study by Perutz and co-workers[17] notes that the M-H bending modes for the *neutral* analogues show the expected trend in that the Mo complex $(\eta\text{-}C_5H_5)_2MoH_2$ exhibits a M-H bending mode ca. 60 cm^{-1} lower in frequency than that of $(\eta\text{-}C_5H_5)_2WH_2$. It is not unreasonable to attribute the large differences in coupling observed in the Mo and W systems to relatively subtle changes in the M-H bending modes, which are indicative of the vibrational potentials experienced by the hydride ligands. Our previous work on quantitative models for exchange coupling predicted that a decrease in the M-H bending frequency of 100 cm^{-1} would reduce the exchange coupling by two orders of magnitude.[3] While the comparison of known bending frequencies of the neutral molecules is not strictly valid for the cationic trihydride complexes considered here, it is reasonable to expect that a similar trend may also hold for the cations.

In conclusion, it is clear that exchange coupling is an important factor in understanding the ^1H NMR spectra of certain metallocene trihydride complexes. In general, "normal" values (<20 Hz) for two-bond H-M-H couplings observed in some polyhydride complexes may not be entirely due to magnetic couplings. Further examination of such complexes may reveal a temperature dependence of the coupling due to an exchange coupling component. In addition, this work has shown that the sign of the two-bond magnetic coupling between hydride ligands attached to a metal is negative in the case of $(\eta\text{-}C_5H_5)_2NbH_3$. This conclusion is consistent with the very limited data available for such couplings in the literature and may be a general observation. Further work is in progress to investigate these possibilities.

Experimental Section

All manipulations were conducted under dry nitrogen following standard Schlenk techniques or in a drybox. $(\eta\text{-}C_5H_5)_2NbH_3$ was prepared from $(\eta\text{-}C_5H_5)_2NbCl_2$ by the method of Curtis and co-workers.[9] $(\eta\text{-}C_5H_5)_2TaH_3$[18] and $(\eta\text{-}C_5H_5)_2MoCl_2$[19] were prepared according to Green and co-workers. Proton NMR spectra were recorded on a modified Bruker instrument at 490 MHz. Probe temperatures were calibrated by comparison to the observed chemical shift differences in the spectrum of pure methanol with use of the data reported by Van Geet.[11] Temperatures below the freezing point of methanol were obtained by extrapolation.

Preparation of $(\eta\text{-}C_5H_5)_2MoH_2$. The procedure of Dias and Ramão was followed, with some modification.[20] To a suspension of $(\eta\text{-}C_5H_5)_2MoCl_2$ (297 mg, 1 mmol) in 30 mL of 1,2-dimethoxyethane (DME) was added an excess of $NaBH_4$ (380 mg, 10 mmol). After 18 h of stirring at room temperature, the yellow brown solution was taken to dryness. Sublimation (75 °C, 10^{-3} mmHg) affords the product as bright yellow crystals (200 mg, 90%).

Preparation of $[(\eta\text{-}C_5H_5)_2MoH_3]BH_4$. $(\eta\text{-}C_5H_5)_2MoH_2$ (100 mg) was dissolved in 25 mL of Et_2O. Excess 85% $HBF_4{\cdot}Et_2O$ was added, affording a flocculent white precipitate of $[(\eta\text{-}C_5H_5)_2MoH_3]BF_4$, which was collected by filtration. A similar procedure was employed to prepare $[(\eta\text{-}C_5H_5)_2WH_3]BF_4$. The precursor $(\eta\text{-}C_5H_5)_2WH_2$ was the generous gift of Professor J. R. Norton.

Acknowledgment. This work was supported by the National Science Foundation. We thank Professor J. R. Norton for a generous gift of $(\eta\text{-}C_5H_5)_2WH_2$.

---

[17] Girling, R. B.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1986**, *25*, 31-36.

[18] Bunker, M. J.; De Cian, A.; Green, M. L. H.; Moreau, J. J. E.; Siganporia, N. *J. Chem. Soc., Dalton Trans.* **1980**, 2155-2161.

[19] Green, M. L. H.; Poveda, M. L.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 30-31.

[20] Dias, A. R.; Romão, C. C. *J. Organomet. Chem.* **1982**, *233*, 223-231.

Structure of a Carbon Monoxide Adduct of a "Capped" Porphyrin: Fe(C_2-Cap)(CO)(1-methylimidazole)

Kimoon Kim[†] and James A. Ibers[*]

Contribution from the Departments of Chemistry, Pohang Institute of Science and Technology, P.O. Box 125, Pohang City, Kyungbook, South Korea, and Northwestern University, Evanston, Illinois 60208-3113. *Received December 17, 1990*

Abstract: The structure of Fe(C_2-Cap)(CO)(1-MeIm) has been determined by single-crystal X-ray diffraction methods. It consists of the packing of two crystallographically independent porphyrin molecules and solvate molecules. Both porphyrin molecules display the expected connectivity in which the benzene caps are slanted with respect to the mean porphyrin planes (dihedral angles of 15.5 and 11.5° for molecules 1 and 2, respectively). The centroids of the cap atoms are 5.57 and 5.68 Å from the mean porphyrin planes. Since this distance is 3.96 Å in $H_2(C_2\text{-Cap})$, the cap moves 1.6-1.7 Å further away from the porphyrin upon binding a CO ligand inside the cavity. The coordinated CO ligand is slightly but detectably distorted from linearity, being both bent and tilted off the axis normal to the porphyrin. The Fe-C-O bond angle and the off-axis displacements for the C and O atoms of CO are 173.1 (9)°, 0.17 Å, and 0.41 Å, respectively, for molecule 1, and 175.8 (8)° and 0.12 and 0.28 Å, respectively, for molecule 2. Crystallographic data: triclinic $P\bar{1}$, $Z = 4$, $a = 18.022$ (2) Å, $b = 20.017$ (1) Å, $c = 20.691$ (2) Å, $\alpha = 70.507$ (7)°, $\beta = 76.232$ (10)°, $\gamma = 82.549$ (7)° at −150 °C, 18 468 observations, 1740 variables, $R(F) = 0.096$ ($F_o^2 > 3\sigma(F_o^2)$).

Introduction

Modeling of oxygen-binding heme proteins has been an active field of research in the last two decades.[1] Numerous model systems have been synthesized, and their affinities for axial bases and small molecules have been measured.[1] Many such model systems have contributed markedly to our understanding of structure-function relationships of natural systems, especially to current ideas about O_2/CO discrimination.[2] Recent attention has focused on the distorted geometry of the bound CO ligand

---

[†] Pohang Institute of Science and Technology.

[*] Northwestern University.

[1] Recent reviews: (a) Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181-220. (b) Morgan, B.; Dolphin, D. *Struct. Bonding* (*Berlin*) **1987**, *64*, 115-203. (c) Jameson, G. B.; Ibers, J. A. *Comments Inorg. Chem.* **1983**, *2*, 97-126. (d) David, S.; Dolphin, D.; James, B. R. In *Frontiers in Bioinorganic Chemistry*; Xavier, A. V., Ed.; VCH: Weinheim, 1986; pp 163-182. (e) Jameson, G. B.; Ibers, J. A. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Valentine, J., Eds.; University Science Books: Mill Valley, CA, 1991.

0002-7863/91/1513-6077$02.50/0

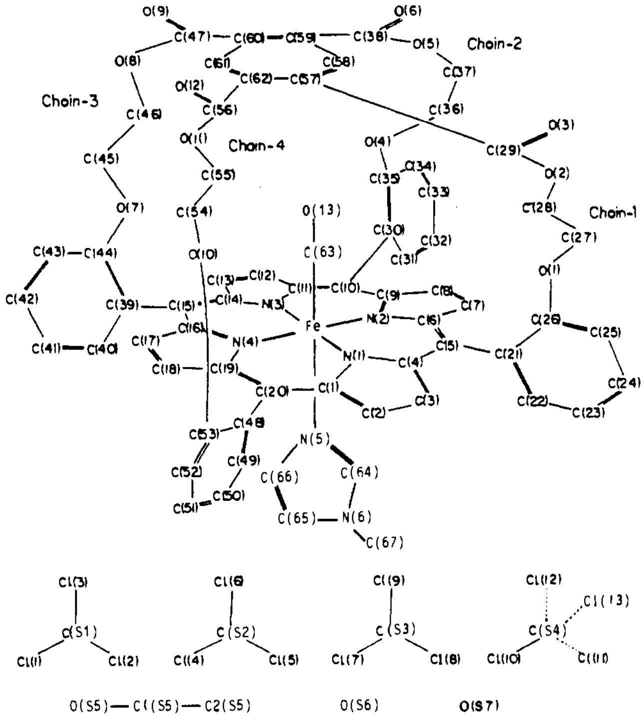

Figure 1. Atom-labeling scheme for Fe(C_2-Cap)(CO)(1-MeIm) and solvate molecules.

Table 1. Crystallographic Data for Fe(C_2-Cap)(CO)(1-MeIm)

formula	$C_{67}H_{48}FeN_6O_{13}\cdot 1.57CHCl_3\cdot 0.50C_2H_6O\cdot 0.63H_2O$
fw	1422
space group	C_i^1-$P\bar{1}$
a, Å	18.022 (2)
b, Å	20.017 (1)
c, Å	20.691 (2)
α, deg	70.507 (7)
β, deg	76.232 (10)
γ, deg	82.549 (7)
vol, α^3	6824 (1)
Z	4
temp, °C	-150^a
density (calcd), g/cm^3	1.384
density (measd), g/cm^3	1.38
cryst size, mm	~0.60 × 0.70 × 0.37
cryst vol, mm^3	0.122
radiation ($\lambda(K\alpha_1)$, Å)	Ni-filtered Cu Kα (1.540 56)
linear abs coeff, cm^{-1}	40.7
trans factors	0.162–0.365
detector aperture	2.0 mm wide × 3.0 mm high
takeoff angle, deg	3.5
scan mode	ω–2θ scan
scan speed, deg/min	2.75; for reflections with $I < 3\sigma(I)$ rescans forced to achieve $I > 3\sigma(I)$, up to 100 s total scan time
2θ limits, deg	$8.0 \leq 2\theta \leq 120.0$
bkgd counts	one-fourth of scan range on each side of reflection
scan width, deg	±0.35 in ω
data collected	$+h,\pm k,\pm l$
no. of unique data	23 517
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	18 468
no. of variables in final refinement	1740
$R(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.096
$R_w(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.134
error in observn of unit wt, e	4.20

[a] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. 1. de Vic, 31320 Castanet-Tolosan, France.

in heme proteins. Most X-ray studies of CO adducts of heme proteins have suggested a substantial distortion of the Fe–C–O linkage: either a bend at the C atom of the Fe–C–O bond or a tilt of the linear Fe–C–O bond from the normal to the heme plane or both.[3] Such distortion presumably stems from nonbonding interactions of the CO ligand with nearby distal amino acid residues, since CO preferentially binds to Fe in a linear, perpendicular fashion in unconstrained heme model systems.[4] Since O_2 preferentially binds to hemes[5] and to model systems[6] in a bent fashion, it is thought that the distal steric interaction is an important factor in O_2/CO discrimination. A number of encumbered porphyrin systems have been prepared in an effort to delineate the structural details of small ligand binding.[7-17] Unfortunately, as yet, only few X-ray structures of these encumbered models with bound small ligands have been reported. These include those with

---

(2) Baltzer, L.; Landergren, M. *J. Am. Chem. Soc.* **1990**, *112*, 2804–2805. (b) Nagai, K.; Luisi, B.; Shih, D.; Miyazaki, G.; Imai, K.; Poyart, C.; De Young, A.; Kwiatkowsky, L.; Noble, R. W.; Lin, S.-H.; Yu, N.-T. *Nature (London)* **1987**, *329*, 858–860. (c) Olson, J. S.; Mathews, A. J.; Rohlfs, R. J.; Springer, B. A.; Egeberg, K. D.; Sligar, S. G.; Tame, J.; Renaud, J.-P.; Nagai, K. *Nature (London)* **1988**, *336*, 265–266.

(3) (a) A typical example: Kuriyan, J.; Wilz, S.; Karplus, M.; Petsko, G. A. *J. Mol. Biol.* **1986**, *192*, 133–154. (b) An example of a nearly linear arrangement: Derewenda, Z.; Dodson, G.; Emsley, P.; Harris, D.; Nagai, K.; Perutz, M.; Reynaud, J.-P. *J. Mol. Biol.* **1990**, *211*, 515–519.

(4) (a) Peng, S.-M.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8032–8036. (b) Scheidt, W. R.; Haller, K. J.; Fons, M.; Mashiko, T.; Reed, C. A. *Biochemistry* **1981**, *20*, 3653–3657.

(5) (a) Steigemann, W.; Weber, E. *J. Mol. Biol.* **1979**, *127*, 309–338. (b) Phillips, S. E. V. *J. Mol. Biol.* **1980**, *142*, 531–554. (c) Phillips, S. E. V.; Schoenborn, B. P. *Nature (London)* **1981**, *292*, 81–82. (d) Shaanan, B. *J. Mol. Biol.* **1983**, *171*, 31–59. (e) Brzozowski, A.; Derewenda, Z.; Dodson, E.; Dodson, G.; Grabowski, M.; Liddington, R.; Skarżyński, T.; Vallely, D. *Nature (London)* **1984**, *307*, 74–76. (f) Liddington, R.; Derewenda, Z.; Dodson, G.; Harris, D. *Nature (London)* **1988**, *331*, 725–728. (g) Luisi, B.; Liddington, B.; Fermi, G.; Shibayama, N. *J. Mol. Biol.* **1990**, *214*, 7–14.

(6) (a) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 3224–3237. (b) Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Collman, J. P. *Inorg. Chem.* **1978**, *17*, 850–857.

(7) (a) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450–2452. (b) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B. L.; Lang, G.; Pettman, R. B.; Sessler, J. L.; Walters, M. A. *J. Am. Chem. Soc.* **1983**, *105*, 3038–3052. (c) Collman, J. P.; Brauman, J. I.; Iverson, B. L.; Sessler, J. L.; Morris, R. M.; Gibson, Q. H. *J. Am. Chem. Soc.* **1983**, *105*, 3052–3064. (d) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3477–3486. (e) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3486–3495.

(8) (a) Battersby, A. R.; Buckley, D. G.; Hartley, S. G.; Turnbull, M. D. *J. Chem. Soc., Chem. Commun.* **1976**, 879–881. (b) Battersby, A. R.; Hartley, S. G.; Turnbull, M. D. *Tetrahedron Lett.* **1978**, *19*, 3169–3172. (c) Battersby, A. R.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1980**, 117–119.

(9) (a) Almog, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227–228. (b) Baldwin, J. E.; Klose, T.; Peters, M. *J. Chem. Soc., Chem. Commun.* **1976**, 881–883. (c) Almog, J.; Baldwin, J. E.; Crossley, M. J.; Debernardis, J. F.; Dyer, R. L.; Huff, J. R.; Peters, M. K. *Tetrahedron* **1981**, *37*, 3589–3601. (d) Baldwin, J. E.; Crossley, M. J.; Klose, T.; O'Rear, E. A., III; Peters, M. K. *Tetrahedron* **1982**, *38*, 27–39. (e) Baldwin, J. E.; Cameron, J. H.; Crossley, M. J.; Dagley, I. J.; Hall, S. R.; Klose, T. *J. Chem. Soc., Dalton Trans.* **1984**, 1739–1746.

(10) (a) Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1896–1904. (b) Hashimoto, T.; Dyer, R. L.; Crossley, M. J.; Baldwin, J. E.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 2101–2109. (c) Rose, E. J.; Venkatasubramanian, P. N.; Swartz, J. C.; Jones, R. D.; Basolo, F.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 5742–5745. (d) Shimizu, M.; Basolo, F.; Vallejo, M. N.; Baldwin, J. L. *Inorg. Chim. Acta* **1984**, *91*, 247–250.

(11) (a) Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102–109 and references therein. (b) Traylor, T. G.; Mitchell, M. J.; Tsuchiya, S.; Campbell, D. H.; Stynes, D. V.; Koga, N. *J. Am. Chem. Soc.* **1981**, *103*, 5234–5236. (c) Traylor, T. G.; Koga, N.; Deardurff, L. A.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5132–5143. (d) Traylor, T. G.; Tsuchiya, S.; Campbell, D.; Mitchell, M.; Stynes, D.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 604–614. (e) Traylor, T. G.; Koga, N.; Deardurff, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6504–6510.

(12) (a) Momenteau, M.; Lavalette, D. *J. Chem. Soc., Chem. Commun.* **1982**, 341–343. (b) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans. 1* **1983**, 189–196. (c) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J.-M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 221–231.

(13) (a) Ward, B.; Wang, C.-B.; Chang, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 5236–5238. (b) Chang, C. K.; Kondylis, M. P. *J. Chem. Soc., Chem. Commun.* **1986**, 316–318.

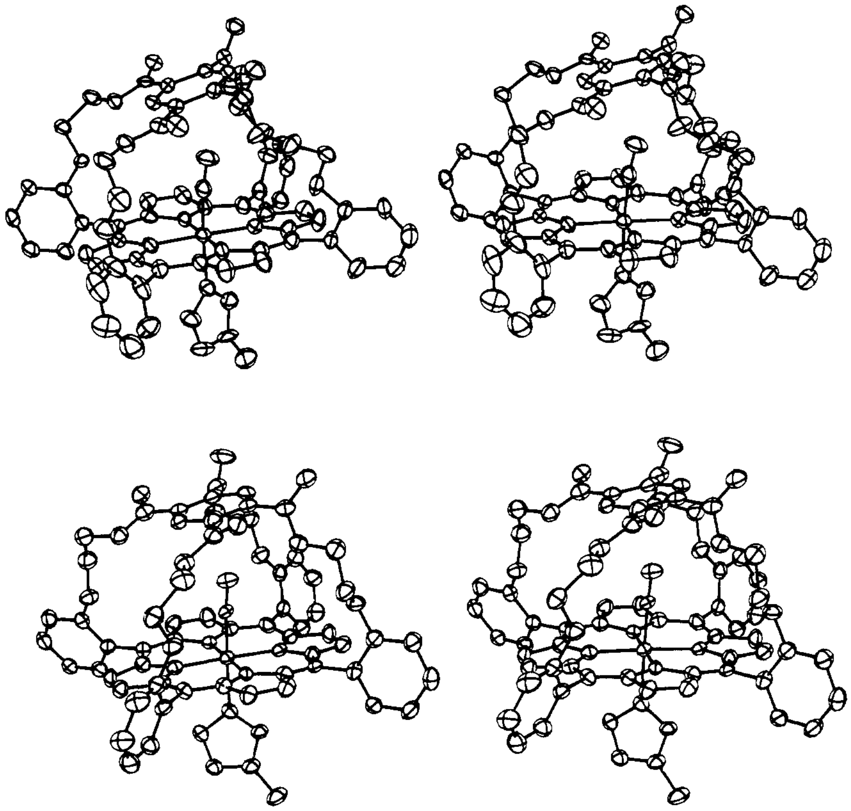

Figure 2. Stereoviews of two independent Fe(C_2-Cap)(CO)(1-MeIm) molecules: (top) molecule 1; (bottom) molecule 2.

O_2,[6] CN^-,[18] and CO.[19] Here we report the crystal structure of Fe(C_2-Cap)(CO)(1-MeIm) (Figure 1), the first such structure of a "capped" system to be determined in which there is any ligand bound inside the cap. The structure reveals (i) a largely expanded cavity to accommodate a CO ligand and (ii) a CO ligand slightly but detectably distorted from linearity owing to the steric interaction with the "cap".

Experimental Section

Preparation of Fe(C_2-Cap)(CO)(1-MeIm). All chemicals were reagent grade and were used without purification. FeCl(C_2-Cap) was a gift from F. Basolo. In a test tube, 15 mg of FeCl(C_2-Cap) was dissolved in 3 mL of chloroform and the solution was purged with CO to remove oxygen. After one drop of 1-MeIm and 1 mL of 2 M aqueous sodium dithionite solution (saturated with CO) were added, the solution was shaken vigorously for 5 min. During this period, the color of the solution turned red. The aqueous layer was discarded, and the organic layer was washed twice with CO-saturated water, dried over anhydrous sodium sulfate, and then transferred to several diffusion tubes. Crystals suitable for X-ray work were obtained in 2 months by diffusion of *n*-hexane through the solution under a CO atmosphere.

X-ray Crystal Structure Determination. When a crystal was exposed to air at room temperature, solvate loss occurred rapidly. Accordingly, a crystal was coated with Nujol and mounted quickly in the cold stream (−150 °C) of an Enraf Nonius CAD4 diffractometer. Unit cell parameters were determined by least-squares refinement of 25 reflections that had been automatically centered on the diffractometer. Cell reduction did not suggest higher symmetry, and hence the crystal was assigned to the triclinic system. Intensity data were collected by methods standard in this laboratory.[20] Intensities of six standard reflections, measured every 3 h of X-ray exposure, decayed linearly by 11.5% on average by the end of the data collection. Crystallographic details are given in Table 1.

Standard procedures and programs were used to develop and refine the structure.[20] The unit cell volume and measured density indicated that two independent molecules of Fe(C_2-Cap)(CO)(1-MeIm) and solvent molecules exist in the asymmetric unit. The positions of two Fe atoms were obtained from the Patterson function, and the rest of the atoms, except for the disordered solvate molecules, were located by the direct-methods program DIRDIF.[21] After several cycles of isotropic full-matrix least-squares refinement, large peaks in difference electron density maps were interpreted as resulting from two partially occupied chloroform molecules (S3,S4). Anisotropic refinement of the Fe and Cl atoms and isotropic refinement of the rest of the atoms led to an R index of 0.12. The difference electron density map after this refinement still showed significant density. No satisfactory model was found, but the largest peaks were interpreted as resulting from partially occupied water molecules and a partially occupied ethanol molecule; these could have come from the solvents used. Hydrogen atom parameters (except for those of the solvate molecules) were idealized (C–H = 0.95 Å, H–C–H = 109.5°; $B(H) = B_{eq}(C) + 1$ Å^2) and included as fixed contributions. In the final cycle of refinement, all non-hydrogen atoms, with the exception of some of those of the solvent molecules, were refined anisotropically and occupancies of the solvent molecules were varied. This refinement, which involved 18 468 observations and 1740 variables, was carried out on a Stellar G2000 computer; it converged to the R indices given in Table 1. Peaks on a final difference electron density map range in height from +2.0 to −1.6 e/Å^3. The atom-labeling scheme for the Fe(C_2-Cap)(CO)(1-MeIm) molecule and solvate molecules is given in Figure 1. Positional parameters and equivalent isotropic thermal parameters for nonhydrogen atoms are listed in Table SI.[22] Anisotropic thermal pa-

---

(14) (a) Wijesekera, T. P.; Paine, J. B., III; Dolphin, D.; Einstein, F. W. B.; Jones, T. *J. Am. Chem. Soc.* **1983**, *105*, 6747–6749. (b) David, S.; Dolphin, D.; James, B. R.; Paine, J. B., III; Wijesekera, T. P.; Einstein, F. W. B.; Jones, T. *Can. J. Chem.* **1986**, *64*, 208–212. (c) David, S.; James, B. R.; Dolphin, D. *J. Inorg. Biochem.* **1986**, *28*, 125–134.

(15) Simonis, U.; Walker, F. A.; Lee, P. L.; Hanquet, B. J.; Meyerhoff, D. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2659–2668.

(16) (a) Lecas, A.; Renko, Z.; Rose, E. *Tetrahedron Lett.* **1985**, *26*, 1019–1022. (b) Boitrel, B.; Lecas, A.; Renko, Z.; Rose, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1820–1821.

(17) Uemori, Y.; Kyuno, E. *Inorg. Chim. Acta* **1987**, *138*, 9–10.

(18) Schappacher, M.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1989**, *28*, 389–390.

(19) (a) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. C.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919–5923. (b) bhp = "basket-handle porphyrin": Ricard, L.; Weiss, R.; Momenteau, M. *J. Chem. Soc., Chem. Commun.* **1986**, 818–820. (c) Kim, K.; Fettinger, J.; Sessler, J. L.; Cyr, M.; Hugdahl, J.; Collman, J. P.; Ibers, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 403–405.

(20) For example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(21) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. *DIRDIF 81*; Crystallographic Laboratory, University of Nijmegen, Toernooiveld: 6525 ED Nijmegen, The Netherlands, 1981.

(22) Supplementary material.

Table II. Selected Bond Distances (Å) and Angles (deg) for Fe(C_2-Cap)(CO)(1-MeIm)

atoms	mol 1	mol 1
C(63)–O(13)	1.161 (8)	1.158 (8)
Fe–C(63)	1.742 (7)	1.748 (7)
Fe–N(5)	2.043 (6)	2.041 (5)
Fe–N(1)	1.997 (6)	1.971 (6)
Fe–N(2)	1.980 (6)	2.001 (6)
Fe–N(3)	1.991 (6)	1.993 (6)
Fe–N(4)	1.995 (6)	1.988 (5)
av Fe–N_{Por}	1.990 (7)[a]	1.988 (13)
av N–C_a	1.381 (10)	1.385 (9)
av C_a–C_b	1.446 (17)	1.441 (10)
av C_b–C_b	1.349 (30)	1.346 (10)
av C_a–C_m	1.388 (10)	1.389 (13)
av C_m–C_α	1.501 (10)	1.490 (9)
av C–C(cap)	1.394 (15)	1.389 (13)
O(13)–C(63)–Fe	172.9 (6)	175.9 (6)
C(63)–Fe–N(1)	89.0 (3)	89.6 (3)
C(63)–Fe–N(2)	86.4 (3)	89.0 (3)
C(63)–Fe–N(3)	90.5 (3)	90.3 (3)
C(63)–Fe–N(4)	95.6 (3)	93.8 (3)
C(63)–Fe–N(5)	174.7 (3)	177.8 (3)
N(5)–Fe–N(1)	88.4 (2)	88.4 (2)
N(5)–Fe–N(2)	89.0 (2)	90.0 (2)
N(5)–Fe–N(3)	92.2 (2)	91.7 (2)
N(5)–Fe–N(4)	89.0 (2)	87.2 (2)
N(1)–Fe–N(2)	90.4 (2)	89.9 (2)
N(1)–Fe–N(4)	90.1 (2)	90.1 (2)
N(2)–Fe–N(3)	90.3 (2)	90.0 (2)
N(3)–Fe–N(4)	89.3 (2)	90.1 (2)
N(1)–Fe–N(3)	179.1 (3)	179.8 (5)
N(2)–Fe–N(4)	178.0 (2)	177.1 (2)

[a] The estimated standard deviation in parentheses is the larger of that calculated for an individual observation from the inverse matrix or on the assumption that the values averaged are from the same population.

rameters, hydrogen atom parameters, and final values of $10|F_o|$ vs $10|F_c|$ are given in Tables SII–SIV, respectively.[22]

Results

General Description. The crystal structure of the title compound consists of the packing of two crystallographically independent Fe(C_2-Cap)(CO)(1-MeIm) molecules and solvate molecules. There are no unusual intermolecular contacts. Stereoviews of the two main molecules, designated arbitrarily molecule 1 and molecule 2, are shown in Figure 2. Both molecules have the expected connectivity. Selected bond distances and bond angles are tabulated in Table II; complete tabulations are available in Tables SV and SVI, respectively.[22] In neither molecule is the phenyl cap parallel to the porphyrin plane, and the two molecules are distinguished mainly by the orientation of the 1-MeIm ligand with respect to the tilt of the cap: in molecule 1 the 1-MeIm plane is nearly perpendicular to the direction of tilt, while in molecule 2 it is nearly parallel to that direction (see Figure 2).

In H_2(C_2-Cap)[23] and FeCl(C_2-Cap)[24] the phenyl cap is essentially parallel to the mean porphyrin plane (dihedral angles 0.03 and 3.0°, respectively), but in the present instance, the dihedral angles are 15.5 and 11.5° for molecules 1 and 2, respectively (see Table SVII[22] (least-squares planes) and Table SVIII[22] (dihedral angles)). This slant of the cap appears to be related to the conformation of the ester linkages that are directly attached to it. In both molecules 1 and 2, two of the ester groups (chains 3 and 4) are nearly coplanar with the cap with torsion angles O(8)-C(47)-C(60)-C(61) of -13.6 (9), -19.9 (9)° and O(11)-C(56)-C(62)-C(57) of -169.4 (6), -154.5 (6)°, while the other two (chains 1 and 2) are nearly perpendicular to the cap with torsion angles O(2)-C(29)-C(57)-C(58) of -96.3 (7), -108.1 (8)° and O(5)-C(38)-C(59)-C(60) of -66.2 (8), -65.9(9)° for molecules 1 and 2, respectively. (See Table SIX[22] for a complete listing of torsion angles.) The latter pair of ester groups "lift up" one side of the cap to make room for the coordinated CO molecule, and consequently the cap is no longer parallel to the porphyrin plane. The separations between the centroids of the cap and the porphyrin core are 5.57 and 5.68 Å for molecules 1 and 2, respectively. These may be compared with a separation of 3.96 Å in H_2(C_2-Cap) and 4.01 Å in FeCl(C_2-Cap).

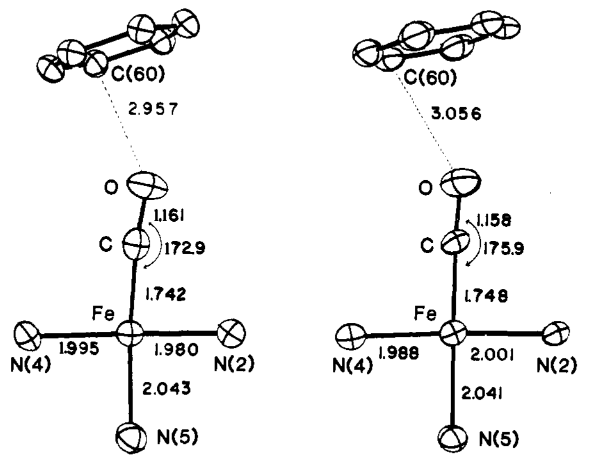

Figure 3. Coordination geometries of iron in (a) molecule 1 and (b) molecule 2.

Coordination Geometry around the Iron Atoms. The Fe–C(CO) bond distances are 1.742 (7) Å for molecule 1 and 1.748 (7) Å for molecule 2. A wide range (1.706–1.792 Å) of Fe–C(CO) bond distances has been observed in Fe(porphyrin)(CO) complexes (Tables III). The C–O bond distances of 1.161 (8) and 1.158 (8) Å for molecules 1 and 2, respectively, are a little longer than those of any other Fe(porphyrin)(CO) complexes, probably because of the present low-temperature data set. One of the interesting features of the present structures is that the coordinated CO ligands are slightly but detectably distorted from linearity, being both bent and tilted off the axis normal to the mean porphyrin plane (Figure 3). A larger distortion is observed in molecule 1 than in molecule 2. In molecule 1, the Fe–C–O bond angle is 172.9 (6)° and the off-axis displacements for the C and O atoms of the carbonyl group are 0.17 and 0.41 Å, respectively. The corresponding values for molecule 2 are 175.9 (6)°, 0.12 Å, and 0.28 Å, respectively. The distortion parameters of the Fe–C–O unit in molecule 1 are comparable to those of Fe(β-PocPiv)(CO)(1,2-Me_2Im)[19c] and [Fe(lacunar)(CO)(py)][PF_6]$_2$:[19a] 172.5 (6)°, 0.18 Å, and 0.36 Å for the former and 170.6 (5)°, 0.13 Å, and 0.40 Å for the latter. In the present instance, this distortion stems from the short nonbonding interactions between the cap and the CO ligand (Table IV). The carbonyl stretching frequency of Fe(C_2-Cap)(CO)(1-MeIm) in Nujol agrees with that in solution[25] within experimental error (2000 cm^{-1}). This result suggests that the distortions of the Fe-C-O linkage should be similar in solution and in the solid state. Such a large shift to higher frequency compared with 1970 cm^{-1} for Fe(OEP)(CO)(1-MeIm)[26] may be a consequence of strong electronic interactions between the cap and the bound CO.[25]

Other bond parameters associated with the iron center are typical of six-coordinate iron(II) porphyrin complexes. The average Fe-N(porphyrin) bond distances are 1.990 (7) Å for molecule 1 and 1.988 (13) Å for molecule 2. The Fe-N(imidazole) bond distances of 2.043 (6) and 2.041 (5) Å for molecules 1 and 2, respectively, are somewhat shorter than that in Fe(bhp)(CO)(1-MeIm)[19b] (2.062 (5) Å). The iron atoms are displaced 0.01 Å out of the plane of the four nitrogen atoms toward the CO ligand in molecule 1 and 0.02 Å away from the CO ligand in molecule 2. The porphyrin cores are slightly S_4-ruffled[27] with

---

(23) Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831.

(24) Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3715–3721.

(25) Jones, R. D.; Budge, J. R.; Ellis, P. E., Jr.; Linard, J. E.; Summerville, D. A.; Basolo, F. *J. Organomet. Chem.* **1979**, *181*, 151–158.

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

Table III. Metrical Data for Fe(CO) Heme Model Compounds

compd	Fe–C, Å	C–O, Å	Fe–C–O, deg	av Fe–N_{pyr}, Å	Fe–N_{ax} or Fe–O_{ax}, Å	C–Fe–N_{ax} or C–Fe–O_{ax}, deg	ref
Fe(TPP)(CO)(py)	1.77 (2)	1.12 (2)	179 (2)	2.02 (3)	2.10 (1)	177.5 (8)	*a*
Fe(deut)(CO)(THF)	1.706 (5)	1.144 (5)	178.3 (1.4)	1.98 (3)	2.127 (4)	177.4 (9)	*b*
Fe(bhp)(CO)(1-MeIm)	1.728 (6)	1.149 (6)	180.0 (0)	1.999 (3)	2.062 (5)	180.0 (0)	*c*
[Fe(lacunar)(CO)(py)][PF_6]$_2$	1.792 (4)	1.150 (5)	170.6 (5)	1.992 (5)	2.052 (3)		*d*
Fe(C_2-Cap)(CO)(1-MeIm)							
mol 1	1.742 (7)	1.161 (8)	172.9 (6)	1.990 (7)	2.043 (6)	174.7 (3)	*e*
mol 2	1.748 (7)	1.158 (8)	175.9 (6)	1.988 (13)	2.041 (5)	177.8 (3)	*e*
Fe(β-PocPiv)(CO)(1,2-Me_2Im)	1.768 (7)	1.148 (7)	172.5 (6)	1.973 (8)	2.079 (5)	176.3 (3)	*f*

[a] Reference 4a. [b] Reference 4b. [c] Reference 19b. [d] Reference 19a. [e] This work. [f] Reference 19c.

Table IV. Distances between CO Oxygen Atoms and the "Cap" Atoms

atoms	mol 1	mol 2
O(13)···C(57)	3.241 (8)	3.189 (9)
O(13)···C(58)	3.231 (8)	3.191 (9)
O(13)···C(59)	3.086 (8)	3.091 (9)
O(13)···C(60)	2.957 (9)	3.056 (8)
O(13)···C(61)	2.980 (8)	3.079 (9)
O(13)···C(62)	3.110 (9)	3.132 (9)
O(13)···center	2.772	2.798

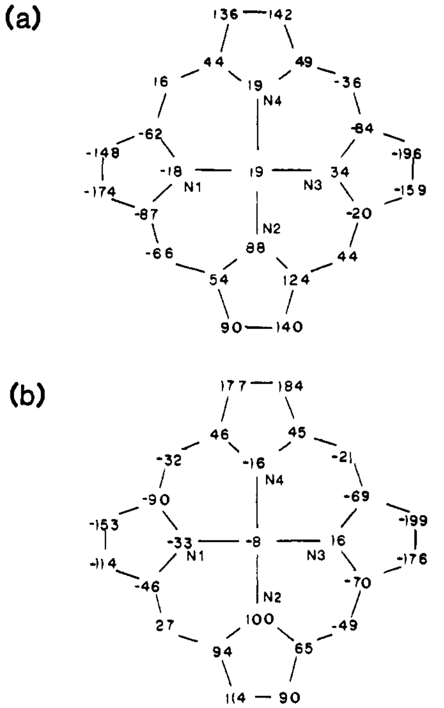

Figure 4. Deviations (×10^3 Å) of the porphyrin atoms from the least-squares plane of the 24-atom porphyrin skeleton: (a) molecule 1; (b) molecule 2.

mean deviations from the 24-atom least-squares plane of 0.085 and 0.084 Å for molecules 1 and 2, respectively. The deviations of individual atoms from the least-squares planes are shown in Figure 4.

Discussion

Conformational Reorganization Associated with CO Binding. NMR studies suggest that the structures of the C_2- and C_3-capped porphyrins in solution are similar to those in the solid state, at least as far as the cap-to-porphyrin distances are concerned.[28] Furthermore, one can expect that the five-coordinate complex, Fe(C_2-Cap)(1-MeIm), would have a structure similar to that of H_2(C_2-Cap) or FeCl(C_2-Cap): the cap unit is nearly parallel to the porphyrin plane with a separation of about 4 Å. The present structures represent two possibilities that Fe(C_2-Cap)(1-MeIm) might adopt upon ligation by CO. Obviously, the most signficant structural change is the expansion of the cavity: the center of the cap moves about 1.6–1.7 Å further away from the porphyrin, and the cap is no longer parallel to the porphyrin plane (vide supra). The expansion of the cavity upon coordination of small molecules, such as O_2 or CO, has been anticipated in these systems, but this is the first structure that demonstrates the large conformational reorganization associated with ligand binding in model systems.

Structure and Affinity for CO. The affinities of the capped porphyrin complexes for O_2 and CO are known.[10] It has been argued that these capped systems discriminate in favor of CO over O_2, since the O_2 affinities of the capped systems are lower while the CO affinities are about the same as those in the flat-open systems. The lower O_2 affinity was thought to result from a peripheral steric effect between the bound O_2 molecule and the atoms in the chain connecting the porphyrin to the cap.[10b] This argument suggests that CO should bind with capped systems in its stable, normal linear structure without any marked steric hindrance. However, the present structures of Fe(C_2-Cap)(CO)(1-MeIm) reveal that significant steric interactions exist between the cap and the oxygen atom of CO. We believe that this should be reflected in the affinity for CO in this system. In fact, Fe(C_2-Cap)(1-MeIm) has even lower CO affinity than does Fe(PocPivP)(1-MeIm), which discriminates against CO binding if we take a "protected", unencumbered system such as (tetramesitylporphyrinato)iron(II) as a control.[7c] Indeed, the CO affinity of the capped porphyrin is at least an order of magnitude lower than that of the control. But there are at least two caveats here: (1) The Fe(PocPivP)(CO)(1-MeIm) molecule exhibits a nearly linear Fe–C–O arrangement despite discrimination against CO binding and (2) the energy required for the large conformational reorganization of the capped and pocket systems associated with CO binding may also contribute significantly to the decrease in CO affinity. More structural information on these model systems will contribute significantly to our understanding of structure–function relationships in these systems.

Acknowledgment. We are indebted to Prof. Fred Basolo for his gift of the sample of FeCl(C_2-Cap). This research was kindly supported by the U.S. National Institutes of Health (Grant HL-13157).

Supplementary Material Available: Table SI (positional and equivalent isotropic thermal parameters for the non-hydrogen atoms), Table SII (anisotropic thermal parameters), Table SIII (hydrogen atom parameters), Table SV (bond distances), Table SVI (bond angles), Table SVII (least-squares planes), Table SVIII (dihedral angles), and Table SIX (torsional angles) (21 pages); Table SIV (observed and calculated structure amplitudes (×10)) (75 pages). Ordering information is given on any current masthead page.

---

(27) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1–70.

(28) Clayden, N. J.; Moore, G. R.; Williams, R. J. P.; Baldwin, J. E.; Crossley, M. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1863–1868.