ond-difference method is not capable of locating this coordinate very well since the $\Delta\Delta I$ value is too dependent on small errors in the rotational constant measurements. The accuracy of these results then does not appear to show any distortion of the $B-H_\mu-B$ moiety by the substitution of the methyl group.

Comparison of $r(B_1-B_2)$ with similar molecules in Table VI does indicate that this bond length in methyldiborane is longer than it is in similar molecules. If the B–B bond length is set at 1.77 Å by displacing $B_2$ along the *a* axis, then its *a* coordinate becomes −0.04 Å. With use of this value for the *a* coordinate of $B_2$, the $B_2-H_\mu$ bond length is reduced to 1.31 Å. A determination of $r(C-B_2)$ by electron diffraction and a reanalysis of the combined microwave and electron diffraction data would elucidate this structure.

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**Registry No.** $CH_3B_2H_5$, 23777-55-1; $(^{10}B_1)CH_3B_2H_5$, 80082-37-7; $(^{10}B_2)CH_3B_2H_5$, 80082-38-8; $(^{10}B_1,{}^{10}B_2)CH_3B_2H_5$, 80082-39-9; $(^{10}B_2,D_\mu)CH_3B_2H_5$, 80082-40-2; $(D_\mu)CH_3B_2H_5$, 80106-01-0; $(D_6)CH_3B_2H_5$, 80082-41-3; $(D_7)CH_3B_2H_5$, 80082-42-4; $(C_8)CH_3B_2H_5$, 80082-43-5; $(D_\mu,D_\mu)CH_3B_2H_5$, 80082-44-6; $(D_\mu,D_8)CH_3B_2H_5$, 80082-45-7.

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# Molecular Stereochemistry of a Low-Spin Five-Coordinate Iron(II) Porphyrinate. (Thiocarbonyl)(octaethylporphinato)iron(II)

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The molecular stereochemistry of the low-spin five-coordinate (porphinato)iron(II) complex (thiocarbonyl)(octaethylporphinato)iron(II) has been determined by X-ray diffraction methods. The molecule crystallizes as the toluene solvate in the triclinic system, space group $P\bar{1}$. The unit cell has $a$ = 12.396 (3) Å, $b$ = 15.393 (3) Å, $c$ = 10.726 (2) Å, $\alpha$ = 93.08 (1)°, $\beta$ = 98.62 (2)°, $\gamma$ = 75.53 (1)°, and $Z$ = 2. Diffraction data were collected by the $\theta-2\theta$ scan technique, and a total of 6919 unique observed reflections were used in refinement of the structure. The final values of the discrepancy indices are $R_1$ = 0.070 and $R_2$ = 0.092. The Fe–C–S group is essentially linear. The FeC(CS) distance is 1.662 (3) Å, and the average Fe–N distance is 1.982 (5) Å. The low-spin iron(II) atom is displaced by 0.23 Å from the mean plane of the porphinato core.

We and others have been investigating the structures of iron porphyrinate derivatives with the view of completely establishing the spin-state/stereochemical relationships of these species.[1] In the iron(II) and iron(III) derivatives, variation in the nature and number of axial ligands allows the isolation of all possible spin states, (for iron(II) these are low spin ($S$ = 0), intermediate spin ($S$ = 1), and high spin ($S$ = 2)). Most of the experimentally accessible possibilities have now been adequately characterized structurally. A possible exception is the low-spin five-coordinate porphinato complexes of iron(II). The only structurally characterized species, Fe(TPP)(NO),[2,3] suffers from possible ambiguity in the oxidation state of iron and in any event has an electronic structure that is unusual for an iron(II) species. (This molecule has an $S = {}^1/_2$ spin state owing to the odd electron originally on the NO ligand.)

Other ligands that can lead to low-spin five-coordinate (porphinato)iron(II) species include CO,[4] CS,[5,6] and in special circumstances, isocyanides, phosphines, and phosphites.[7] The preparation of the monocarbonyl complexes in solution has been described. Isolation of the complex is complicated by relatively unfavorable equilibria:[4,8]

$$\mathrm{Fe(P) + CO \rightleftarrows Fe(P)(CO) + CO \rightleftarrows Fe(P)(CO)_2}$$

Table I. Summary of Crystal Data and Intensity Collection Parameters for $Fe(OEP)(CS)\cdot C_7H_8$

| | | | |
|---|---|---|---|
| formula | $FeSN_4C_{44}H_{52}$ | $\alpha$, deg | 93.08 (1) |
| fw, amu | 724.8 | $\beta$, deg | 98.62 (2) |
| crystal dimensions, mm | 0.7 × 0.3 × 0.1 | $\gamma$, deg | 75.53 (1) |
| space group | $P\bar{1}$ | $V$, Å$^3$ | 1959.2 |
| temp, K | 293 | $Z$ | 2 |
| $a$, Å | 12.396 (3) | $d_{calcd}$, g/cm$^3$ | 1.229 |
| $b$, Å | 15.393 (3) | $d_{obsd}$, g/cm$^3$ | 1.26 |
| $c$, Å | 10.726 (2) | | |
| radiation | graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) | | |
| scan technique | $\theta-2\theta$ | | |
| scan range | 0.55° below K$\alpha_1$ to 0.55° above K$\alpha_2$ | | |
| scan rate, deg/min | 2–12 | | |
| bckgrd | equal scan time at extremes of scan | | |
| $2\theta$ limits, deg | 3.5–54.9 | | |
| criterion for observation | $F_o > 3\sigma(F_o)$ | | |
| unique obsd data | 6919 | | |
| $\mu$, mm$^{-1}$ | 0.468 | | |
| $R_1$ | 0.070 | | |
| $R_2$ | 0.092 | | |
| goodness of fit | 2.691 | | |

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(1) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543-555 and references cited therein.

(2) Scheidt, W. R.; Frisse, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 17-21.

(3) Abreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; OEP, the dianion of octaethylporphyrin; P, the dianion of any porphyrin; TTP, the dianion of *meso*-tetratolylporphyrin; deut, the dianion of deuteroporphyrin IX dimethyl ester; py, pyridine; THF, tetrahydrofuran; $N_p$, porphinato nitrogen atom.

(4) Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379-2384.

(5) Buchler, J. W.; Kokisch, W.; Smith, P. D.; Tonn, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1371-1380.

(6) Mansuy, D.; Battioni, J. P.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4311-4312.

(7) Ellis, P. E., Jr.; Jones, R. D.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1980**, 54-55.

Thus a solution containing the monocarbonyl complex also contains the dicarbonyl species and the four-coordinate starting material. To date, we have not been able to obtain satisfactory crystals of the monocarbonyl for structural analysis. We have obtained single crystals of the thiocarbonyl complex (thiocarbonyl)(octaethylporphinato)iron(II), hereinafter written as Fe(OEP)(CS). We believe that this complex provides stereochemical information equivalent to that of the analogous carbonyl complex.

In this paper, we report the molecular stereochemistry of Fe(OEP)(CS). We compare this structure with those obtained for the six-coordinate carbonyl complexes Fe(TPP)(CO)(py)[9] and Fe(deut)(CO)(THF)[10] and examine the effect of the axial ligands on the position of the iron atom with respect to the porphinato plane.

## Experimental Section

Fe(OEP)(CS) was prepared by the method of Buchler et al.[5] and was obtained in crystalline form as the toluene solvate by the slow evaporation of concentrated toluene solutions. Preliminary X-ray examination on a Syntex P$\bar{1}$ diffractometer established a two-molecule triclinic unit cell, space group $P1$ or $P\bar{1}$. Least-squares refinement of the setting angles of 60 automatically centered reflections, at $\pm 2\theta$, led to the cell constants reported in Table I.[11]

Intensity data were collected by the $\pm$–$2\theta$ scan technique; details of the intensity data collection are summarized in Table I. Four standard reflections, well separated in reciprocal space, were examined every 50 reflections during data collection to monitor the long-term stability. A linear decrease in the intensity of the check reflections (~40%) was observed as a function of the X-ray exposure time. The observed intensities were corrected for this decomposition. As a check on the validity of the correction, the low-$2\theta$ data between 3.5 and 24.7° were recollected and corrected as above. A comparison of the separately collected data showed the validity of the correction. Intensity data were otherwise reduced as previously described.[12]

The structure was solved in the centrosymmetric space group $P\bar{1}$ with the direct methods program MULTAN 78.[13] An $E$ map calculated from the largest 300 $E$ values gave positions of the iron atom, the 24 atoms of the porphinato core, and a number of the ethyl group atoms. The positions of the thiocarbonyl ligand, the remaining ethyl group atoms, and a disordered toluene of solvation were found in subsequent difference Fourier syntheses. The disordered toluene molecule was refined by using rigid-group techniques, with occupancies of 0.70 and 0.30 for the two rigid groups. The rigid groups utilized a six-membered ring with C–C distances of 1.395 Å and a C–$CH_3$ distance of 1.500 Å. After several cycles of least-squares refinement, difference Fourier maps revealed the positions of the meso hydrogen atoms and many of the hydrogen atoms of the ethyl groups. All hydrogen atoms were included in subsequent cycles of least-squares refinement as fixed contributors (C–H = 0.95 Å and $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å$^2$). Least-squares refinement was then carried to convergence for the 414 parameters which included anisotropic temperature factors for all heavy atoms. At convergence, the final values for the discrepancy indices[14] were $R_1 = 0.070$ and $R_2 = 0.092$, with a final

**Table II.** Atomic Coordinates for Fe(OEP)(CS)[a]

| atom | $x$ | $y$ | $z$ | $B$,[b] Å$^2$ |
|---|---|---|---|---|
| Fe | 0.35096 (4) | 0.45840 (3) | 0.12327 (4) | 2.92 |
| S | 0.19232 (8) | 0.52669 (7) | 0.33837 (10) | 4.69 |
| C | 0.27112 (26) | 0.49623 (20) | 0.23550 (29) | 3.09 |
| $N_1$ | 0.26313 (23) | 0.54257 (17) | −0.00962 (24) | 3.16 |
| $N_2$ | 0.45946 (22) | 0.53546 (17) | 0.15933 (25) | 3.12 |
| $N_3$ | 0.45941 (22) | 0.36375 (17) | 0.22709 (25) | 3.15 |
| $N_4$ | 0.26303 (22) | 0.37036 (17) | 0.05804 (24) | 3.13 |
| $C_{m1}$ | 0.36947 (29) | 0.65728 (22) | 0.01444 (31) | 3.41 |
| $C_{m2}$ | 0.59427 (27) | 0.44785 (23) | 0.32476 (32) | 3.43 |
| $C_{m3}$ | 0.36427 (30) | 0.24150 (22) | 0.18488 (32) | 3.53 |
| $C_{m4}$ | 0.11560 (28) | 0.46592 (22) | −0.08957 (31) | 3.40 |
| $C_{a1}$ | 0.16184 (27) | 0.53886 (21) | −0.08304 (30) | 3.14 |
| $C_{a2}$ | 0.27929 (28) | 0.62394 (21) | −0.03858 (30) | 3.33 |
| $C_{a3}$ | 0.45277 (28) | 0.61640 (22) | 0.10638 (31) | 3.26 |
| $C_{a4}$ | 0.55255 (26) | 0.52342 (21) | 0.25142 (31) | 3.17 |
| $C_{a5}$ | 0.55315 (27) | 0.37252 (22) | 0.31102 (31) | 3.29 |
| $C_{a6}$ | 0.44986 (28) | 0.27768 (22) | 0.24453 (31) | 3.35 |
| $C_{a7}$ | 0.27739 (28) | 0.28441 (22) | 0.09931 (31) | 3.33 |
| $C_{a8}$ | 0.16385 (27) | 0.38643 (22) | −0.02646 (30) | 3.22 |
| $C_{b1}$ | 0.11530 (28) | 0.61915 (22) | −0.15573 (30) | 3.40 |
| $C_{b2}$ | 0.18802 (29) | 0.67151 (22) | −0.12862 (31) | 3.48 |
| $C_{b3}$ | 0.54289 (28) | 0.65650 (22) | 0.16723 (32) | 3.35 |
| $C_{b4}$ | 0.60336 (27) | 0.59866 (22) | 0.25731 (32) | 3.30 |
| $C_{b5}$ | 0.60394 (27) | 0.29059 (22) | 0.37959 (32) | 3.45 |
| $C_{b6}$ | 0.54128 (29) | 0.23075 (23) | 0.33599 (32) | 3.68 |
| $C_{b7}$ | 0.18934 (29) | 0.24440 (22) | 0.03512 (32) | 3.44 |
| $C_{b8}$ | 0.11826 (29) | 0.30758 (23) | −0.04143 (31) | 3.38 |
| $C_{11}$ | 0.00715 (29) | 0.63745 (23) | −0.24618 (34) | 3.86 |
| $C_{12}$ | 0.02343 (34) | 0.60160 (31) | −0.37868 (37) | 5.13 |
| $C_{21}$ | 0.17974 (32) | 0.76278 (25) | −0.17707 (36) | 4.27 |
| $C_{22}$ | 0.14587 (41) | 0.83883 (28) | −0.08300 (49) | 5.95 |
| $C_{31}$ | 0.55943 (31) | 0.74500 (25) | 0.13168 (37) | 4.10 |
| $C_{32}$ | 0.48557 (42) | 0.82688 (26) | 0.18842 (47) | 5.59 |
| $C_{41}$ | 0.70177 (29) | 0.61122 (25) | 0.35017 (38) | 3.97 |
| $C_{42}$ | 0.66727 (37) | 0.66506 (31) | 0.46526 (47) | 5.88 |
| $C_{51}$ | 0.70469 (30) | 0.27619 (25) | 0.47953 (36) | 4.07 |
| $C_{52}$ | 0.67064 (36) | 0.29138 (30) | 0.61133 (40) | 5.22 |
| $C_{61}$ | 0.56267 (34) | 0.13500 (25) | 0.37223 (39) | 4.64 |
| $C_{62}$ | 0.61889 (54) | 0.06897 (31) | 0.27915 (60) | 7.64 |
| $C_{71}$ | 0.18444 (34) | 0.14934 (26) | 0.05090 (40) | 4.65 |
| $C_{72}$ | 0.26511 (49) | 0.08116 (30) | −0.01870 (57) | 7.05 |
| $C_{81}$ | 0.01641 (31) | 0.29944 (25) | −0.13044 (36) | 4.08 |
| $C_{82}$ | 0.04006 (37) | 0.27857 (30) | −0.26570 (40) | 5.24 |

[a] The numbers in parentheses are the estimated standard deviations. [b] Isotropic thermal parameters as calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

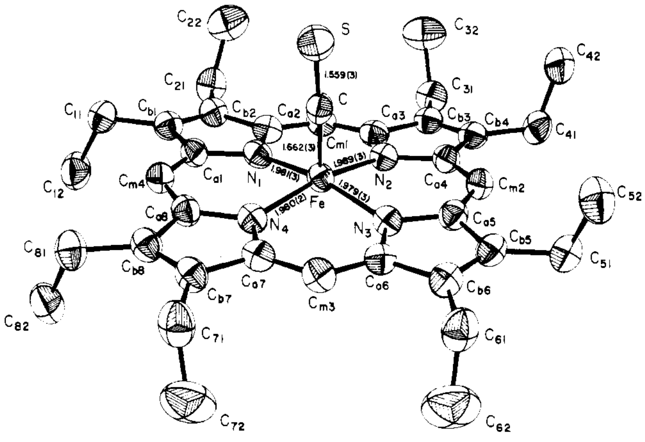

**Figure 1.** Computer-drawn model in perspective of the Fe(OEP)(CS) molecule in the crystal. The labeling scheme for the atoms is given. Bond distances in the coordination group are shown. Ellipsoids are contoured to enclose 50% of the electron density.

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(8) Rougee, M.; Brault, D. *Biochemistry* **1975**, *14*, 4100–4105.

(9) Peng, S.-M.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8032–8036.

(10) Scheidt, W. R.; Haller, K. J.; Fons, M.; Mashiko, T.; Reed, C. A. *Biochemistry* **1981**, *20*, 3653–3657.

(11) The cell reported in Table I is the reduced cell according to the convention of Donnay et al. (Donnay, J. D. H., et al. "Crystal Data Determinative Tables", ACA Monograph No. 5, American Crystallographic Association: Washington, D.C.; 1963. The reduced cell according to the convention given in the International Tables ("International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. I, pp 530–535) is $a = 10.726$ Å, $b = 12.396$ Å, $c = 15.393$ Å, $\alpha = 75.53°$, $\beta = 86.92°$, and $\gamma = 81.28°$ and is obtained by the transformation 001, $\bar{1}$00, 0$\bar{1}$0.

(12) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84–89.

(13) Programs used in this study included local modifications of Main et al.'s MULTAN 78, Jacobson's ALFF and ALLS, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP 2. Atomic form factors were from Cromer and Mann (Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–323), with real and imaginary corrections for anomalous dispersion in the form factor of the iron and sulfur atoms from: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891–1898. Scattering factors for hydrogen were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175–3187.

(14) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table IV. Bond Distances[a] (Å) in Fe(OEP)(CS)

| | | | | | |
|---|---|---|---|---|---|
| Fe–C | 1.662 (3) | $N_4-C_{a7}$ | 1.378 (4) | $C_{a2}-C_{b2}$ | 1.444 (5) |
| $Fe-N_1$ | 1.981 (3) | $N_4-C_{a8}$ | 1.390 (4) | $C_{a3}-C_{b3}$ | 1.462 (5) |
| $Fe-N_2$ | 1.989 (3) | $C_{m1}-C_{a2}$ | 1.379 (5) | $C_{a4}-C_{b4}$ | 1.445 (4) |
| $Fe-N_3$ | 1.979 (3) | $C_{m1}-C_{a3}$ | 1.368 (5) | $C_{a5}-C_{b5}$ | 1.446 (4) |
| $Fe-N_4$ | 1.980 (2) | $C_{m2}-C_{a4}$ | 1.384 (5) | $C_{a6}-C_{b6}$ | 1.450 (5) |
| C–S | 1.559 (3) | $C_{m2}-C_{a5}$ | 1.371 (5) | $C_{a7}-C_{b7}$ | 1.453 (4) |
| $N_1-C_{a1}$ | 1.391 (4) | $C_{m3}-C_{a6}$ | 1.378 (5) | $C_{a8}-C_{b8}$ | 1.454 (4) |
| $N_1-C_{a2}$ | 1.375 (4) | $C_{m3}-C_{a7}$ | 1.361 (5) | $C_{b1}-C_{b2}$ | 1.344 (5) |
| $N_2-C_{a3}$ | 1.376 (4) | $C_{m4}-C_{a8}$ | 1.384 (5) | $C_{b3}-C_{b4}$ | 1.353 (5) |
| $N_2-C_{a4}$ | 1.383 (4) | $C_{m4}-C_{a1}$ | 1.377 (4) | $C_{b5}-C_{b6}$ | 1.369 (5) |
| $N_3-C_{a5}$ | 1.390 (4) | $C_{a1}-C_{b1}$ | 1.442 (4) | $C_{b7}-C_{b8}$ | 1.355 (5) |
| $N_3-C_{a6}$ | 1.384 (4) | | | | |

[a] The numbers in parentheses are the estimated standard deviations.

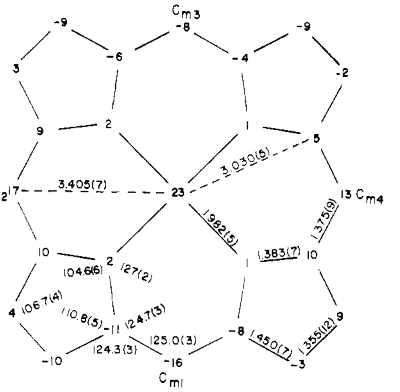

**Figure 2.** Formal diagram of a porphinato core displaying the average values of the bond parameters. Also displayed are the perpendicular displacements, in units of 0.01 Å, of each atom of the core from the mean plane of the 24-atom core. In this diagram, the atom symbol has been replaced by the value of the displacement. The orientation of the core with respect to that shown in Figure 1 is indicated by the labeled methine carbon atoms.

data/parameter ratio of 16.7.[15] A final difference Fourier map had its five highest peaks (0.6–1.0 e/Å$^3$) associated with the iron atom; the map was judged to be otherwise featureless. Final atomic coordinates are reported in Table II. Final anisotropic temperature factors are reported in Table III (supplementary material). Tables of hydrogen atom positions, rigid-group parameters, and a listing of the final observed and calculated structure factor amplitudes (×10) are also available as supplementary material.

## Results and Discussion

Figure 1 provides an overall perspective view of the five-coordinate Fe(OEP)(CS) molecule. Figure 1 also displays the special symbols assigned to the atoms in the molecule. Tables IV and V provide listings of the individual bond lengths and angles of the molecule. Average values for each chemically unique type of bond length and angle in the porphinato core are displayed in Figure 2, a formal diagram of the porphinato core. The numbers in parentheses following these averaged values, here and elsewhere in the paper, are the estimated standard deviations calculated on the assumption that the individual values are drawn from the same population. The values of the averaged bond parameters of the core are unremarkable. Figure 2 also displays the perpendicular displacement of the atoms from the mean plane of the 24-atom core. It can be seen that the porphinato core exhibits a modest quasi-$D_{2d}$ ruffling that is well within the limits of porphinato core conformations observed.

Table V. Bond Angles[a] (Deg) in Fe(OEP)(CS)

| | | | |
|---|---|---|---|
| FeCS | 176.3 (2) | $N_3C_{a5}C_{b5}$ | 110.0 (3) |
| $N_1FeC$ | 97.3 (1) | $N_3C_{a6}C_{b6}$ | 110.9 (3) |
| $N_2FeC$ | 99.5 (1) | $N_4C_{a7}C_{b7}$ | 110.6 (3) |
| $N_3FeC$ | 95.2 (1) | $N_4C_{a8}C_{b8}$ | 110.7 (3) |
| $N_4FeC$ | 93.0 (1) | $N_1C_{a1}C_{m4}$ | 124.0 (3) |
| $N_1FeN_2$ | 89.3 (1) | $N_1C_{a2}C_{m1}$ | 124.4 (3) |
| $N_2FeN_3$ | 88.9 (1) | $N_2C_{a3}C_{m1}$ | 125.0 (3) |
| $N_3FeN_4$ | 89.7 (1) | $N_2C_{a4}C_{m2}$ | 124.6 (3) |
| $N_4FeN_1$ | 89.4 (1) | $N_3C_{a5}C_{m2}$ | 124.7 (3) |
| $FeN_1C_{a1}$ | 130.2 (2) | $N_3C_{a6}C_{m3}$ | 124.8 (3) |
| $FeN_1C_{a2}$ | 126.8 (2) | $N_4C_{a7}C_{m3}$ | 124.8 (3) |
| $FeN_2C_{a3}$ | 125.0 (2) | $N_4C_{a8}C_{m4}$ | 124.9 (3) |
| $FeN_2C_{a4}$ | 128.7 (2) | $C_{m4}C_{a1}C_{b1}$ | 124.8 (3) |
| $FeN_3C_{a5}$ | 129.8 (2) | $C_{m1}C_{a2}C_{b2}$ | 124.1 (3) |
| $FeN_3C_{a6}$ | 126.0 (2) | $C_{m1}C_{a3}C_{b3}$ | 123.9 (3) |
| $FeN_4C_{a7}$ | 128.3 (2) | $C_{m2}C_{a4}C_{b4}$ | 124.4 (3) |
| $FeN_4C_{a8}$ | 125.1 (2) | $C_{m2}C_{a5}C_{b5}$ | 124.3 (3) |
| $C_{a1}N_1C_{a2}$ | 103.8 (3) | $C_{m3}C_{a6}C_{b6}$ | 124.3 (3) |
| $C_{a3}N_2C_{a4}$ | 104.8 (3) | $C_{m3}C_{a7}C_{b7}$ | 124.5 (3) |
| $C_{a5}N_3C_{a6}$ | 104.8 (3) | $C_{m4}C_{a8}C_{b8}$ | 124.4 (3) |
| $C_{a7}N_4C_{a8}$ | 105.0 (3) | $C_{a1}C_{b1}C_{b2}$ | 106.7 (3) |
| $C_{a3}C_{m1}C_{a2}$ | 125.2 (3) | $C_{a2}C_{b2}C_{b1}$ | 106.9 (3) |
| $C_{a5}C_{m2}C_{a4}$ | 124.6 (3) | $C_{a3}C_{b3}C_{b4}$ | 106.1 (3) |
| $C_{a7}C_{m3}C_{a6}$ | 125.2 (3) | $C_{a4}C_{b4}C_{b3}$ | 107.2 (3) |
| $C_{a1}C_{m4}C_{a8}$ | 125.0 (3) | $C_{a5}C_{b5}C_{b6}$ | 106.5 (3) |
| $N_1C_{a1}C_{b1}$ | 111.1 (3) | $C_{a6}C_{b6}C_{b5}$ | 106.7 (3) |
| $N_1C_{a2}C_{b2}$ | 111.5 (3) | $C_{a7}C_{b7}C_{b8}$ | 107.2 (3) |
| $N_2C_{a3}C_{b3}$ | 110.9 (3) | $C_{a8}C_{b8}C_{b7}$ | 106.4 (3) |
| $N_2C_{a4}C_{b4}$ | 110.9 (3) | | |

[a] The numbers in parentheses are the estimated standard deviations.

The average Fe–$N_p$ bond distance observed is 1.982 (5) Å. This is slightly shorter than the average 1.998 (11) Å distance found[1] for six-coordinate low-spin iron(II) species and the 2.001 (3) Å value observed for Fe(TPP)(NO).[2] The value is comparable to the 1.988-Å distance found in Fe(TPP)(CS)(py).[16] It is thus clear that changing the coordination number (from 6 to 5) of low-spin iron(II) porphyrinates will have a very modest effect of the equatorial bond distances. This stereochemical change is of interest because such a change occurs in the α subunits of nitrosylhemoglobin under certain conditions.[17]

The Fe–C–S group is nearly linear (Figure 1), with an angle of 176.3 (2)°. The Fe–C vector is tipped by ~4° from the normal to the heme plane. The C–S distance of 1.559 (3) Å is within the range of values normally observed for thiocarbonyl complexes. We observe a C–S stretching frequency of 1292 cm$^{-1}$, in agreement with the value previously reported.[5] The observed C–S distance and C–S stretching frequency do not agree with the correlation proposed[18] for these two quantities. It is to be noted that this correlation was based on a limited number of data.

The Fe–C(CS) distance in Fe(OEP)(CS) is 1.662 (3) Å. This distance is shorter than the Fe–C(CO) distances observed in a number of five- and six-coordinate iron(II) porphyrinates and related macrocyclic complexes. The shortest Fe–C(CO) distance of this type is the 1.694 (4) Å value observed by Goedken et al.[19] in a five-coordinate macrocycle, and the shortest Fe–C(CO) distance observed in a porphinato complex is the 1.706 (5) Å distance found in Fe(deut)(CO)(THF).[10] It is pertinent to consider the relationship to be expected be-

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(15) The final value of the "goodness of fit" parameter is somewhat larger than usual for structures of this type from this laboratory. An analysis of the weighting scheme as a function of setting angles and classes of indices showed reasonable values. However, the weighting scheme as a function of (sin θ)/λ apeared to overweight the low-angle data. Additional refinement with a value of 0.05 for the "ignorance factor" rather than the original 0.04 gave lower values for the goodness of fit (~2.4). However, structural parameters and derived results differed only slightly, and consequently this refinement was not pursued further.

(16) The value of Fe–$N_p$ and the displacement of the iron atom are given in Table II of: Chottard, G.; Battioni, P.; Battioni, J.-P.; Lange, M.; Mansuy, D. *Inorg. Chem.* **1981**, *20*, 1718–1722.

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tween M–C(CO) and M–C(CS) distances. There appear to be only a few cases in which M–C(CO) and M–C(CS) distances can be directly compared. A comparison[20-23] of these few structures in which a carbonyl or a thiocarbonyl ligand is found in very similar chemical environments suggests that the M–C(CS) distance will be only slightly shorter ($\Delta \approx$ 0.0–0.10 Å). It would thus appear that the Fe–C(CO) distance in a five-coordinate Fe(P)(CO) complex would be within the range 1.66–1.70 Å. The axial bond distance in the isoelectronic complex Mn(TTP)(NO)[24] is 1.641 (2) Å.

The displacement of a metal atom from the $N_4$ porphinato plane is a function of the spin state of the metal, the number of axial ligands (one or two), and their relative bonding strengths. In Fe(OEP)(CS), the low-spin iron(II) atom is displaced 0.23 Å from the mean plane of the core (Figure 2) and 0.22 Å from the $N_4$ mean plane. These displacements are quite comparable to those observed (0.21 Å) for Fe(TPP)(NO).[2] Is is thus reasonable to expect that a similar displacement of the iron atom would be found for an Fe(P)(CO) complex. With these data, the effect of various sixth ligands on the displacement of the iron atom can be examined. The coordination of a sixth ligand (pyridine) to Fe(TPP)(CS) leads to[16] virtual centering of the iron atom. A similar lack of iron displacement is also seen[9] in Fe(TPP)(CO)(py). Replacement of pyridine with the weak-field and weakly binding ligand tetrahydrofuran leads to[10] a displacement of the iron atom of 0.10 Å toward the CO ligand. Thus even one of the weakest possible sixth-ligand interactions decreases the iron atom displacement by about half compared to the displacement expected for the case of no sixth-ligand interaction.

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**Registry No.** Fe(OEP)(CS)·$C_7H_8$, 80327-76-0.

**Supplementary Material Available:** Table III (anisotropic temperature factors), Table VI (rigid-group and derived atomic coordinates for the disordered toluene molecule), Table VII (calculated hydrogen atom positions), Table VIII (additional bond distances and angles), and a listing of the structure factor amplitudes (×10) (29 pages). Ordering information is given on any current masthead page.

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# Structure of Yttrium Octachloroditechnetate Nonahydrate

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The crystal structure of the title compound, $YTc_2Cl_8\cdot 9H_2O$, has been determined, and from the structure of the $[Tc_2Cl_8]^{3-}$ anion some hypotheses concerning the factors determining metal–metal multiple-bond lengths may be suggested. The compound crystallizes in space group $P42_12$, with cell dimensions of $a$ = 11.712 (2) Å, $c$ = 7.661 (2) Å, $V$ = 1050.9 (4) Å$^3$, and $Z$ = 4. The structure was refined to $R_1$ = 0.031 and $R_2$ = 0.039 with 621 reflections with $I > 3\sigma(I)$ and 51 parameters. The correct enantiomer was chosen. The crystal consists of equal numbers of $[Tc_2Cl_8]^{3-}$ ions at sites of $C_4$ symmetry, slightly distorted square antiprismatic $[Y(H_2O)_8]^{3+}$ ions on sites of $D_2$ symmetry, and $H_2O$ molecules on sites of $C_2$ symmetry. The Tc–Tc distance is 2.105 (1) Å; the Tc–Cl distances average 2.364 (2) Å, and the Tc–Tc–Cl angles average 104.34 (6)°. The ion has symmetry approximating closely to $D_{4h}$. The independent Y–O distances are 2.346 (5) and 2.373 (5) Å. The shortness of the Tc–Tc bond compared to that in the $[Tc_2Cl_8]^{2-}$ ion where the formal bond order is higher is attributed mainly to the decreased effective positive charge on the metal atoms in the $[Tc_2Cl_8]^{3-}$ ion, which leads to stronger $\pi$ bonding.

## Introduction

In a recent paper[2] the structure of $(N\text{-}n\text{-}Bu_4)_2Tc_2Cl_8$ was reported, providing for the first time a structural characterization of $[Tc_2Cl_8]^{2-}$. Previously, there had been two X-ray crystallographic studies[4,5] of compounds containing the $[Tc_2Cl_8]^{3-}$ ion; the results of these two are not entirely independent since the two compounds $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$[3] and $K_3[Tc_2Cl_8]\cdot nH_2O$[4] are isotypic. The structural data provided by these investigations gave rise to an apparent inconsistency. In $[Tc_2Cl_8]^{3-}$, where the Tc–Tc bond order is believed[5,6] to be 3.5, the metal–metal bond length is 2.117 (2) Å, while in $[Tc_2Cl_8]^{2-}$, where the Tc–Tc bond order should be 4.0, the distance is 2.151 (1) Å.

One of several possible explanations for this unexpected result might have been that the above comparison of Tc–Tc bond lengths is invalid, either because one (or both) structures are crystallographically in error or because these bonds are subject to the influences of drastically different surroundings (hard and highly polar in the case of $[Tc_2Cl_8]^{3-}$ but soft and diffuse for $[Tc_2Cl_8]^{2-}$) in the two cases. To determine whether either of these factors is pertinent, it is obviously necessary to carry out additional structural studies, preferably on substances in which the surroundings of the anions are changed in nature. Efforts to prepare suitable compounds are under way, but there are difficulties because of the lability of both

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