPP)] showed a decline of about 18% while [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)] displayed no significant trends. Structure amplitudes and their standard deviations were calculated from the intensity data as described previously.¹³ Since the crystals of [Na(THF) $_3$] $_2$ [Fe(TPP)] were thin plates, an absorption correction was applied to the data, by using the analytical method of de Meulenaer and Tompa.¹⁴ A correction for the crystal decomposition was also applied. No absorption correction was applied to the data from [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)].

Structure Solution and Refinement. The structure of [Na(THF) $_3$] $_2$ [Fe(TPP)] was solved by placing the iron atom on the inversion center at 0, 0, 0 and calculating a series of electron density difference maps to locate the remaining 40 atoms.¹⁵ The structure of [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)] was solved by locating the iron atom from a Patterson map and calculating a series of electron density difference maps to locate the remaining 47 atoms in the cation and anion. The oxygen atoms and the α -carbon atoms of one of the THF molecules lie on the mirror plane. The β -carbon atoms of both THF molecules are disordered (the disorder in the first molecule is symmetry imposed). Both structures were refined by a combination of full-matrix and block-diagonal least-squares methods. Both structures were initially refined to convergence with isotropic thermal parameters for all atoms. A difference electron density map for [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)] revealed a solvent molecule of THF located on the mirror plane. Difference electron density maps also revealed, for both structures, electron densities appropriately located for many of the hydrogen atoms. All hydrogen atom positions were idealized (C-H = 0.95 Å), and each was assigned an isotropic thermal parameter 1.0 Å 2 larger than the isotropic equivalent of the carbon atom to which it was bonded. In the final cycles of refinement all non-hydrogen atoms were refined with anisotropic thermal parameters. For [Na(THF) $_3$] $_2$ [Fe(TPP)], a final difference electron density map showed no significant features not closely associated with the iron atom position. There were no significant features on the final electron density difference map for [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)].

Listings of observed and calculated structure factors ($\times 10$), the coordinates for the fixed hydrogen atoms (Tables X and XI), and the

Table II. Fractional Monoclinic Coordinates in [Na(DB-18-crown-6)(THF) $_2$][Fe(TPP)] \cdot THF a

atom	x	y	z
Fe	0	1/2	0
N $_1$	0.14258 (11)	0.52369 (14)	-0.02439 (27)
N $_2$	-0.06927 (22)	0.53037 (14)	-0.15325 (26)
C $_{a1}$	0.24328 (27)	0.51670 (18)	0.0514 (3)
C $_{a2}$	0.16588 (27)	0.54888 (17)	-0.1216 (4)
C $_{a3}$	-0.01890 (29)	0.55574 (17)	-0.2333 (4)
C $_{a4}$	-0.17925 (28)	0.53034 (20)	-0.2070 (3)
C $_{b1}$	0.32581 (28)	0.53611 (21)	-0.0007 (4)
C $_{b2}$	0.27944 (29)	0.55535 (19)	-0.1057 (4)
C $_{b3}$	-0.0981 (3)	0.57212 (20)	-0.3349 (3)
C $_{b4}$	-0.1940 (3)	0.55646 (20)	-0.3176 (3)
C $_{m1}$	0.09066 (28)	0.56364 (16)	-0.2197 (3)
C $_{m2}$	-0.26023 (27)	0.50711 (19)	-0.1597 (3)
C $_1$	0.12923 (27)	0.52542 (16)	-0.3186 (4)
C $_2$	0.1210 (3)	0.55286 (17)	-0.4168 (4)
C $_3$	0.1565 (3)	0.57351 (20)	-0.5084 (4)
C $_4$	0.2014 (4)	0.62904 (26)	-0.5054 (5)
C $_5$	0.2133 (4)	0.66506 (22)	-0.4142 (6)
C $_6$	0.1769 (3)	0.64522 (20)	-0.3199 (5)
C $_7$	-0.37206 (29)	0.50674 (22)	-0.2327 (3)
C $_8$	-0.4306 (3)	0.55927 (24)	-0.2580 (4)
C $_9$	-0.5361 (4)	0.5567 (3)	-0.3291 (4)
C $_{10}$	-0.5807 (4)	0.5042 (4)	-0.3694 (5)
C $_{11}$	-0.5234 (4)	0.4527 (3)	-0.3427 (5)
C $_{12}$	-0.4199 (3)	0.45332 (25)	-0.2761 (4)
Na	0.14456 (16)	1/4	0.84415 (16)
O $_1$	0.33963 (19)	0.30856 (11)	0.89603 (21)
O $_2$	0.14644 (20)	0.36744 (11)	0.83130 (22)
O $_3$	-0.04715 (19)	0.30853 (10)	0.80979 (21)
C $_{13}$	0.5523 (3)	0.28065 (22)	1.1510 (4)
C $_{14}$	0.4826 (3)	0.31324 (2)	1.0666 (4)
C $_{15}$	0.41235 (24)	0.28122 (16)	0.98278 (29)
C $_{16}$	0.3334 (3)	0.37400 (19)	0.8954 (4)
C $_{17}$	0.2404 (4)	0.39125 (18)	0.8042 (4)
C $_{18}$	0.0494 (3)	0.39172 (17)	0.7626 (4)
C $_{19}$	-0.0400 (3)	0.37377 (17)	0.8138 (3)
C $_{20}$	-0.12161 (29)	0.28185 (16)	0.8596 (3)
C $_{21}$	-0.1921 (4)	0.31389 (21)	0.9092 (4)
C $_{22}$	-0.2635 (4)	0.28124 (22)	0.9572 (5)
O $_4$	0.1376 (3)	1/4	0.6527 (3)
C $_{23}$	0.2238 (7)	1/4	0.6000 (8)
C $_{24}$	0.1807 (10)	0.2763 (6)	0.4926 (9)
C $_{25}$	0.0676 (9)	0.2702 (10)	0.4761 (8)
C $_{26}$	0.0446 (6)	1/4	0.5631 (6)
O $_5$	0.1587 (4)	1/4	1.0353 (3)
C $_{27}$	0.1471 (5)	0.30200 (23)	1.1003 (4)
C $_{28}$	0.0568 (8)	0.2836 (4)	1.1503 (7)
C $_{282}$	0.150 (4)	0.2843 (7)	1.1903 (12)
O $_6$	0.5036 (17)	1/4	0.4610 (14)
C $_{29}$	0.4869 (11)	0.2004 (5)	0.5270 (16)
C $_{30}$	0.5606 (10)	0.2228 (5)	0.6243 (11)

^a The estimated standard deviations of the least significant digits are given in parentheses.

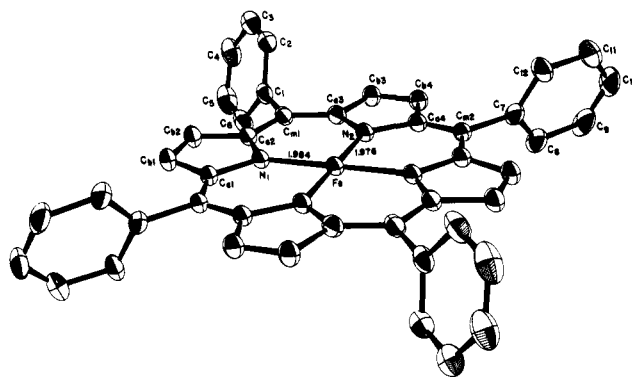


Figure 1. Perspective view of the [Fe(TPP)] $^-$ anion showing 50% probability ellipsoids.

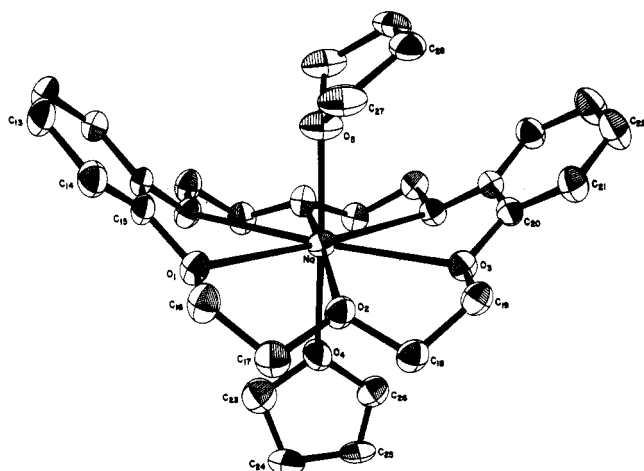
anisotropic temperature factors for the non-hydrogen atoms (Tables VIII and IX) are available as supplementary material. The final

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 (14) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014-1018.
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Table III. Fractional Triclinic Coordinates for the Non-Hydrogen Atoms in $[\text{Na}(\text{THF})_3]_2[\text{Fe}(\text{TPP})]^\text{a}$

atom	x	y	z
Fe	0	0	0
Na	-0.10609 (17)	0.20647 (15)	-0.06251 (18)
O ₁	-0.2529 (4)	0.2412 (3)	-0.2426 (4)
O ₂	0.0492 (4)	0.1747 (3)	-0.1600 (4)
O ₃	-0.0763 (3)	0.39336 (29)	0.0630 (4)
N ₁	0.17258 (26)	-0.00135 (25)	0.09892 (29)
N ₂	-0.03500 (27)	0.13010 (25)	0.15201 (29)
C _{a1}	0.2690 (3)	-0.0725 (3)	0.0548 (4)
C _{a2}	0.2294 (3)	0.0742 (3)	0.2250 (4)
C _{a3}	0.0472 (4)	0.1854 (3)	0.2760 (4)
C _{a4}	-0.1477 (3)	0.1867 (3)	0.1659 (4)
C _{b1}	0.3812 (4)	-0.0371 (4)	0.1502 (5)
C _{b2}	0.3561 (4)	0.0518 (4)	0.2540 (4)
C _{b3}	-0.0152 (4)	0.2699 (4)	0.3627 (4)
C _{b4}	-0.1343 (4)	0.2718 (4)	0.2959 (4)
C _{m1}	0.1708 (4)	0.1605 (3)	0.3095 (4)
C _{m2}	-0.2575 (3)	0.1608 (3)	0.0679 (4)
C ₁	0.2464 (4)	0.2313 (4)	0.4437 (4)
C ₂	0.2983 (5)	0.1921 (4)	0.5484 (5)
C ₃	0.3687 (5)	0.2580 (5)	0.6727 (5)
C ₄	0.3864 (5)	0.3612 (5)	0.6925 (5)
C ₅	0.3381 (5)	0.4029 (4)	0.5910 (6)
C ₆	0.2664 (5)	0.3360 (4)	0.4656 (5)
C ₇	0.6301 (4)	0.2293 (3)	0.0971 (4)
C ₈	0.5780 (5)	0.2142 (5)	0.1776 (7)
C ₉	0.4730 (6)	0.2768 (6)	0.2061 (7)
C ₁₀	0.4226 (4)	0.3559 (4)	0.1494 (6)
C ₁₁	0.4711 (4)	0.3716 (4)	0.0666 (5)
C ₁₂	0.5758 (4)	0.3089 (4)	0.0408 (5)
C ₁₃	-0.2642 (8)	0.3344 (6)	-0.2718 (7)
C ₁₄	-0.2995 (9)	0.3019 (9)	-0.4201 (9)
C ₁₅	-0.3540 (7)	0.1985 (7)	-0.4729 (7)
C ₁₆	-0.3150 (6)	0.1566 (6)	-0.3574 (8)
C ₁₇	0.0345 (8)	0.0953 (8)	-0.2938 (8)
C ₁₈	0.1508 (11)	0.0358 (9)	-0.3017 (13)
C ₁₉	0.2389 (9)	0.0897 (10)	-0.1770 (14)
C ₂₀	0.1731 (6)	0.1770 (6)	-0.0856 (9)
C ₂₁	0.0391 (6)	0.4154 (5)	0.1563 (7)
C ₂₂	0.0193 (7)	0.5107 (6)	0.2816 (8)
C ₂₃	-0.0902 (7)	0.5676 (6)	0.2295 (8)
C ₂₄	-0.1604 (6)	0.4813 (5)	0.1091 (7)

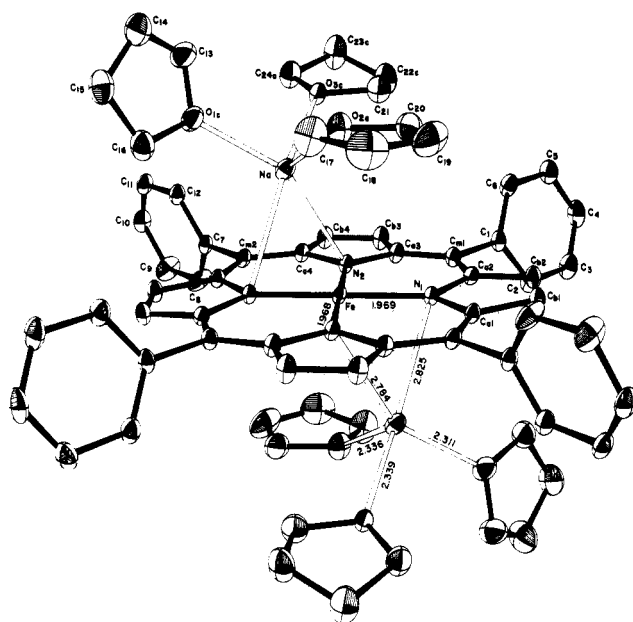
^a The standard deviations of the least significant digits are given in parentheses.

**Figure 2.** Perspective view of the $[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2]^\text{+}$ cation.

atomic coordinates are listed in Tables II and III.

Description of the Structures

Figure 1 displays a perspective view of the $[\text{Fe}(\text{TPP})]^\text{-}$ anion. Figure 2 gives a perspective view of the $[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2]^\text{+}$ cation. The $[\text{Fe}(\text{TPP})]^\text{-}$ anion has a crystallographically required inversion center at the iron atom, and the

**Figure 3.** ORTEP plot of $[\text{Na}(\text{THF})_3]_2[\text{Fe}(\text{TPP})]$.

$\text{Na}(\text{DB-18-crown-6})(\text{THF})_2]^\text{+}$ cation has a required mirror plane of symmetry perpendicular to the plane of the macrocycle and bisecting the two benzo rings. Individual bond distances and angles for $[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2][\text{Fe}(\text{TPP})]$ are given in Tables IV and V of the supplementary material.

The sodium ion in $[\text{Na}(\text{DB-18-crown-6})(\text{THF})_2]^\text{+}$ is coordinated to eight oxygen atoms in a hexagonal-bipyramidal environment; the six oxygen atoms of the crown ether provide the equatorial plane atoms and THF oxygen atoms occupy the apical positions. The six oxygen atoms of the crown are approximately planar and the sodium ion is in the center of this plane. The equatorial Na-O distances range from 2.573 (3) to 2.745 (3) Å and are within the normal range of values observed in this type of sodium crown complex.^{16,17} The apical Na-O(THF) distances are 2.299 (4) and 2.279 (4) Å and are typical of the separations for THF¹⁸⁻²¹ or water^{16,17} ligands. The DB-18-crown-6 ligand has the usual umbrella shape, with the shorter apical distance on the handle side of the umbrella as is typically observed.²²

The conformation of the porphinato core in the four-coordinate $[\text{Fe}(\text{TPP})]^\text{-}$ anion is unremarkable; the atoms of the 24-atom core deviate from exact planarity by less than ± 0.05 Å. The dihedral angles between the two unique peripheral phenyls and the mean plane of the core are 68.3 and 72.6°. The average Fe-N_p distance is 1.980 (6) Å. Bond parameters within the porphinato core display some unusual trends; this matter will be discussed subsequently. The anion and cation are well separated in the crystal; there is only one interionic contact less than 3.6 Å.

Figure 3 is an ORTEP plot of $[\text{Na}(\text{THF})_3]_2[\text{Fe}(\text{TPP})]$. There is a crystallographically required center of symmetry at the iron atom, and consequently the two $[\text{Na}(\text{THF})_3]^\text{+}$ cations are equivalently located above and below the plane of the $[\text{Fe}(\text{TPP})]^\text{-}$ anion.

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(TPP)]²⁻ anion. Selected individual bond distances and angles for [Na(THF)₃]₂[Fe(TPP)] are given in Table VI of the supplementary material.

The porphinato core in the quasi-four-coordinate [Fe(TPP)]²⁻ anion has an effectively planar geometry; the maximum deviation from exact planarity of any atom in the 24-atom core is <0.08 Å. The dihedral angles between the peripheral phenyl groups and the core are 74.0 and 78.9°. The average Fe-N_p distance is 1.968 (1) Å. As also noted for [Fe(TPP)]⁻, there are interesting trends for bond parameters within the porphinato core in [Fe(TPP)]²⁻.

The interaction of the two [Na(THF)₃]⁺ cations with the [Fe(TPP)]²⁻ anion appears to be best described as tight ion pairs. The sodium ion of the [Na(THF)₃]⁺ moiety is positioned almost exactly above the center of a six-membered chelate ring (defined by Fe, N₂, C_{a4}, C_{m2}, C_{a1}, and N₁'). This leads to Na-N(porphyrin) distances of 2.784 (4) and 2.825 (4) Å. Although these distances are longer than the observed Na-N separations (2.444–2.610 Å) in a number of complexes in which the nitrogen atoms are in a relatively unconstrained ligand,^{23–28} they are comparable to those observed in a cryptate complex²⁹ and probably correspond to a bonding interaction. The skeletal constraints of the porphinato ligand also lead to rather close separations between the sodium ion and the other atoms of the six-membered chelate ring: Na...C = 2.90–2.95 Å; Na...Fe = 3.00 Å. Strong ion pairing between sodium ions and salen complexes has also been reported.^{19,20,30} The coordination geometry around a sodium ion in [Na(THF)₃]₂[Fe(TPP)] can be roughly described as square pyramidal, with two oxygen atoms and two nitrogen atoms defining the basal plane and O₂ the apical atom. The observed Na-O(THF) distances range from 2.311 (4) to 2.339 (4) Å and are normal distances. The three THF oxygen atoms define a plane that is parallel to the porphinato plane with an interplanar separation of ~3.70 Å. There are no unusually short nonbonded contacts between [Na(THF)₃]₂[Fe(TPP)] units.

Results and Discussion

It is apparent to us that the extreme air sensitivity of the anions [Fe(TPP)]⁻ and [Fe(TPP)]²⁻ has until now prevented their proper characterization. Crystalline solids of satisfactory analytical purity¹⁰ have now been obtained. By careful anaerobic measurement of the magnetic susceptibility, the spin state of [Fe(TPP)]⁻ has been determined as $S = 1/2$, suggesting that reports of higher spin multiplicities^{3,6} can be safely disregarded. Oxygen uptake by [Fe(TPP)]⁻ to give the high-spin $S = 5/2$ ferric peroxo complex [Fe(O₂)(TPP)]⁻ is a relatively clean reaction¹⁰ and provides one reasonable explanation for higher observed magnetic moments. Interestingly, we find that the doubly reduced species [Fe(TPP)]²⁻ is diamagnetic.

One observation worthy of note is that the crystals of unliganded [Fe(TPP)]⁻ used for X-ray analysis were grown by using pyridine as a cosolvent. Reports of axial ligation by THF⁴ and CO⁶ are unsubstantiated,¹⁰ and the lack of axial ligation even by good nitrogen donors such as imidazole or

Table VII. Comparison of Averaged Bond Distances and Angles^a

	[Fe(TPP)L ₂] ^b	[Fe(TPP)] ⁻	[Fe(TPP)] ²⁻
Distances, Å			
Fe-N _p	2.000	1.980 (6)	1.968 (1)
N _p -C _a	1.384	1.401 (6)	1.409 (5)
C _a -C _b	1.439	1.429 (12)	1.421 (4)
C _a -C _m	1.393	1.385 (5)	1.380 (3)
C _b -C _b	1.341	1.338 (1)	1.352 (5)
Angles, deg			
FeNC _a	127.2	127.7 (4)	128.1 (4)
CaNC _a	105.2	104.6 (1)	103.7 (1)
N _p CaC _b	110.1	109.8 (3)	110.4 (2)
N _p CaC _m	125.6	125.2 (5)	125.1 (2)
C _m C _a C _b	124.3	124.9 (7)	124.4 (2)
C _a C _b C _b	107.3	107.9 (8)	107.7 (8)
C _a C _m C _a	124.0	124.0 (3)	123.4 (2)

^a The numbers in parentheses are the estimated standard deviations calculated from the deviation of the averaged value from the population. ^b Data from ref 34 and 35.

pyridine is consistent with EPR studies. As in one earlier study,⁴ we find that different solvents and ligand solutes can cause some variation of g_{\perp} (2.15–2.30) but at 77 K the basic pattern of the EPR signal ($g_{\perp} = 2.3$, $g_{\parallel} = 1.98$) remains essentially constant and devoid of readily identifiable hyperfine splitting. The lack of a significant axial ligation chemistry must result from the overall negative charge on the complex and possibly also from a (d_{z^2})¹ configuration, the proposed candidate⁴ for the ground state.

It is often the case in iron porphyrin chemistry that it takes an X-ray structure determination to elevate the characterization of a compound to the desired level of confidence. The present situation is no exception. But in addition to confirmation of the true identity of a complex, bond distances in iron porphyrins always contain considerable information about spin states and oxidation states.³¹ In the present complexes, [Fe(TPP)]⁻ and [Fe(TPP)]²⁻, we can look for consistency of the Fe-N distances with the low-spin $S = 1/2$ and $S = 0$ assignments, respectively. We can also inspect the bond distances throughout the molecule for insight into the question of the appropriate formulation and the site of reduction. Should [Fe(TPP)]⁻ be considered an iron(I) porphyrin or an iron(II) π -radical anion? Should [Fe(TPP)]²⁻ be thought of as an iron(0) porphyrin, an iron(I) radical anion, an iron(II) diradical dianion, or some resonance admixture of all of these? In general,³² it is possible to assign metal-based or ligand-based reduction (or oxidation) to a particular redox process in a metalloporphyrin species. Indeed, *oxidation* seems to be distinctly either metal or ligand based once the proper criteria are used to make the determination.^{10,33} However, for *reduction* we shall conclude that resonance forms allow a hybrid description.

Table VII compares, in order, the average Fe-N_p distances and average porphinato core dimensions for three species: *planar* low-spin Fe(TPP)L₂ complexes,^{34,35} [Fe(TPP)]⁻, and [Fe(TPP)]²⁻. A comparison is not made with Fe(TPP)³⁶ because the core in this complex is ruffled, rather than planar, and such conformational differences lead to changes in core parameters.³⁷ We consider first the Fe-N_p distances in the

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reduced species. The observed Fe–N_p distances are clearly inconsistent with a populated d_{x²-y²} orbital³¹ in agreement with the observed low-spin magnetic properties. Two approaches appear reasonable for establishing expectations for low-spin Fe–N_p distances in these reduced species. The decrease in the formal oxidation state would be expected to lead to small increases in Fe–N_p (relative to Fe(II)), with each successive reduction step owing to the decreased effective nuclear charge on the central iron atom. Such a trend is observed for Fe(III) (average low-spin Fe–N_p = 1.990 Å) and Fe(II) porphyrinates (average low-spin Fe–N_p = 2.000 Å).³¹ The observed trend (Table VII) is seen to be opposite to that expected with Fe(II) (2.000 Å) > Fe(I) (1.980 Å) > Fe(0) (1.968 Å). Alternatively, expected values could be based on the distances observed for the isoelectronic d⁷ Co(II) and d⁸ Ni(II) species with an appropriate allowance for the decreased effective nuclear charge in the iron complexes. For planar Co(TPP)³⁸ the Co–N_p distance is ~1.98 Å, and for planar Ni(TPP) the distance is about 1.96 Å. The expected Fe–N_p distances would be slightly longer. Either way, it appears that the observed Fe–N_p distances are shorter than predicted for iron(I) and iron(0) formulations.

In addition, the pattern of bond distances in the core also appear anomalous with respect to normal metalloporphyrins. Table VII presents values, averaged in accordance with assumed D_{4h} symmetry, for the chemically distinct classes. The N–C_a bond distances in the reduced iron complexes are longer than those observed in *any* metalloporphyrin species of reasonable precision. The lengthening of the N–C_a bonds and the shortening of the C_a–C_b bonds are qualitatively consistent³⁹ with the bond length changes expected for populating the porphyrin LUMO of e_g symmetry, i.e., a π-anion species.⁴⁰ The precise bond length changes that would occur upon formation of porphyrin π-anions are unknown since there are no structural data for species of this type. The structure of a π-anion radical in which metal atom reduction is unlikely (such as a Zn derivative) would be helpful in establishing the expected structural changes in the core. The magnitudes of the observed changes in the N–C_a and C_a–C_b bonds are actually larger than the calculated changes⁴¹ and appear to provide

strong evidence for some population of the porphyrin LUMO.

The question of iron vs. porphyrin reduction in [Fe(TPP)]⁻ and [Fe(TPP)]²⁻ is seen to have no simple answer. We view the former complex as a resonance hybrid of a d⁷ iron(I) porphyrin and an S = 1 d⁶ iron(II) π-radical anion having sufficient metal/radical orbital overlap to give an overall S = 1/2 state:



The latter complex can be viewed as a resonance hybrid of three spin-paired formulations with the higher oxidation states as the major contributors:



There is no compelling evidence for an iron(0) contribution; it is included in the resonance description only because it cannot presently be ruled out. The π-radical anion character in these species deduced from the structural data above is also required by the UV-vis spectral comparison of Fe(TPP), [Fe(TPP)]⁻, and [Fe(TPP)]²⁻ (see Figure 1 of ref 10) where an almost fourfold diminution in the Soret band intensity at 419 nm occurs with each successive reduction. On the other hand, iron(I) character is consistent with the Mössbauer spectra and the lack of any significant axial ligation chemistry.

These considerations suggest that the iron(I) and iron(0) designations for singly and doubly reduced iron(II) porphyrinates should be used guardedly, as labels of convenience only. That the averaged valencies resulting from resonance structures are needed to properly describe radical *anion* structures but not radical *cation* structures is probably a consequence of orbital symmetry.¹⁰ Unlike the a_u HOMO of a porphyrin,⁴² the e_g LUMO of a porphyrin has the correct symmetry to engage in significant bonding overlap with the metal d_{xz} and d_{yz} orbitals.

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Registry No. [Na(THF)₃][Fe(TPP)], 91711-74-9; [Na(DB-18-crown-6)(THF)₂][Fe(TPP)], 91741-69-4; [Na(THF)₃]₂[Fe(TPP)], 91711-75-0; FeCl(TPP), 16456-81-8; sodium anthracene, 12261-48-2.

Supplementary Material Available: Table IV, bond distances and angles for [Fe(TPP)]⁻, Table V, distances and angles for [Na(DB-18-crown-6)(THF)₂]⁺, Table VI, distances and angles for [Na(THF)₃]₂[Fe(TPP)], Tables VIII and IX, anisotropic temperature factors, Tables X and XI, idealized hydrogen atom positions, and listings of observed and calculated structure amplitudes (×10) for [Na(DB-18-crown-6)(THF)₂][Fe(TPP)] and [Na(THF)₃]₂[Fe(TPP)] (53 pages). Ordering information is given on any current masthead page.

- (37) These conformational changes lead to a decrease of about 0.03 Å in M–N_p for species with ruffled cores vs. those with planar cores. Cf., for example: Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2095–2102. Meyer, E. F., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 2162–2167. Other parameters of the porphyrin core also change, principally bond angles in the ring.
- (38) An increase of 0.03 Å is given from the observed distances for ruffled Co(TPP) (Madura, P.; Scheidt, W. R. *Inorg. Chem.* **1976**, *15*, 3182–3184) and ruffled Ni(TPP) (Saylor, A. A.; Hoard, J. L., unpublished results) to allow for the conformational effects of planar and ruffled cores on the M–N bond distances.
- (39) See the four-orbital diagram given in: Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1, p 93. In addition, this qualitative picture predicts lengthening of the C_b–C_b and C_a–C_m bonds.
- (40) The population of an e_g π* orbital would lead to a species with maximum D_{2h} symmetry. However, in the crystalline state such species are likely to be disordered yielding effective D_{4h} symmetry species.

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