

- Ellman, G. L. (1959) *Arch. Biochem. Biophys.* 82, 70-77.
- Fabian, F., & Mühlrad, A. (1968) *Biochim. Biophys. Acta* 162, 596-603.
- Hegyi, G., & Mühlrad, A. (1968) *Acta Biochim. Biophys. Acad. Sci. Hung.* 3, 425-428.
- Hoare, D. G., & Koshland, D. E., Jr. (1967) *J. Biol. Chem.* 242, 2447-2453.
- Itaya, K., & Ui, M. (1966) *Clin. Chim. Acta* 14, 361-366.
- Jones, J. M., & Perry, S. V. (1966) *Biochem. J.* 100, 120-130.
- Khorana, H. G. (1953) *Chem. Rev.* 53, 145-166.
- Kinoshita, N., Kubo, S., Onishi, H., & Tonomura, Y. (1969) *J. Biochem. (Tokyo)* 65, 285-301.
- Klotz, C., Lèger, J. J., & Marotte, F. (1976) *Eur. J. Biochem.* 65, 607-611.
- Lynn, R. W., & Taylor, E. W. (1970) *Biochemistry* 9, 2975-2983.
- Morkin, E., Flink, I. L., & Banerjee, S. K. (1979) *J. Biol. Chem.* 254, 12647-12652.
- Mornet, D., Pantel, P., Audemard, E., & Kassab, R. (1979) *Eur. J. Biochem.* 100, 421-431.
- Nauss, K. M., Kitagawa, S., & Gergely, J. (1969) *J. Biol. Chem.* 244, 755-765.
- Offer, G., Moos, C., & Starr, R. (1973) *J. Mol. Biol.* 74, 653-676.
- Pfister, M., Schaub, M. C., Watterson, J. G., Knecht, M., & Waser, P. G. (1975) *Biochim. Biophys. Acta* 410, 193-209.
- Pick, U., & Racker, E. (1979) *Biochemistry* 18, 108-113.
- Ramirez, F., Shukla, K. K., & Levy, H. M. (1979) *J. Theor. Biol.* 76, 351-357.
- Ray, W. J., & Koshland, D. E., Jr. (1961) *J. Biol. Chem.* 236, 1973-1979.
- Reisler, E., Burke, M., & Harrington, W. F. (1974) *Biochemistry* 13, 2014-2022.
- Satre, M., Lunardi, J., Pougeois, R., & Vignais, P. V. (1979) *Biochemistry* 18, 3134-3410.
- Schliselfeld, L. H., & Barany, M. (1968) *Biochemistry* 7, 3206-3213.
- Sekine, T., & Kielley, W. W. (1964) *Biochim. Biophys. Acta* 81, 336-345.
- Shimada, T. (1970) *J. Biochem. (Tokyo)* 67, 185-198.
- Sokolovsky, M., Riordan, J. I., & Vallee, B. I. (1966) *Biochemistry* 5, 3582-3589.
- Vanaman, T. C., & Stark, G. R. (1970) *J. Biol. Chem.* 245, 3565-3573.
- Van Thiem, N., Lacombe, G., & Swynghedauw, B. (1978) *Eur. J. Biochem.* 91, 243-248.
- Wagner, P. D., & Weeds, A. G. (1977) *J. Mol. Biol.* 109, 455-473.
- Weeds, A. G., & Taylor, R. S. (1975) *Nature (London)* 257, 54-56.
- Weeds, A. G., & Pope, B. (1977) *J. Mol. Biol.* 111, 129-157.
- Wells, J. A., & Yount, R. G. (1979) *Proc. Natl. Acad. Sci. U.S.A.* 76, 4966-4970.
- Wells, J. A., & Yount, R. G. (1980) *Biochemistry* 19, 1711-1717.
- Wells, J. A., Werber, M. M., & Yount, R. G. (1979) *Biochemistry* 18, 4800-4805.
- Wiedner, H., Wetzel, R., & Eckstein, F. (1978) *J. Biol. Chem.* 253, 2763-2768.
- Wolcott, R. G., & Boyer, P. D. (1973) *Biochim. Biophys. Acta* 303, 292-297.
- Yoshino, H. (1976) *J. Biochem. (Tokyo)* 80, 1117-1128.

## A (Carbonmonoxy)heme Complex with a Weak Proximal Bond. Molecular Stereochemistry of Carbonyl(deuteroporphinato)(tetrahydrofuran)iron(II)<sup>†</sup>

W. Robert Scheidt,\* Kenneth J. Haller, M. Fons, Toshio Mashiko, and Christopher A. Reed\*

**ABSTRACT:** The synthesis and structural characterization of a six-coordinate (carbonmonoxy)(porphyrin)iron(II), carbonyl(deuteroporphinato)(tetrahydrofuran)iron(II), is described. The choice of tetrahydrofuran as the sixth ligand represents one of the weakest field and weakest binding ligands possible and leads to stronger than usual bonding of CO to the heme. The Fe-C(CO) bond distance is 1.706 Å, unusually short. The Fe-O(THF) bond distance in the low-spin complex is 2.127 Å. The Fe-C-O and O-Fe-C groups are essentially

linear with angles of 178.3° and 177.4°, respectively. The iron atom is displaced out of plane 0.10 Å toward the tightly bound CO. The results suggest that the different CO stretching frequencies observed in myoglobin might result from modulating the bonding of the histidine trans to CO. Crystal data are as follows:  $a = 11.524(3)$  Å,  $b = 14.915(5)$  Å,  $c = 10.583(2)$  Å;  $\alpha = 91.51(2)^\circ$ ,  $\beta = 108.99(2)^\circ$ ,  $\gamma = 102.86(3)^\circ$ ; triclinic, space group  $P\bar{1}$ ,  $Z = 2$ ;  $\rho_{\text{calcd}} = 1.363$  g/cm<sup>3</sup>,  $\rho_{\text{obsd}} = 1.370$  g/cm<sup>3</sup>.

**B**inding of the strong-field ligand carbon monoxide has been frequently exploited in studies of hemoproteins and porphyrin species. These studies have focused particularly on exploring the nature of the heme binding site and the evaluation of cis and trans effects (Caughey et al., 1972; Buchler et al., 1978).

Such studies have shown, for example, that there are spectroscopically distinguishable (and probably structurally distinct) components of (carbonmonoxy)myoglobin, both in solution (McCoy & Caughey, 1971; Alben, 1978) and in the crystalline state (Makinen et al., 1979). The affinity of CO for a deuteroheme has been found to be significantly influenced by the nature of the ligand trans to the CO (Rougee & Brault, 1975).

Crystallographic study of carbon monoxide liganded hemoglobins and myoglobins (Huber et al., 1970; Heidner et al., 1976; Norvell et al., 1975; Tucker et al., 1978; Steigemann & Weber, 1979; Baldwin, 1980) has shown that the CO ligand

<sup>†</sup> From the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 (W.R.S., K.J.H., and M.F.), and the Department of Chemistry, University of Southern California, Los Angeles, California 90007 (T.M. and C.A.R.). Received September 25, 1980. The work done at Notre Dame was supported by National Institutes of Health Grant HL-15627 and that done at Southern California by National Science Foundation Grant CHE-78-09813.

exhibits a bent or tilted configuration with respect to the heme plane. This ligand geometry is not expected for unconstrained heme derivatives since this stereochemical feature of the hemoproteins is associated with nonbonded interactions of the axial ligand with nearby amino acid residues. In heme derivatives, the substantial differences in affinities of CO as a function of the trans ligand, as well as variations in the infrared stretching frequencies, do suggest, however, that the trans ligand may lead to structurally significant differences in CO bonding to iron of the heme. As part of a program to investigate such possible effects, we have prepared and structurally characterized carbonyl(deuteroporphinato)(tetrahydrofuran)iron(II), hereinafter abbreviated as Fe(CO)-(deut)(THF).<sup>1</sup> The use of tetrahydrofuran as the sixth (trans) ligand represents one of the weakest field and weakest binding ligands. The equilibrium constant for the reaction Fe(CO)(deut) + THF  $\rightarrow$  Fe(CO)(deut)(THF) has been reported to be  $\sim 290 \text{ M}^{-1}$ . For comparison, the equilibrium constant for a stronger binding ligand such as 1-methylimidazole is  $6.5 \times 10^5 \text{ M}^{-1}$  (Rougee & Braut, 1975).

### Experimental Procedures

**Synthesis.** Deuteroporphyrin IX dimethyl ester was prepared by the method of Adler et al. (1977) and converted to Fe(deut) by standard methods (Collman et al., 1975). Anaerobic treatment with carbon monoxide in THF solution, followed by heptane addition, gave a purple crystalline product: IR (KBr)  $\nu(\text{CO})$ ,  $1955 \text{ cm}^{-1}$ .

**Structure Determination.** A single crystal of Fe(CO)-(deut)(THF) with dimensions  $0.30 \times 0.35 \times 0.60 \text{ mm}$  was mounted in a thin-walled glass capillary under dinitrogen. Preliminary examination on a Syntex PI four-circle diffractometer established a two-molecule triclinic unit cell. A Delaunay reduction did not reveal any hidden symmetry. The unit cell parameters, at  $20 \pm 1^\circ \text{C}$ , were obtained from a least-squares refinement based on the setting angles of 41 reflections ( $24.5^\circ < 2\theta < 35.5^\circ$ ), each centered at  $\pm 2\theta$ :  $a = 11.524(3) \text{ \AA}$ ,  $b = 14.915(5) \text{ \AA}$ ,  $c = 10.583(2) \text{ \AA}$ ;  $\alpha = 91.51(2)^\circ$ ,  $\beta = 108.99(2)^\circ$ ,  $\gamma = 102.86(3)^\circ$  ( $\lambda \text{ Mo K}\alpha = 0.71073 \text{ \AA}$ ). The unit cell volume of  $1667 \text{ \AA}^3$  and a cell content of two Fe(CO)(deut)(THF) molecules led to a calculated density of  $1.363 \text{ g/cm}^3$ ; the experimental density, determined by flotation ( $\text{CCl}_4/\text{hexane}$ ), was  $1.370 \text{ g/cm}^3$ .

X-ray intensity data were collected by using graphite-monochromated Mo K $\alpha$  radiation and  $\theta$ - $2\theta$  scanning. Variable scan rates ( $2$ – $12^\circ/\text{min}$ ) with scans of  $0.9^\circ$  below K $\alpha_1$  to  $1.0^\circ$  above K $\alpha_2$  and backgrounds collected at the extremes of the scan each for 0.25 times the time required for the scan were used. Four standard reflections from diverse regions of reciprocal space were monitored every 50 reflections throughout the data collection. The intensities of the standard reflections did not exhibit any systematic variation during the time required to collect the data. The intensity data were reduced and standard deviations calculated as described previously (Scheidt, 1974). With a linear absorption coefficient of only  $0.456 \text{ mm}^{-1}$  for Mo K $\alpha$  radiation, no absorption correction was made. A total of 4209 unique reflections having  $\sin(\theta/\lambda) \leq 0.65 \text{ \AA}^{-1}$  and  $F_o > 3\sigma(F_o)$  were retained as observed and used in the solution and refinement of structure.

The structure was solved by the heavy-atom method and refined by block-diagonal and full-matrix least-squares tech-

niques.<sup>2</sup> Atomic form factors were taken from Cromer & Mann (1968) and for hydrogen from Stewart et al. (1965). The effects of anomalous scattering of the iron atom were included in the calculated structure amplitudes (Cromer & Liberman, 1970). After initial refinement, a difference electron-density map showed a second orientation of the coordinated THF molecule approximately perpendicular to the first. The peak heights suggested occupancy factors of 0.6 and 0.4 for the first and second orientations, respectively. The model was refined to convergence by allowing the occupancies of the THF carbon atoms to vary. All atoms were anisotropic except for the THF carbon atoms. The occupancies of the two THF groups were reset to the averages of the individual atoms after every second cycle. Final occupancy factors for the two THF groups were 0.58 and 0.42. Fixed idealized hydrogen atom positions were included in the final cycles of refinement [ $d(\text{C-H}) = 0.95 \text{ \AA}$ ,  $B(\text{H}) = B(\text{C}) + 1.0 \text{ \AA}^2$ ]. During the course of refinement, it was noted that the positions of N<sub>1</sub> and N<sub>3</sub> appeared to be systematically too close to the iron atom as judged by deviations from expected values for Fe-N and N-C<sub>a</sub> distances. The positions of N<sub>1</sub> and N<sub>3</sub> were manually adjusted so that the Fe-N distances were  $2.00 \text{ \AA}$ . However, the positions of N<sub>1</sub> and N<sub>3</sub> refined back to their original positions. The discrepancy indices at convergence were  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.083$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.084$ . The final electron-density difference map was judged to be free of significant features. The error in an observation of unit weight was 2.26, and the final data/parameter ratio was 8.0.

The values of the final atomic coordinates are reported in Table I. The final values of the fixed hydrogen atom coordinates and the anisotropic  $B$  values for the unique atoms are reported in Tables III and IV and are available as supplementary material (see paragraph at end of paper regarding supplementary material). Final values of the observed and calculated structure amplitudes are also available as supplementary material.

### Results and Discussion

Figure 1 presents an overall view of the Fe(CO)(deut)(THF) molecule displaying the numbering scheme used for the atoms. Figure 1 also displays the bond distances in the coordination group. Selected individual bond distances and angles for the Fe(CO)(deut)(THF) molecule are given in Table II. A complete listing of bond distances and angles is given in Table V of the supplementary material. Figure 1 shows only one of the two observed orientations of the THF ligand. The two orientations are displayed in Figure 2 which gives a view down the Fe-O(THF) axis. The diagram clearly shows that the two orientations of the THF ligand are chemically equivalent. Both THF rings show a slight puckering (Figure 2).

In this porphinato complex, the geometry of the 24-atom core is very similar to that found in other metalloporphyrins (Hoard, 1975; Scheidt, 1978), with the possible exception of the bond parameters involving N<sub>1</sub> and N<sub>3</sub> as described under Experimental Procedures. The peripheral substituents of the porphyrin ring appear to be well-behaved with no positional disorder of the type commonly encountered with naturally occurring porphyrin derivatives. The deviations from planarity of the 24-atom core are shown in Figure 3. The pattern of deviations of the core from exact planarity are unremarkable.

The structural features of the coordination sphere of the complex are consistent with low-spin (porphinato)iron(II)

<sup>1</sup> Abbreviations used: deut, dianion of deuteroporphyrin IX dimethyl ester; THF, tetrahydrofuran; TPP, dianion of 5,10,15,20-tetraphenylporphyrin; 1-Melm, 1-methylimidazole; 4-MePip, 4-methylpiperidine; py, pyridine; *t*-BuNC, *tert*-butyl isocyanide.

<sup>2</sup> Details of the computations can be found in Mashiko et al. (1978).

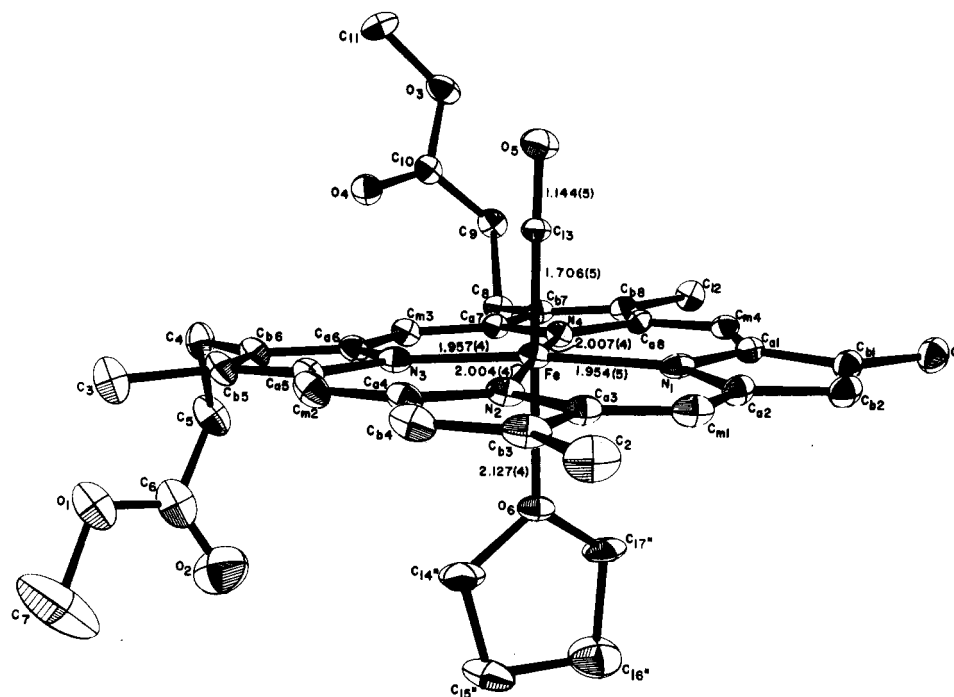


FIGURE 1: ORTEP drawing of  $\text{Fe}(\text{CO})(\text{deut})(\text{THF})$  molecule showing atom numbering scheme. The figure also displays the bond distances in the coordination group. All thermal ellipsoids are drawn at the 50% probability level.

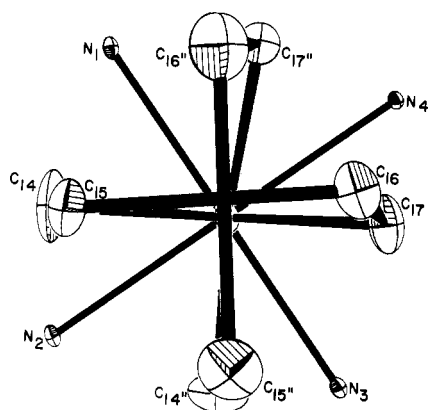


FIGURE 2: Computer-drawn diagram showing the two orientations of the THF ligand. The THF ligand with the double-primed atom labels is the minor orientation (final occupancy 0.42); the THF with the unprimed labels is the major orientation (occupancy factor 0.58).

complexes. The four independent Fe–N distances average to 1.98 (3) Å in agreement with those observed in a number of other low-spin complexes: 2.004 (4) Å for  $\text{Fe}(\text{TPP})(\text{piperidine})_2$  (Radonovich et al., 1972); 2.001 (3) Å for  $\text{Fe}(\text{TPP})(\text{NO})$  (Scheidt & Frisse, 1975); 2.008 (4) Å for  $\text{Fe}(\text{TPP})(\text{NO})(1\text{-MeIm})$  (Scheidt & Piccolo, 1976); 1.999 (10) and 2.004 (10) Å for two forms of  $\text{Fe}(\text{TPP})(\text{NO})(4\text{-MePip})$  (Scheidt et al., 1977); 2.02 (3) Å for  $\text{Fe}(\text{TPP})(\text{CO})(\text{py})$  (Peng & Ibers, 1976); 2.005 (4) Å for  $\text{Fe}(\text{TPP})(t\text{-BuNC})_2$  (Jameson & Ibers, 1979).

The axial Fe–O(THF) distance of 2.127 (4) Å in this low-spin complex is considerably shorter than the 2.351 (3) Å value for the corresponding bond in high-spin  $\text{Fe}(\text{TPP})(\text{THF})_2$  (Reed et al., 1980). This observation of a 0.22-Å bond length difference again points out the importance of the electronic configuration in controlling bond lengths in metalloporphyrin complexes (Scheidt, 1977). The short axial Fe–O bond is correlated with the absence of an electron in the  $d_{z^2}$  orbital and the long Fe–O bond with its presence. It has been suggested (Peng & Ibers, 1976; Goedken et al., 1976) that the CO ligand exerts a structural trans effect leading to long axial

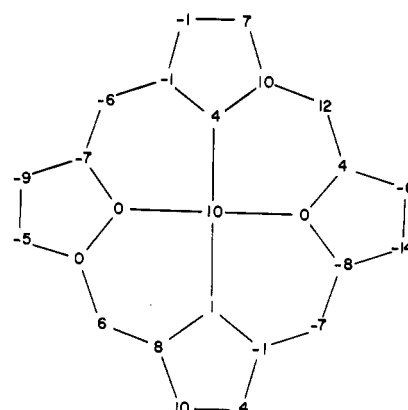


FIGURE 3: Formal diagram of porphinato core having the same relative orientation as Figure 1. The perpendicular displacement of each individual atom, in units of 0.01 Å, from the mean plane of the 24-atom core is given.

bonds trans to the CO. This does not seem to be a significant effect in  $\text{Fe}(\text{CO})(\text{deut})(\text{THF})$ .

The Fe–C(CO) bond distance of 1.706 (5) Å is quite short compared to the 1.77 (3) Å value observed in  $\text{Fe}(\text{TPP})(\text{CO})(\text{py})$  (Peng & Ibers, 1976) and, indeed, when compared to the values observed for all carbonyliron(II) macrocycles (range 1.730–1.779 Å, average 1.76 Å) (Goedken et al., 1976; McCandlish et al., 1979). In fact, the Fe–C(CO) distance is almost as short as the 1.694 (4) Å distance observed in a five-coordinate macrocyclic species (Goedken et al., 1976). This suggests that the bonding to CO in  $\text{Fe}(\text{CO})(\text{deut})(\text{THF})$  is stronger than usual. This is consistent with the CO stretching frequencies observed in a number of carbonyl-(porphinato)iron(II) derivatives. The CO stretching frequency in  $\text{Fe}(\text{CO})(\text{deut})(\text{THF})$  is 1955  $\text{cm}^{-1}$ , considerably lower than that observed for related deuteroporphyrin derivatives, for example, 1973  $\text{cm}^{-1}$  in  $\text{Fe}(\text{CO})(\text{deut})(\text{py})$  (Alben & Caughey, 1968) and  $[\text{Fe}(\text{CO})(\text{deut})]_2(\mu\text{-hydrazine})$  (Caughey et al., 1972) and the 1980- $\text{cm}^{-1}$  stretching frequency of  $\text{Fe}(\text{TPP})(\text{CO})(\text{py})$ .

Further evidence for the strong interaction of CO with iron

Table I: Fractional Triclinic Coordinates for Fe(CO)(deut)(THF)<sup>a</sup>

atom	x	y	z
Fe	0.19761 (7)	0.30756 (6)	0.13953 (7)
O <sub>1</sub>	0.3062 (7)	-0.0861 (5)	-0.1844 (7)
O <sub>2</sub>	0.4053 (9)	0.0491 (6)	-0.2219 (8)
O <sub>3</sub>	-0.3124 (4)	0.1988 (3)	-0.5158 (4)
O <sub>4</sub>	-0.1524 (4)	0.1315 (3)	-0.4318 (4)
O <sub>5</sub>	-0.0491 (4)	0.27372 (28)	0.1587 (4)
O <sub>6</sub>	0.3858 (3)	0.3374 (3)	0.1359 (4)
N <sub>1</sub>	0.2329 (4)	0.4365 (3)	0.2116 (4)
N <sub>2</sub>	0.2670 (4)	0.2731 (3)	0.3263 (4)
N <sub>3</sub>	0.1798 (4)	0.1811 (3)	0.0675 (4)
N <sub>4</sub>	0.1407 (4)	0.34426 (27)	-0.0477 (4)
C <sub>a1</sub>	0.2078 (5)	0.5138 (4)	0.1415 (5)
C <sub>a2</sub>	0.2858 (5)	0.4771 (4)	0.3444 (5)
C <sub>a3</sub>	0.3096 (5)	0.3313 (4)	0.4435 (5)
C <sub>a4</sub>	0.2713 (5)	0.1862 (5)	0.3621 (6)
C <sub>a5</sub>	0.2008 (5)	0.1034 (4)	0.1357 (6)
C <sub>a6</sub>	0.1394 (5)	0.1436 (4)	-0.0684 (6)
C <sub>a7</sub>	0.1044 (5)	0.2863 (4)	-0.1655 (5)
C <sub>a8</sub>	0.1244 (5)	0.4286 (4)	-0.0844 (5)
C <sub>b1</sub>	0.2477 (5)	0.5967 (4)	0.2291 (6)
C <sub>b2</sub>	0.2966 (5)	0.5734 (4)	0.3537 (6)
C <sub>b3</sub>	0.3427 (5)	0.2781 (5)	0.5574 (6)
C <sub>b4</sub>	0.3185 (6)	0.1909 (5)	0.5058 (6)
C <sub>b5</sub>	0.1734 (6)	0.0228 (4)	0.0455 (6)
C <sub>b6</sub>	0.1351 (5)	0.0476 (4)	-0.0807 (6)
C <sub>b7</sub>	0.0672 (5)	0.3398 (4)	-0.2799 (5)
C <sub>b8</sub>	0.0787 (5)	0.4256 (4)	-0.2302 (5)
C <sub>m1</sub>	0.3198 (5)	0.4235 (4)	0.4516 (5)
C <sub>m2</sub>	0.2422 (6)	0.1088 (4)	0.2755 (6)
C <sub>m3</sub>	0.1036 (5)	0.1950 (4)	-0.1743 (5)
C <sub>m4</sub>	0.1539 (5)	0.5067 (4)	0.0025 (5)
C <sub>1</sub>	0.2362 (6)	0.6887 (4)	0.1859 (6)
C <sub>2</sub>	0.3919 (6)	0.3177 (5)	0.7016 (6)
C <sub>3</sub>	0.1864 (7)	-0.0705 (5)	0.0879 (7)
C <sub>4</sub>	0.0922 (6)	-0.0114 (4)	-0.2110 (6)
C <sub>5</sub>	0.1809 (8)	0.0101 (5)	-0.2924 (7)
C <sub>6</sub>	0.3073 (12)	-0.0078 (9)	-0.2286 (9)
C <sub>7</sub>	0.4413 (17)	-0.1000 (15)	-0.1269 (15)
C <sub>8</sub>	0.0313 (5)	0.3028 (4)	-0.4248 (5)
C <sub>9</sub>	-0.1115 (6)	0.2828 (4)	-0.5046 (5)
C <sub>10</sub>	-0.1890 (6)	0.1970 (5)	-0.4774 (6)
C <sub>11</sub>	-0.4001 (7)	0.1151 (6)	-0.4985 (8)
C <sub>12</sub>	0.0519 (6)	0.5072 (4)	-0.3046 (5)
C <sub>13</sub>	0.0493 (5)	0.2862 (4)	0.1496 (5)
C <sub>14</sub>	0.4941 (11)	0.3789 (16)	0.2464 (15)
C <sub>15</sub>	0.6083 (14)	0.3897 (23)	0.2125 (18)
C <sub>16</sub>	0.5636 (16)	0.3639 (25)	0.0675 (20)
C <sub>17</sub>	0.4241 (15)	0.3233 (18)	0.0338 (16)
C <sub>14'</sub>	0.4645 (18)	0.2768 (15)	0.166 (3)
C <sub>15'</sub>	0.5912 (29)	0.3216 (25)	0.149 (6)
C <sub>16'</sub>	0.582 (4)	0.425 (3)	0.120 (6)
C <sub>17'</sub>	0.4424 (15)	0.4169 (15)	0.0898 (22)

<sup>a</sup> The standard deviations of the least significant digits are given in parentheses.

comes from the displacement of the iron atom from the mean plane of the porphyrato core. The iron(II) atom is displaced 0.10 Å from the mean plane of the core, toward the CO ligand. This is compared with the virtual centering of the iron atom in Fe(TPP)(CO)(py). In six-coordinate (porphyrin)iron(II) derivatives, iron atom displacements as large as 0.10 Å are found only in species with quite dissimilar axial interactions, for example, 0.07 Å in Fe(TPP)(NO)(1-Melm) (Scheidt & Piciulo, 1976) and 0.11 Å in Fe(TPP)(NO)(4-MePip) (Scheidt et al., 1977), and where the displacements are toward the tightly bound NO ligand.

The C-O distance of 1.144 (5) Å is normal as is the nearly linear angle for the two axial ligands, O-Fe-C = 177.4 (9)°. As expected, the Fe-C-O group is essentially linear with an observed angle of 178.3 (14)°. In distinct contrast to the carbonyl heme proteins, the Fe-C-O vector is within 2° of being perpendicular to the heme plane. In the proteins, the

Table II: Selected Interatomic Distances (Å) and Angles (deg) for Fe(CO)(deut)(THF)<sup>a</sup>

Distances			
Fe-N <sub>1</sub>	1.954 (5)	N <sub>4</sub> -C <sub>a7</sub>	1.386 (6)
Fe-N <sub>2</sub>	2.004 (4)	N <sub>4</sub> -C <sub>a8</sub>	1.360 (6)
Fe-N <sub>3</sub>	1.957 (4)	C <sub>a1</sub> -C <sub>m4</sub>	1.389 (7)
Fe-N <sub>4</sub>	2.007 (4)	C <sub>a1</sub> -C <sub>b1</sub>	1.417 (7)
Fe-C <sub>13</sub>	1.706 (5)	C <sub>a2</sub> -C <sub>m1</sub>	1.405 (7)
Fe-O <sub>6</sub>	2.127 (4)	C <sub>a2</sub> -C <sub>b2</sub>	1.412 (7)
N <sub>1</sub> -C <sub>a1</sub>	1.420 (6)	C <sub>a3</sub> -C <sub>m1</sub>	1.353 (8)
N <sub>1</sub> -C <sub>a2</sub>	1.396 (6)	C <sub>a3</sub> -C <sub>b3</sub>	1.454 (7)
N <sub>2</sub> -C <sub>a3</sub>	1.375 (7)	C <sub>a4</sub> -C <sub>m2</sub>	1.362 (8)
N <sub>2</sub> -C <sub>a4</sub>	1.366 (7)	C <sub>a4</sub> -C <sub>b4</sub>	1.443 (7)
N <sub>3</sub> -C <sub>a5</sub>	1.406 (7)	C <sub>a5</sub> -C <sub>m2</sub>	1.393 (8)
N <sub>3</sub> -C <sub>a6</sub>	1.416 (6)	C <sub>a5</sub> -C <sub>b5</sub>	1.425 (8)
		C <sub>a6</sub> -C <sub>m3</sub>	1.378 (7)
		C <sub>a6</sub> -C <sub>b6</sub>	1.423 (7)
		C <sub>a7</sub> -C <sub>m3</sub>	1.360 (7)
		C <sub>a7</sub> -C <sub>b7</sub>	1.467 (7)
		C <sub>a8</sub> -C <sub>m4</sub>	1.372 (7)
		C <sub>a8</sub> -C <sub>b8</sub>	1.456 (7)
		C <sub>b1</sub> -C <sub>b2</sub>	1.344 (7)
		C <sub>b3</sub> -C <sub>b4</sub>	1.331 (8)
		C <sub>b5</sub> -C <sub>b6</sub>	1.353 (8)
		C <sub>b7</sub> -C <sub>b8</sub>	1.332 (7)
Angles			
N <sub>1</sub> -Fe-N <sub>2</sub>	90.04 (17)	Fe-N <sub>2</sub> -C <sub>a3</sub>	126.3 (4)
N <sub>1</sub> -Fe-N <sub>3</sub>	174.25 (27)	Fe-N <sub>2</sub> -C <sub>a4</sub>	126.6 (4)
N <sub>1</sub> -Fe-N <sub>4</sub>	89.70 (16)	Fe-N <sub>3</sub> -C <sub>a6</sub>	129.6 (4)
N <sub>2</sub> -Fe-N <sub>3</sub>	89.57 (17)	Fe-N <sub>3</sub> -C <sub>a7</sub>	128.7 (4)
N <sub>2</sub> -Fe-N <sub>4</sub>	175.92 (22)	Fe-N <sub>4</sub> -C <sub>a7</sub>	126.0 (4)
N <sub>3</sub> -Fe-N <sub>4</sub>	90.29 (17)	Fe-N <sub>4</sub> -C <sub>a8</sub>	127.3 (3)
C <sub>13</sub> -Fe-O <sub>6</sub>	177.4 (9)	C <sub>a1</sub> -N <sub>1</sub> -C <sub>a2</sub>	101.4 (5)
Fe-C <sub>13</sub> -O <sub>5</sub>	178.3 (14)	C <sub>a3</sub> -N <sub>2</sub> -C <sub>a4</sub>	106.9 (5)
Fe-N <sub>1</sub> -C <sub>a1</sub>	128.8 (3)	C <sub>a5</sub> -N <sub>3</sub> -C <sub>a6</sub>	101.7 (5)
Fe-N <sub>1</sub> -C <sub>a2</sub>	129.8 (4)	C <sub>a7</sub> -N <sub>4</sub> -C <sub>a8</sub>	106.7 (4)

<sup>a</sup> The standard deviations of the least significant digits are given in parentheses.

Fe-C-O group is either bent or more likely tilted (Deatherage et al., 1976) with respect to the heme plane. In the most recent results of Baldwin (1980) [for human (carbonmonoxy)-hemoglobin] an assumed linear Fe-C-O group was found to be tilted by 13° from the heme normal. Other heme protein derivatives have even larger apparent deviations from idealized geometry. It has been suggested (Collman, 1977; Moffat et al., 1979) that the decreased CO affinity and kinetics of ligand binding are influenced by steric hindrance in the ligand binding pocket of the heme proteins compared to heme complexes.

## Conclusion

This study of Fe(CO)(deut)(THF) demonstrates that the bonding and structure between CO and iron is sensitive to the ligand field strength of the trans ligand. It suggests that the different CO stretching frequencies observed in crystalline (Makinen et al., 1979) and solution state (McCoy & Caughey, 1971) carbonylmyoglobin could result, at least in part, from modulating the bonding of the proximal histidine trans to the CO. Such modulation may arise either from changes in the bonding relationships of the proximal histidine trans to CO as suggested by Makinen et al. (1979) or from different degrees of hydrogen bonding by the exo N-H of the proximal histidine which can provide a mechanism for both decreasing [Reed et al. (1979) and references cited therein] or increasing [Landrum et al. (1980) and references 3-10 therein; Peisach, 1975] the field strength of histidyl imidazole.

## Supplementary Material Available

Table III, hydrogen atom positions, Table IV, anisotropic temperature factors, Table V, bond distances and angles, and a listing of observed and calculated structure factors (×10) (27 pages). Ordering information is given on any current masthead page.

## References

- Adler, A. D., Ostfeld, D. L., & Abbot, E. H. (1977) *Bioinorg. Chem.* 7, 187-188.
- Alben, J. O. (1978) in *The Porphyrins* (Dolphin, D., Ed.) Vol. 3, pp 323-345, Academic Press, New York.

- Alben, J. O., & Caughey, W. A. (1968) *Biochemistry* 7, 175-183.
- Baldwin, J. M. (1980) *J. Mol. Biol.* 136, 103-128.
- Buchler, J. W., Kokisch, W. E., & Smith, P. D. (1978) *Struct. Bonding (Berlin)* 34, 79-134.
- Caughey, W. S., Barlow, C. H., O'Keeffe, D. H., & O'Toole, M. C. (1972) *Ann. N.Y. Acad. Sci.* 206, 296-309.
- Collman, J. P. (1977) *Acc. Chem. Res.* 10, 265-272.
- Collman, J. P., Hoard, J. L., Kim, N., Lang, G., & Reed, C. A. (1975) *J. Am. Chem. Soc.* 97, 2676-2681.
- Cromer, D. T., & Mann, J. B. (1968) *Acta Crystallogr., Sect. A* 24, 321-323.
- Cromer, D. T., & Liberman, D. (1970) *J. Chem. Phys.* 53, 1891-1898.
- Deatherage, J. F., Loe, R. S., Anderson, C. M., & Moffat, K. (1976) *J. Mol. Biol.* 104, 687-706.
- Goedken, V. L., Peng, S.-M., Molin-Norris, J., & Park, Y. (1976) *J. Am. Chem. Soc.* 98, 8391-8400.
- Heidner, E. J., Ladner, R. C., & Perutz, M. F. (1976) *J. Mol. Biol.* 104, 707-722.
- Hoard, J. L. (1975) in *Porphyrins and Metalloporphyrins* (Smith, K. M., Ed.) pp 317-380, Elsevier, Amsterdam.
- Huber, R., Epp, O., & Formanek, H. (1970) *J. Mol. Biol.* 52, 349-354.
- Jameson, G. B., & Ibers, J. A. (1979) *Inorg. Chem.* 18, 1200-1208.
- Landrum, J. T., Hatano, K., Scheidt, W. R., & Reed, C. A. (1980) *J. Am. Chem. Soc.* 102, 6729-6735.
- Makinen, M. W., Houtchens, R. A., & Caughey, W. S. (1979) *Proc. Natl. Acad. Sci. U.S.A.* 76, 6042-6046.
- Mashiko, T., Kastner, M. E., Spartalian, K., Scheidt, W. R., & Reed, C. A. (1978) *J. Am. Chem. Soc.* 100, 6354-6361.
- McCandlish, L. E., Santarsiero, B. D., Rose, N. J., & Lingtafelter, E. C. (1979) *Acta Crystallogr., Sect. B* 35, 3053-3056.
- McCoy, S., & Caughey, W. S. (1971) *Probes Struct. Funct. Macromol. Membr., Proc. Colloq. Johnson Res. Found., 5th* 2, 289-291.
- Moffat, K., Deatherage, J. F., & Seybert, D. W. (1979) *Science (Washington, D.C.)* 206, 1035-1042.
- Norvell, J. C., Nunes, A. C., & Schoenborn, B. P. (1975) *Science (Washington, D.C.)* 190, 568-570.
- Peisach, J. (1975) *Ann. N.Y. Acad. Sci.* 244, 187-203.
- Peng, S.-M., & Ibers, J. A. (1976) *J. Am. Chem. Soc.* 98, 8032-8036.
- Radonovich, L. J., Bloom, A., & Hoard, J. L. (1972) *J. Am. Chem. Soc.* 94, 2073-2078.
- Reed, C. A., Mashiko, T., Bentley, S. P., Kastner, M. E., Scheidt, W. R., Spartalian, K., & Lang, G. (1979) *J. Am. Chem. Soc.* 101, 2948-2958.
- Reed, C. A., Mashiko, T., Scheidt, W. R., Spartalian, K., & Land, G. (1980) *J. Am. Chem. Soc.* 102, 2302-2306.
- Rougee, M., & Brault, D. (1975) *Biochemistry* 14, 4100-4106.
- Scheidt, W. R. (1974) *J. Am. Chem. Soc.* 96, 84-89.
- Scheidt, W. R. (1977) *Acc. Chem. Res.* 10, 339-345.
- Scheidt, W. R. (1978) in *The Porphyrins* (Dolphin, D., Ed.) Vol. 3, pp 463-511, Academic Press, New York.
- Scheidt, W. R., & Frisse, M. E. (1975) *J. Am. Chem. Soc.* 97, 17-21.
- Scheidt, W. R., & Piciulo, P. L. (1976) *J. Am. Chem. Soc.* 98, 1913-1919.
- Scheidt, W. R., Brinegar, A. C., Ferro, E. B., & Kirner, J. F. (1977) *J. Am. Chem. Soc.* 99, 7315-7322.
- Steigemann, W., & Weber, E. (1979) *J. Mol. Biol.* 127, 309-338.
- Stewart, R. F., Davidson, E. R., & Simpson, W. T. (1965) *J. Chem. Phys.* 42, 3175-3187.
- Tucker, P. W., Phillips, S. E. V., Perutz, M. F., Houtchens, R. A., & Caughey, W. S. (1978) *Proc. Natl. Acad. Sci. U.S.A.* 75, 1076-1080.