# Structure of the Cobalt(II)-"Capped" Porphyrin, $Co(C_3\text{-}Cap)\cdot 3CHCl_3$

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**Abstract:** The structure of $Co(C_3\text{-}Cap)\cdot 3CHCl_3$ consists of the packing of discrete porphyrin and solvate molecules. The $Co(C_3\text{-}Cap)$ moiety displays its expected connectivity in which the mean planes of the benzene cap and the porphyrin are nearly coplanar (dihedral angle, 2.4°) with the center of the cap nearly over the Co site. The Co atom is 3.436 Å from the mean cap plane; the centroid of the cap atoms is 3.494 Å from the mean porphyrin plane. Thus this $C_3$-cap displays a cap-to-porphyrin separation that is about 0.5 Å *less* than that found in the known $C_2$-cap structures. The porphyrin in $Co(C_3\text{-}Cap)$ is severely ruffled with an average deviation of the atoms from the mean porphyrin plane of 0.30 Å and individual deviations as large as 0.6 Å. Implications of structural results on the $C_2$-caps and the present $C_3$-cap for $O_2$ and CO affinities are discussed. Crystallographic data: monoclinic, $P2_1/n$, $Z = 4$, $a = 20.111$ (13) Å, $b = 15.660$ (11) Å, $c = 22.796$ (16) Å, $\beta = 110.49$ (2)° at −150 °C, 8153 observations, 443 variables, $R(F)$ ($F_o^2 > 3\sigma(F_o^2)$) = 0.100. The solvate molecules are badly disordered.

Model systems have contributed markedly to our understanding of structure–function relationships of oxygen-binding hemoproteins.[2–4] Among such model are the so-called "capped" porphyrins[5,6] (Figure 1) which form a very useful homologous series. Ligand binding and small molecule ($O_2$, CO, NO) affinities of these "capped" porphyrins have been determined.[7–12] The binding of $O_2$ to $MB(C_x\text{-}Cap)$ for a given metal M and base B is particularly sensitive to $x$, with affinity decreasing as $x$ increases (Table I), while the affinities of CO and NO are much less dependent upon $x$. Although various conjectures[4,12–15] have been offered to explain these trends with cap size, evolution of meaningful structure–function relationships has been hampered by the dearth of structural information on such systems. For the $C_2$-caps two structures are known: $H_2(C_2\text{-}Cap)$[16] and $FeCl(C_2\text{-}Cap)$.[17] Here we report the first structural results on a higher member of the series, namely $Co(C_3\text{-}Cap)\cdot 3CHCl_3$. Remarkably, the cap-to-porphyrin separation in this $C_3$-cap is nearly 0.5 Å *less* than that in the known $C_2$-cap structures.

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(2) Perutz, M. F. *Annu. Rev. Biochem.* **1979**, *48*, 327–386.
(3) Jameson, G. B.; Robinson, W. T.; Ibers, J. A. In *Hemoglobin and Oxygen Binding*; Ho, C., Ed.; Elsevier North Holland: New York, 1982; pp 25–35.
(4) Jameson, G. B.; Ibers, J. A. *Comments Inorg. Chem.* **1983**, *2*, 97–126.
(5) Almog, J.; Baldwin, J. E.; Dyer, R. L.; Peters, M. *J. Am. Chem. Soc.* **1975**, *97*, 226–227.
(6) Almog, J.; Baldwin, J. E.; Huff, J. *J. Am. Chem. Soc.* **1975**, *97*, 227–228.
(7) Elis, P. E., Jr.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889–1896.
(8) Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1896–1904.
(9) Hashimoto, T.; Dyer, R. L.; Crossley, M. J.; Baldwin, J. E.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 2101–2109.
(10) Shimizu, M.; Basolo, F.; Vallejo, M. N.; Baldwin, J. E. *Inorg. Chim. Acta* **1984**, *91*, 247–250.
(11) Shimizu, M.; Basolo, F.; Vallejo, M. N.; Baldwin, J. E. *Inorg. Chim. Acta* **1984**, *91*, 251–255.
(12) Hashimoto, T.; Basolo, F. *Comments Inorg. Chem.* **1981**, *4*, 199–205.
(13) Traylor, T. G.; Campbell, D.; Tsuchiya, S.; Mitchell, M.; Stynes, D. V. *J. Am. Chem. Soc.* **1980**, *102*, 5939–5941.
(14) Traylor, T. G.; Mitchell, M. J.; Tsuchiya, S.; Campbell, D. H.; Stynes, D. V.; Koga, N. *J. Am. Chem. Soc.* **1981**, *103*, 5234–5236.
(15) Clayden, N. J.; Moore, G. R.; Williams, R. J. P.; Baldwin, J. E.; Crossley, M. J. *J. Chem. Soc., Perkin Trans. II*, **1982**, 1693–1698.
(16) Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831.
(17) Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3715–3721.
(18) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

**Table I.** Affinities[a] for Small Molecules of Some "Capped" Porphyrin Systems

| system | $P_{1/2}^{CO}$(25 °C) | $P_{1/2}^{NO}$(25 °C) |
|---|---|---|
| Fe(1,2-Me$_2$Im)(C$_2$-Cap) | $2.0 \times 10^{-1}$ [b] | $2.0 \times 10^{-6}$ [d] |
| Fe(1,2-Me$_2$Im)(C$_3$-Cap) | $1.4 \times 10^{-1}$ [b] | $3.3 \times 10^{-6}$ [d] |
| Fe(1,2-Me$_2$Im)(C$_4$-Cap) | 4.1[c] | $4.1 \times 10^{-5}$ [d] |
| | $P_{1/2}^{O_2}$(0 °C) | |
| Fe(1-MeIm)(C$_2$-Cap) | 4.5[e] | |
| Fe(1-MeIm)(C$_3$-Cap) | 120–180[e] | |
| | $P_{1/2}^{O_2}$(−78 °C) | |
| Co(1-MeIm)(C$_2$-Cap) | 140[e] | |
| Co(1-MeIm)(C$_3$-Cap) | $>5 \times 10^{3}$ [e] | |

[a] The solvent is toluene. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 8.

## Experimental Section

$Co(C_3\text{-}Cap)$ was prepared as previously described.[7] Over a period of about 3 years modest sized crystals were grown by diffusion at 5 °C of methanol into a dilute chloroform solution of $Co(C_3\text{-}Cap)$.

Solvate loss occurs rapidly at room temperature when the crystals are taken from their mother liquor. Accordingly, a crystal was mounted directly in the cold stream (−150 °C) of an Enraf-Nonius CAD4 diffractometer. Intensity data were collected by methods standard at Northwestern.[17] Details are given in Table II.

The structure was solved by a combination of Patterson and direct methods. Refinement of the structure proceeded smoothly, except for problems with the solvate molecules. No thoroughly satisfactory model for these solvate molecules was found. In the best model the three chloroform molecules were given variable occupancies and the Cl atoms were allowed anisotropic motion. While such motion remained positive definite, some of the $B_{eq}$ values for these Cl atoms exceed 20 Å$^2$ for data collected at −150 °C; moreover, the resultant geometries are non-representative. Clearly, the chloroform molecules are badly disordered. The occupancies of the three solvent molecules refined to 0.87 (1), 0.77 (1), and 0.96 (1), respectively. In view of the general problems with the solvent molecules and the high correlation between occupancies and thermal parameters we choose to denote the composition of the compound as $Co(C_3\text{-}Cap)\cdot 3CHCl_3$ rather than 2.60 $CHCl_3$. In the final model, in addition to the Cl atoms, the Co atom was refined anisotropically. All other non-hydrogen atoms were refined isotropically. Hydrogen-atom positions (with the exception of the $CHCl_3$ H atoms) were idealized (C–H = 0.95 Å; $B(H) = B_{eq}(C) + 1$ Å$^2$) and their contributions included. The final refinement on $F_o^2$ involved 8153 observations and 443 variables; it converged to the agreement indices given in Table II. An analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of setting angles, Miller indices, and $F_o^2$ shows poorer agreement at low Bragg angles. This is consistent with residual electron density of the order of 1.5 e/Å$^3$ in the vicinity of the Cl atoms. Such density is about 20% that of a typical Cl atom in this structure. Final positional and equivalent isotropic thermal parameters

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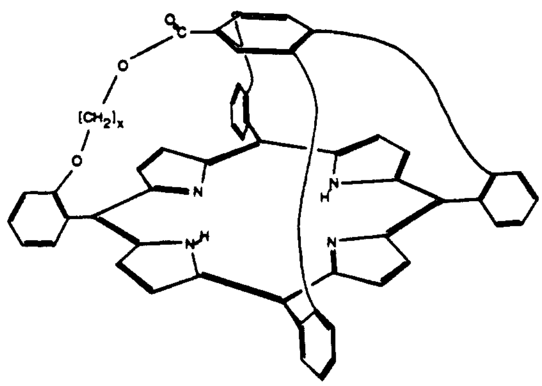


**Figure 1.** "Capped" porphyrin molecules. For $x = 3$ we term the molecule $C_3$-cap. The four chains linking the phenyl "cap" to the tetraphenylporphyrin moiety are identical.

**Table II.** Crystal Data and Data Collection Procedures for $Co(C_3\text{-}Cap)\cdot 3CHCl_3$

| | |
|---|---|
| formula | $C_{69}H_{53}Cl_9CoN_4O_{12}$ |
| formula wt, amu | 1508.2 |
| space group | $C_{2h}^5$-$P2_1/n$ |
| *a*, Å | 20.111 (13) |
| *b*, Å | 15.660 (11) |
| *c*, Å | 22.796 (16) |
| *β*, deg | 110.49 (2) |
| vol, Å$^3$ | 6725 |
| *Z* | 4 |
| temp, °C | −150[a] |
| density (calcd), g/cm$^3$ | 1.489 |
| crystal planes | {101}, (0.107),[b] {1$\bar{1}$0}, (0.106), ($\bar{1}$01), (0.245), (00$\bar{1}$), (0.245) |
| crystal vol, mm$^3$ | 0.0067 |
| radiation | graphite-monochromated Mo K$\alpha$ ($\lambda$(Mo K$\alpha_1$) = 0.7093 Å) |
| linear abs coeff, cm$^{-1}$ | 6.77 |
| transmission factors | 0.919–0.938 |
| detector aperture | 2 mm wide, 2 m high, 17 cm from crystal |
| take-off angle, deg | 2.3 |
| scan mode | $\omega$ |
| scan speed, deg/min | 2 in $\omega$; reflections having $F_o^2 < 3\sigma(F_o^2)$ were rescanned to achieve a $3\sigma$ level up to a maximum scan time of 100 s |
| $2\theta$ limits | $4 \leq 2\theta \leq 44$ |
| bkg counts | 1/4 of scan range on each side of reflection |
| stand reflctns | 6 in diverse regions of reciprocal space remeasured every 3.0 h of X-ray exposure time |
| scan range | ±1.1 in $\omega$ |
| data collected | $\pm h + k + l$ |
| unique data | 8153 |
| *p* factor for $\sigma(F_o^2)$ | 0.03 |
| unique data with $F_o^2 > 3\sigma t(F_o^2)$ | 4476 |
| no. of variables | 443 |
| $R(F^2)$ | 0.168 |
| $R_w(F^2)$ | 0.210 |
| $R(F)$ ($F_o^2 > 3\sigma(F_o^2)$) | 0.100 |
| error in observation of unit wt, e$^2$ | 1.90 |

[a] The low-temperature system is from a design by Prof. J. J. Bonnet and S. Askenazy and is commerically available from Soterem, Z. I. de Vic, 31320 Castanet-Tolosan, France. [b] The numbers in parentheses are the distances in mm between Friedel pairs of the preceding form. For ($\bar{1}$01) and (00$\bar{1}$) it is the distance from the center of the crystal to the face.

are given in Table SI.[19] Anisotropic thermal parameters are given in Table SII,[19] hydrogen atom positions in Table SIII,[19] and values of $10|F_o|$ versus $10|F_c|$ in Table SIV.[19]

## Description of the Structure and Discussion

The crystal structure of $Co(C_3\text{-}Cap)\cdot 3CHCl_3$ consists of the packing of discrete, monomeric molecules of $Co(C_3\text{-}Cap)$ and $CHCl_3$ solvent. There are no unusual intermolecular contacts.

The $Co(C_3\text{-}Cap)$ molecule has its expected connectivity (Figure 1). A stereoview of the molecule is shown in Figure 2, while the numbering scheme is shown in Figure 3. The following metrical data are tabulated: bond distances (Table III), bond angles (Table IV), selected least-squares planes (Table V), interplanar angles

(19) Supplementary material.

**Table III.** Bond Distances (Å) for $Co(C_3\text{-}Cap)\cdot 3CHCl_3$

| | | | |
|---|---|---|---|
| Co–N(1) | 1.942 (8)[a] | Co–N(3) | 1.931 (7) |
| Co–N(2) | 1.931 (8) | Co–N(4) | 1.932 (8) |
| av Co–N | 1.934 (8) | | |
| N(1)–C(1) | 1.382 (11) | N(3)–C(11) | 1.381 (11) |
| N(1)–C(4) | 1.359 (11) | N(3)–C(14) | 1.390 (11) |
| N(2)–C(6) | 1.409 (11) | N(4)–C(16) | 1.407 (11) |
| N(2)–C(9) | 1.380 (12) | N(4)–C(19) | 1.391 (11) |
| av N–$C_a$ | 1.387 (16) | | |
| C(1)–C(2) | 1.444 (12) | C(11)–C(12) | 1.433 (13) |
| C(4)–C(3) | 1.433 (13) | C(14)–C(13) | 1.444 (12) |
| C(6)–C(7) | 1.432 (13) | C(16)–C(17) | 1.426 (13) |
| C(9)–C(8) | 1.436 (13) | C(19)–C(18) | 1.437 (12) |
| av $C_a$–$C_b$ | 1.436 (13) | | |
| C(2)–C(3) | 1.318 (13) | C(12)–C(13) | 1.331 (13) |
| C(7)–C(8) | 1.334 (14) | C(17)–C(18) | 1.361 (13) |
| av $C_b$–$C_b$ | 1.336 (14) | | |
| C(5)–C(4) | 1.377 (12) | C(15)–C(14) | 1.381 (12) |
| C(5)–C(6) | 1.383 (12) | C(15)–C(16) | 1.402 (13) |
| C(10)–C(9) | 1.378 (13) | C(20)–C(19) | 1.388 (12) |
| C(10)–C(11) | 1.374 (13) | C(20)–C(1) | 1.389 (12) |
| av $C_a$–$C_m$ | 1.384 (13) | | |
| C(5)–C(21) | 1.524 (13) | C(15)–C(41) | 1.497 (13) |
| C(10)–C(31) | 1.509 (13) | C(20)–C(51) | 1.496 (12) |
| av $C_m$–$C_\alpha$ | 1.506 (13) | | |
| C(21)–C(22) | 1.394 (13) | C(41)–C(42) | 1.404 (13) |
| C(22)–C(23) | 1.411 (14) | C(42)–C(43) | 1.401 (14) |
| C(23)–C(24) | 1.362 (14) | C(43)–C(44) | 1.385 (13) |
| C(24)–C(25) | 1.352 (13) | C(44)–C(45) | 1.396 (13) |
| C(25)–C(26) | 1.419 (13) | C(45)–C(46) | 1.393 (13) |
| C(26)–C(21) | 1.384 (13) | C(46)–C(41) | 1.396 (12) |
| C(31)–C(32) | 1.360 (14) | C(51)–C(52) | 1.404 (13) |
| C(32)–C(33) | 1.401 (15) | C(52)–C(53) | 1.404 (13) |
| C(33)–C(34) | 1.349 (14) | C(53)–C(54) | 1.374 (14) |
| C(34)–C(35) | 1.352 (14) | C(54)–C(55) | 1.383 (13) |
| C(35)–C(36) | 1.406 (14) | C(55)–C(56) | 1.398 (13) |
| C(36)–C(31) | 1.413 (13) | C(56)–C(51) | 1.376 (13) |
| av $C_{Ph}$–$C_{Ph}$ | 1.389 (21) | | |
| C(26)–O(1) | 1.336 (11) | C(46)–O(7) | 1.361 (10) |
| C(36)–O(4) | 1.345 (12) | C(56)–O(10) | 1.353 (11) |
| O(1)–C(27) | 1.434 (11) | O(7)–C(47) | 1.418 (11) |
| O(4)–C(37) | 1.437 (12) | O(10)–C(57) | 1.414 (12) |
| C(27)–C(28) | 1.483 (14) | C(47)–C(48) | 1.510 (13) |
| C(28)–C(29) | 1.545 (13) | C(48)–C(49) | 1.532 (14) |
| C(37)–C(38) | 1.522 (15) | C(57)–C(58) | 1.509 (13) |
| C(38)–C(39) | 1.527 (14) | C(58)–C(59) | 1.510 (13) |
| C(29)–O(2) | 1.478 (11) | C(49)–O(8) | 1.458 (11) |
| C(39)–O(5) | 1.467 (11) | C(59)–O(11) | 1.467 (11) |
| O(2)–C(30) | 1.318 (11) | O(8)–C(50) | 1.321 (11) |
| O(5)–C(40) | 1.318 (11) | O(11)–C(60) | 1.328 (10) |
| C(30)–O(3) | 1.189 (10) | C(50)–O(9) | 1.202 (10) |
| C(40)–O(6) | 1.198 (11) | C(60)–C(12) | 1.213 (11) |
| C(61)–C(30) | 1.520 (12) | C(64)–C(50) | 1.495 (12) |
| C(65)–C(40) | 1.507 (13) | C(62)–C(60) | 1.480 (13) |
| C(61)–C(62) | 1.406 (12) | C(64)–C(65) | 1.397 (12) |
| C(62)–C(63) | 1.402 (13) | C(65)–C(66) | 1.398 (13) |
| C(63)–C(64) | 1.366 (12) | C(66)–C(61) | 1.376 (12) |
| C(67)–Cl(1) | 2.15 (2) | C(69)–Cl(7) | 1.85 (3) |
| C(67)–Cl(2) | 1.78 (2) | C(69)–Cl(8) | 1.75 (3) |
| C(67)–Cl(3) | 1.68 (2) | C(69)–Cl(9A) | 1.69 (3) |
| C(68)–Cl(4) | 1.57 (3) | | |
| C(68)–Cl(5) | 1.63 (3) | | |
| C(68)–Cl(6) | 1.59 (3) | | |

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

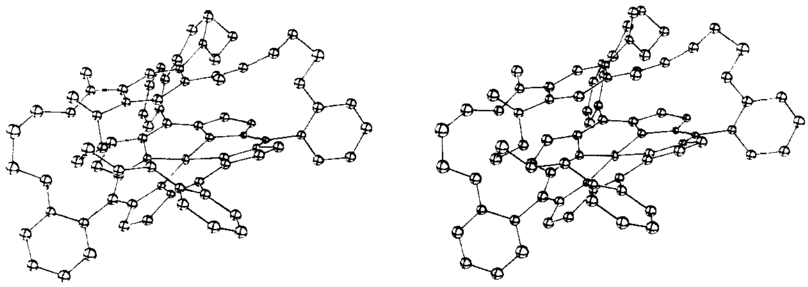

**Figure 2.** A stereoview of the Co($C_3$-Cap) molecule. Here and in Figure 4 the 50% probability ellipsoids have been drawn and H atoms are omitted for the sake of clarity.

**Table IV.** Bond Angles (deg) for Co($C_3$-Cap)·3CHCl$_3$

| | | | |
|---|---|---|---|
| N(1)–Co–N(2) | 89.7 (3) | N(2)–Co–N(3) | 89.8 (3) |
| N(1)–Co–N(4) | 90.8 (3) | N(3)–Co–N(4) | 90.0 (3) |
| av N–Co–N | 90.1 (5) | | |
| N(1)–Co–N(3) | 175.0 (3) | N(2)–Co–N(4) | 176.2 (3) |
| av N–Co–N | 175.6 (8) | | |
| Co–N(1)–C(1) | 125.2 (6) | Co–N(3)–C(11) | 126.7 (6) |
| Co–N(1)–C(4) | 128.8 (6) | Co–N(3)–C(14) | 127.8 (6) |
| Co–N(2)–C(6) | 126.3 (6) | Co–N(4)–C(16) | 127.9 (6) |
| Co–N(2)–C(9) | 127.8 (7) | Co–N(4)–C(19) | 127.5 (6) |
| av Co–N–$C_a$ | 127.2 (10) | | |
| N(1)–C(1)–C(2) | 109.7 (8) | N(3)–C(11)–C(12) | 110.7 (8) |
| N(1)–C(4)–C(3) | 109.9 (8) | N(3)–C(14)–C(13) | 109.1 (8) |
| N(2)–C(6)–C(7) | 108.2 (8) | N(4)–C(16)–C(17) | 110.4 (8) |
| N(2)–C(9)–C(8) | 109.6 (9) | N(4)–C(19)–C(18) | 110.3 (8) |
| av N–$C_a$–$C_b$ | 109.7 (9) | | |
| C(1)–N(1)–C(4) | 105.4 (8) | C(11)–N(3)–C(14) | 105.0 (7) |
| C(6)–N(2)–C(9) | 105.8 (8) | C(16)–N(4)–C(19) | 104.5 (7) |
| av $C_a$–N–$C_a$ | 105.2 (8) | | |
| C(1)–C(2)–C(3) | 106.4 (8) | C(11)–C(12)–C(13) | 106.9 (9) |
| C(2)–C(3)–C(4) | 108.4 (9) | C(12)–C(13)–C(14) | 108.3 (9) |
| C(6)–C(7)–C(8) | 108.5 (10) | C(16)–C(17)–C(18) | 107.1 (9) |
| C(7)–C(8)–C(9) | 107.5 (9) | C(17)–C(18)–C(19) | 107.4 (8) |
| av $C_a$–$C_b$–$C_b$ | 107.6 (10) | | |
| N(1)–C(1)–C(20) | 126.2 (8) | N(3)–C(11)–C(10) | 124.4 (9) |
| N(1)–C(4)–C(5) | 124.5 (9) | N(3)–C(14)–C(15) | 125.5 (9) |
| N(2)–C(6)–C(5) | 124.3 (9) | N(4)–C(16)–C(15) | 123.1 (9) |
| N(2)–C(9)–C(10) | 124.5 (9) | N(4)–C(19)–C(20) | 124.5 (8) |
| av N–$C_a$–$C_m$ | 124.6 (9) | | |
| C(2)–C(1)–C(20) | 123.8 (8) | C(12)–C(11)–C(10) | 124.0 (9) |
| C(3)–C(4)–C(5) | 125.6 (9) | C(13)–C(14)–C(15) | 125.3 (9) |
| C(7)–C(6)–C(5) | 126.6 (9) | C(17)–C(16)–C(15) | 125.6 (9) |
| C(8)–C(9)–C(10) | 125.8 (9) | C(18)–C(19)–C(20) | 125.1 (8) |
| av $C_b$–$C_a$–$C_m$ | 125.2 (9) | | |
| C(4)–C(5)–C(6) | 123.9 (9) | C(14)–C(15)–C(16) | 122.4 (9) |
| C(9)–C(10)–C(11) | 122.9 (9) | C(19)–C(20)–C(1) | 122.0 (8) |
| av $C_a$–$C_m$–$C_a$ | 122.8 (9) | | |
| C(4)–C(5)–C(21) | 117.8 (8) | C(14)–C(15)–C(41) | 116.9 (9) |
| C(6)–C(5)–C(21) | 118.5 (8) | C(16)–C(15)–C(41) | 119.7 (9) |
| C(9)–C(10)–C(31) | 119.3 (9) | C(19)–C(20)–C(51) | 119.6 (8) |
| C(11)–C(10)–C(31) | 117.8 (9) | C(1)–C(20)–C(51) | 118.3 (8) |
| av $C_a$–$C_m$–$C_\alpha$ | 118.5 (10) | | |
| C(21)–C(22)–C(23) | 120.4 (10) | C(41)–C(42)–C(43) | 122.0 (9) |
| C(22)–C(23)–C(24) | 118.8 (10) | C(42)–C(43)–C(44) | 117.9 (9) |
| C(23)–C(24)–C(25) | 121.2 (10) | C(43)–C(44)–C(45) | 121.5 (10) |
| C(24)–C(25)–C(26) | 121.8 (10) | C(44)–C(45)–C(46) | 119.6 (9) |
| C(25)–C(26)–C(21) | 117.5 (9) | C(45)–C(46)–C(41) | 120.6 (9) |
| C(26)–C(21)–C(22) | 120.3 (9) | C(46)–C(41)–C(42) | 118.3 (9) |
| C(31)–C(32)–C(33) | 121.0 (10) | C(51)–C(52)–C(53) | 120.7 (9) |
| C(32)–C(33)–C(34) | 119.0 (10) | C(52)–C(53)–C(54) | 118.7 (9) |
| C(33)–C(34)–C(35) | 121.9 (11) | C(53)–C(54)–C(55) | 121.3 (10) |
| C(34)–C(35)–C(36) | 120.2 (10) | C(54)–C(55)–C(56) | 119.0 (10) |
| C(35)–C(36)–C(31) | 118.3 (10) | C(55)–C(56)–C(57) | 120.0 (9) |
| C(36)–C(31)–C(32) | 119.3 (10) | C(56)–C(51)–C(52) | 119.4 (9) |
| av $C_{Ph}$–$C_{Ph}$–$C_{Ph}$ | 120.0 (13) | | |

| | | | |
|---|---|---|---|
| C(21)–C(26)–O(1) | 118.7 (9) | C(41)–C(46)–O(7) | 117.8 (9) |
| C(31)–C(36)–O(4) | 116.5 (9) | C(51)–C(56)–O(10) | 115.8 (8) |
| C(25)–C(26)–O(1) | 123.9 (9) | C(45)–C(46)–O(7) | 121.6 (9) |
| C(35)–C(36)–O(4) | 125.2 (9) | C(55)–C(56)–O(10) | 124.2 (9) |
| C(26)–O(1)–C(27) | 116.8 (8) | C(46)–O(7)–C(47) | 116.0 (7) |
| C(36)–O(4)–C(37) | 116.5 (8) | C(56)–O(10)–C(57) | 116.6 (8) |
| O(1)–C(27)–C(28) | 110.5 (8) | O(7)–C(47)–C(48) | 110.2 (8) |
| O(4)–C(37)–C(38) | 107.1 (9) | O(10)–C(57)–C(58) | 107.5 (8) |
| C(27)–C(28)–C(29) | 114.8 (9) | C(47)–C(48)–C(49) | 116.0 (9) |
| C(37)–C(38)–C(39) | 114.9 (10) | C(57)–C(58)–C(59) | 115.3 (9) |
| C(28)–C(29)–O(2) | 109.4 (8) | C(48)–C(49)–O(8) | 110.3 (8) |
| C(38)–C(39)–O(5) | 105.9 (9) | C(58)–C(59)–O(11) | 106.7 (8) |
| C(29)–O(2)–C(30) | 113.4 (7) | C(49)–O(8)–C(50) | 115.5 (7) |
| C(39)–O(5)–C(40) | 114.6 (8) | C(59)–O(11)–C(60) | 114.9 (7) |
| C(5)–C(21)–C(26) | 121.2 (9) | C(15)–C(41)–C(46) | 121.3 (9) |
| C(5)–C(21)–C(22) | 118.4 (9) | C(15)–C(41)–C(42) | 120.1 (9) |
| C(10)–C(31)–C(36) | 121.2 (9) | C(20)–C(51)–C(56) | 121.4 (9) |
| C(10)–C(31)–C(32) | 119.5 (9) | C(20)–C(51)–C(52) | 119.2 (8) |
| O(2)–C(30)–O(3) | 127.4 (9) | O(18)–C(50)–O(9) | 125.1 (9) |
| O(5)–C(40)–O(6) | 126.7 (9) | O(11)–C(60)–O(12) | 124.3 (9) |
| O(2)–C(30)–C(61) | 110.3 (8) | O(8)–C(50)–C(64) | 112.4 (8) |
| O(5)–C(40)–C(65) | 110.7 (8) | O(11)–C(60)–C(62) | 112.1 (8) |
| O(3)–C(30)–C(61) | 122.0 (9) | O(9)–C(50)–C(64) | 122.2 (9) |
| O(6)–C(40)–C(65) | 122.6 (9) | O(12)–C(60)–C(62) | 123.5 (9) |
| C(30)–C(61)–C(62) | 122.8 (8) | C(50–C(64)–C(63) | 115.7 (9) |
| C(30)–C(61)–C(66) | 117.2 (8) | C(50)–C(64)–C(65) | 124.7 (8) |
| C(40)–C(65)–C(64) | 123.9 (9) | C(60)–C(62)–C(61) | 123.4 (9) |
| C(40)–C(65)–C(66) | 117.4 (9) | C(60)–C(62)–C(63) | 118.5 (9) |
| C(61)–C(62)–C(63) | 117.9 (9) | C(64)–C(65)–C(66) | 118.7 (9) |
| C(62)–C(63)–C(64) | 122.5 (9) | C(65)–C(66)–C(61) | 121.9 (9) |
| C(63)–C(64)–C(65) | 119.3 (9) | C(66)–C(61)–C(62) | 119.3 (9) |
| Cl(1)–C(67)–Cl(2) | 102.1 (8) | Cl(7)–C(69)–Cl(8) | 118.1 (18) |
| Cl(1)–C(67)–Cl(3) | 106.8 (9) | Cl(7)–C(69)–Cl(9A) | 105.6 (17) |
| Cl(2)–C(67)–Cl(3) | 111.2 (9) | Cl(8)–C(69)–Cl(9A) | 104.6 (17) |
| Cl(4)–C(68)–Cl(5) | 114.6 (17) | | |
| Cl(4)–C(68)–Cl(6) | 119.5 (18) | | |
| Cl(5)–C(68)–Cl(6) | 99.8 (17) | | |

(Table VI), and torsional angles (Table VII).

Apparent in Figure 2, and especially in Figure 4, which is a stereoview down the cap toward the porphyrin, is the striking nonplanarity of the porphyrin core. This nonplanarity is sketched in Figure 5, where deviations from the best weighted least-squares plane are provided. Porphyrin nonplanarity has recently been

**Table V.** Best Weighted Least-Squares Planes for $Co(C_3\text{-Cap})\cdot 3CHCl_3$

| | coefficients $Ax + By + Cz - D = 0$[a] | | | | atoms defining the plane[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $A$ | $B$ | $C$ | $D$ | | | | | | | | |
| I | 8.788 | −13.895 | −0.341 | 0.759 | N(1) | N(2) | N(3) | N(4) | Co | | | |
| | | | | | −074 (7) | 073 (7) | −070 (7) | 075 (7) | 011 | | | |
| II | 8.540 | −14.026 | −0.567 | 0.526 | C(5) | C(10) | C(15) | C(20) | | | | |
| | | | | | 472 (10) | −489 (10) | 443 (10) | −397 (9) | | | | |
| III | 8.932 | −13.858 | −0.549 | 0.677 | C(2) | C(3) | C(7) | C(8) | | | | |
| | | | | | −544 (10) | −183 (10) | 651 (11) | 261 (11) | | | | |
| | | | | | C(12) | C(13) | C(17) | C(18) | | | | |
| | | | | | −519 (10) | −212 (9) | 566 (10) | 167 (10) | | | | |
| py-1 | 3.359 | −15.418 | −0.214 | −1.432 | N(1) | C(1) | C(2) | C(3) | C(4) | | | |
| | | | | | −010 (8) | 021 (9) | −024 (10) | 015 (10) | 002 (10) | | | |
| py-2 | 7.787 | −12.959 | 5.591 | 1.731 | N(2) | C(6) | C(7) | C(8) | C(9) | | | |
| | | | | | 011 (7) | −028 (9) | 038 (11) | −025 (11) | 002 (10) | | | |
| py-3 | 13.457 | −11.139 | −0.745 | 3.387 | N(3) | C(11) | C(12) | C(13) | C(14) | | | |
| | | | | | −009 (7) | 012 (9) | −004 (9) | −005 (9) | 012 (9) | | | |
| py-4 | 8.937 | −13.857 | −6.528 | −0.731 | N(4) | C(16) | C(17) | C(18) | C(19) | | | |
| | | | | | 016 (8) | −033 (10) | 031 (10) | −016 (10) | −004 (9) | | | |
| cap | 8.328 | −13.990 | 0.422 | 4.174 | C(61) | C(62) | C(63) | C(64) | C(65) | C(66) | Co | |
| | | | | | 016 (9) | 013 (9) | −035 (10) | 022 (9) | 007 (10) | −027 (9) | −3436 | |
| Ph-1 | 17.999 | −2.839 | 1.564 | 7.442 | C(21) | C(22) | C(23) | C(24) | C(25) | C(26) | | |
| | | | | | 001 (9) | −005 (10) | 003 (10) | 002 (10) | −006 (10) | 004 (9) | | |
| Ph-2 | −5.711 | −2.715 | 22.403 | 2.434 | C(31) | C(32) | C(33) | C(34) | C(35) | C(36) | | |
| | | | | | −016 (10) | −006 (11) | 030 (12) | −025 (11) | 003 (11) | 018 (10) | | |
| Ph-3 | 6.585 | 14.676 | −0.042 | 4.821 | C(41) | C(42) | C(43) | C(44) | C(45) | C(46) | | |
| | | | | | 009 (10) | −002 (10) | −010 (11) | 014 (11) | −004 (10) | −006 (9) | | |
| Ph-4 | 8.972 | 0.239 | −22.668 | −1.502 | C(51) | C(52) | C(53) | C(54) | C(55) | C(56) | | |
| | | | | | 002 (10) | −002 (10) | −001 (10) | 005 (11) | −005 (10) | 001 (10) | | |
| ester-1 | 18.170 | −0.510 | −16.335 | 4.802 | O(3) | O(2) | C(30) | C(61) | | | | |
| | | | | | 009 (7) | 005 (6) | −028 (9) | 009 (9) | | | | |
| ester-2 | 8.054 | −12.448 | 6.537 | 5.552 | O(5) | O(6) | C(40) | C(65) | | | | |
| | | | | | 001 (7) | 001 (7) | −004 (10) | 001 (10) | | | | |
| ester-3 | 11.622 | 10.044 | −15.387 | 2.282 | O(8) | O(9) | C(50) | C(64) | | | | |
| | | | | | −005 (6) | −008 (7) | 032 (9) | −010 (9) | | | | |
| ester-4 | 8.417 | −14.088 | −5.999 | 2.552 | O(11) | O(12) | C(60) | C(62) | | | | |
| | | | | | −001 (6) | −002 (7) | 008 (10) | −002 (9) | | | | |
| porph | 8.778 | −13.916 | −0.482 | 0.678 | see | Co | C(61) | C(62) | C(63) | C(64) | C(65) | C(66) |
| | | | | | Figure 5 | 052 | 3528 | 3469 | 3406 | 3500 | 3541 | 3523 |

[a] Plane is in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185–189. [b] The displacement (Å) beneath the atom is $\times 10^3$. If no standard deviation of the displacement is given, that atom was not involved in defining the plane.

**Table VI.** Dihedral Angles (deg) between Selected Least-Squares Planes for $Co(C_3\text{-Cap})\cdot 3CHCl_3$

| | porph | I | cap | py-1 | py-2 | py-3 |
|---|---|---|---|---|---|---|
| porph | | | | | | |
| I | 0.4 | | | | | |
| cap | 2.4 | 2.1 | | | | |
| py-1 | 17.2 | 17.4 | 16.7 | | | |
| py-2 | 15.9 | 15.6 | 13.9 | 25.7 | | |
| py-3 | 17.4 | 17.2 | 18.2 | 34.6 | 20.7 | |
| py-4 | 16.1 | 16.5 | 18.2 | 20.3 | 32.1 | 26.3 |
| ester 1 | | | 70.8 | | | |
| ester 2 | | | 17.2 | | | |
| ester 3 | | | 115.0 | | | |
| ester 4 | | | 17.2 | | | |
| Ph-1 | 52.5 | | | | | |
| Ph-2 | 80.6 | | | | | |
| Ph-3 | 132.3 | | | | | |
| Ph-4 | 86.8 | | | | | |

reviewed by Scheidt and Lee.[20] Within their terminology the porphyrin core in $Co(C_3\text{-Cap})$ is "Ruf" (or ruffled). The average absolute displacements of the $C_m$ atoms (C atoms 5, 10, 15, and 20) is 0.45 Å while that of the $C_b$ atoms (C atoms 2, 3, 7, 8, 12, 13, 17, 18) is 0.39 Å with a maximum $C_b$ displacement of 0.60 Å. These values indicate that the current porphyrin is more distorted than most of the 21 examples listed in Table XXII of Scheidt and Lee.[20]

From Figures 4 and 5 it is apparent that the $Co(C_3\text{-Cap})$ molecule has approximate symmetry 2. If we take as a reference point the cap as "up" then the diagonally opposed $C_m$ atoms C(10) and C(20) are down −0.450 (10) and −0.465 (9) Å, respectively, while $C_m$ atoms C(5) and C(15) are up 0.450 (10) and 0.436 (10) Å, respectively. The chains 1 and 3 that connect the up atoms C(5) and C(15) to the cap have the same conformation but this conformation is different from that of the chains 2 and 4 that connect the down atoms C(10) and C(20) to the cap. This is most readily seen in Figure 4 and in Table VI. Chains 1 and 3 originate on phenyl rings 1 and 3, respectively, that make angles of 52.5 and 132.3° (supplement = 47.7°) with the porphyrin mean plane

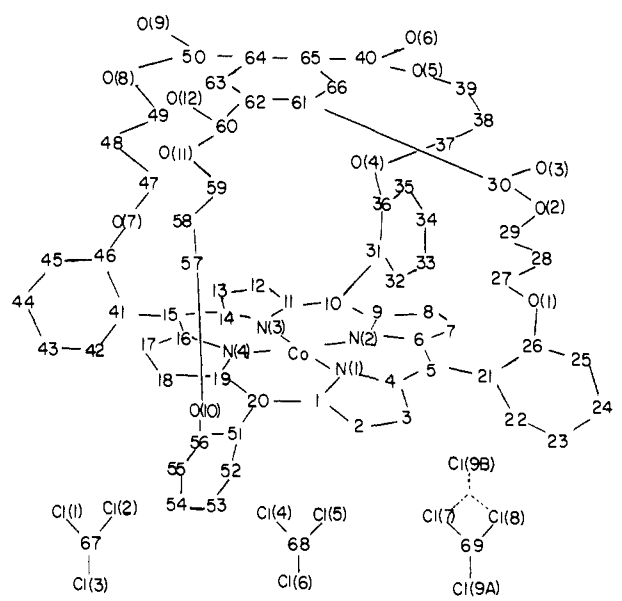


**Figure 3.** Numbering scheme for $Co(C_3\text{-Cap})\cdot 3CHCl_3$. Cl(9A) and Cl(9B) are half positions for atom Cl(9). The counterpart to the half atom C(69) was not located.

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

**Table VII.** Torsional Angles (deg) for the Linkages for Co($C_3$-Cap)·3CHCl$_3$

| | chain 1 | chain 2 | chain 3 | chain 4 |
|---|---|---|---|---|
| C(21)–C(26)–O(1)–C(27) | 160.8 (8)[b] | 172.9 (9) | 161.1 (8) | 165.4 (9) |
| C(26)–O(1)–C(27)–C(28) | −170.8 (8) | −176.0 (9) | −171.5 (8) | −169.5 (8) |
| O(1)–C(27)–C(28)–C(29) | 55.2 (11) | 56.8 (12) | 61.6 (11) | 55.5 (11) |
| C(27)–C(28)–C(29)–O(2) | −77.3 (10) | −87.8 (11) | −80.3 (11) | −89.5 (10) |
| C(28)–C(29)–O(2)–C(30) | −75.5 (10) | −163.2 (8) | −79.2 (10) | −159.7 (8) |
| C(29)–O(2)–C(30)–O(3) | −6.2 (14) | −10.5 (15) | −5.7 (14) | −14.6 (14) |
| C(29)–O(2)–C(30)–O(61) | 168.4 (7) | 168.8 (8) | 168.4 (8) | 166.9 (8) |
| O(3)–C(30)–C(61)–C(62) | −66.8 (14) | −17.7 (15) | −62.4 (14) | −15.6 (15) |
| O(2)–C(30)–C(61)–C(62) | 118.2 (10) | 163.0 (8) | 123.4 (10) | 163.0 (9) |

[a]Only the atoms of chain 1 are listed here; atoms in chains 2, 3, and 4 are defined analogously as shown in Figure 3. [b]The sign is positive if, for a chain of atoms 1-2-3-4, when looking from 2 to 1 a clockwise motion of atom 1 would superimpose it on atom 4.

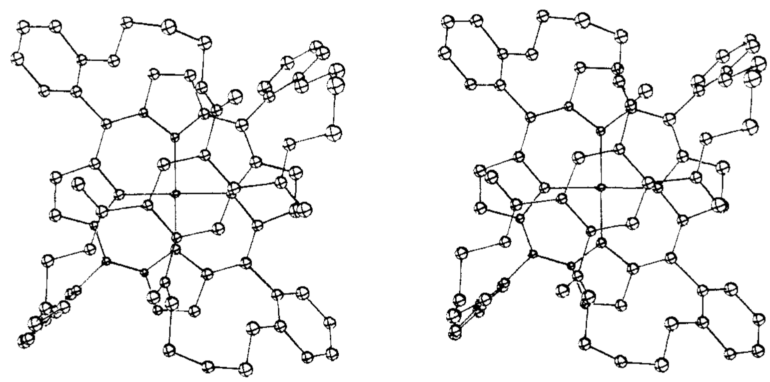

**Figure 4.** A stereoview of Co($C_3$-Cap) looking down the cap toward the porphyrin. In the drawing atom C(5) is near the bottom right-hand corner and atom C(20) the bottom left-hand corner.

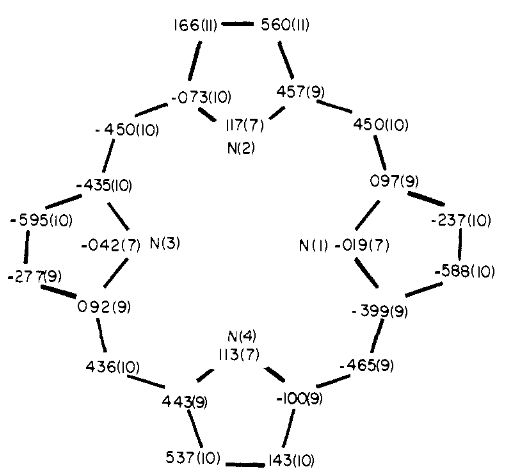


**Figure 5.** Deviations (×10$^3$ Å) of the porphyrin atoms from the best weighted least-squares plane through the 24 atoms. The Co atom is +0.052 Å from the plane.

(Table VI). These chains continue up to the cap to connect with ester linkages that are nearly perpendicular to the cap. On the other hand, chains 2 and 4 originate on phenyl rings 2 and 4, respectively, that make the more usual angles of 80.6 and 86.8° with the porphyrin core and these chains terminate in ester linkages that are nearly coplanar with the cap. These differences are manifested in differences in torsional angles at the cap connections (Table VII). Severe strain is apparent in all the linkages as the torsional angle about the C(26)–O(1) bond (and analogous bonds in the other chains) is close to zero leading to a nearly eclipsed conformation. An eclipsed conformation was seen in only one such chain (chain 3) in $H_2$($C_2$-Cap).[16]

Apparent in Figure 3 and in Table VI is the near coplanarity of the cap and mean porphyrin plane (dihedral angle, 2.4°). Owing to the nonplanarity of the porphyrin core there are various measures that can be used to describe the separation of cap and porphyrin. Two that seem useful are the Co-to-cap distance of 3.436 Å and the separation of 3.494 Å of the centroid of the cap atoms from the mean porphyrin plane. This latter measure can be compared with a separation of 4.01 Å in FeCl($C_2$-Cap)[17] and 3.96 Å in $H_2$($C_2$-Cap).[16] Thus the cap is about 0.5 Å *closer* to the porphyrin in the larger $C_3$ system than in the $C_2$ system. Clayden et al.[21] from paramagnetic shifts in the NMR spectra of Co($C_2$-Cap) and Co($C_3$-Cap) in chloroform concluded that the cap-to-porphyrin distance is smaller in the $C_3$ compound than in the $C_2$ compound. Thus it appears that the separations seen in the solid state persist in solution and are not the result of "packing forces". $\pi$–$\pi$ interactions between cap and porphyrins may be the driving force that leads to coplanarity and close approach of the two groups. It seems likely that there is insufficient flexibility in the shorter chains of the $C_2$ system to permit as close an approach of cap to porphyrin as in the $C_3$ system. Yet the very close approach in the $C_3$ system is achieved through distortion of the porphyrin core with concomitant loss of aromaticity and presumably some weakening of the $\pi$–$\pi$ interaction.

Bond distances (Table III) and bond angles (Table IV) within the Co($C_3$-Cap) molecule are comparable with those in similar molecules, including Co(TPP),[22] although the standard deviations in the present instance are somewhat larger owing to the disordered solvent molecules. As such, it is not possible to discern differences between the two types of chains or to assess the effects, if any, of the asymmetric linkages on the symmetry of the core. On the other hand, the $C_a$–$C_m$–$C_a$ angles (average = 122.8 (9)°) are unusually small, indicative of the severe nonplanarity of the porphyrin core.

From the results on the $C_2$ and $C_3$ systems in solution[21] and in the solid state[16,17] it is clear that upon addition of a small molecule, such as CO or $O_2$, to the metal center the cap-to-porphyrin distance must increase by perhaps 2 Å to accommodate the linear Fe–C–O or bent Fe–O–O groups. Several conjectures[4,11-15] have been offered to explain the affinity results given in Table I. Hashimoto and Basolo[12] suggest that for $O_2$ binding peripheral steric effects[13] are important and that the "capped" systems are destabilized relative to the more open systems because of interactions of the terminal O atom with chain atoms at the periphery of the cavity, with destabilization being greater for the $C_3$ than for the $C_2$ system. It is not apparent from Figure 4 how such peripheral steric effects would arise as the cap is "unwound",

(21) Clayden, N. J.; Moore, G. R.; Williams, R. J. P.; Baldwin, J. E.; Crossley, M. J. *J. Chem. Soc., Perkin Trans. II* **1983**, 1863–1868.
(22) Stevens, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 5087–5095.

but then it is very difficult to guess what the conformation of the molecule would be if the cap were 2 Å or so further from the porphyrin. Hashimoto and Basolo go on to argue that central steric effects[13] should not be important in these systems. Indeed the binding of CO in the "capped" systems is comparable to that in the more open porphyrins.

Clearly there are other effects in addition to possible steric ones that could be important. The "picket-fence"[23] and "basket"[24] porphyrins provide the opportunity for polar interactions with the bound $O_2$ molecule, interactions that are known to be important in the heme proteins.[25] No such polar interactions are possible in the "capped" systems. On this basis one would expect CO binding to be comparable in the various systems while $O_2$ binding should be favored in those systems with polar interactions. Moreover, the more open systems or those with built-in, rigid cavities need not change conformation to accommodate the binding of small molecules. Obviously, the "capped" systems must do so. We think that the necessary expansion of the cavity in the "capped" systems would mainly be enthalpic rather than entropic. The enthalpy penalty paid for expansion should be greater in the $C_3$ system than in the $C_2$ system (and certainly greater than in the open systems) and this would end up as decreased affinity. This penalty could be significant with respect to the enthalpy of the oxygenation reaction and yet small compared to the enthalpy of the carbonylation reaction where the equilibrium ($1/P_{1/2}$) is far to the right. But a caveat is that the increased enthalpy of expansion of the $C_3$ system compared with the $C_2$ system might be compensated for, at least in part, by the return to planarity of the porphyrin. Unfortunately, thermodynamic data for binding of small molecules, especially to the "capped" systems, are generally lacking.

(23) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 564–568.

(24) Mispelter, J.; Momenteau, M.; Lavalette, D.; Lhoste, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 5165–5166.

(25) Phillips, S. E. V.; Schoenborn, B. P. *Nature (London)* **1981**, *292*, 81–82.

How, then, does one explain the poorer affinities for small molecules of the $C_4$-caps compared with the lower caps? The cap-to-porphyrin distance is probably a minimum in the $C_3$ system so that the enthalpic penalty of expansion should not be greater in the $C_4$ system and thus one might expect, contrary to the facts,[11] that the $C_4$ system should bind $O_2$ as well as the $C_3$ system. Moreover, the $C_4$ system binds CO and NO more poorly than does the $C_3$ system (Table I). Here one might turn to the argument of Clayden et al.[15] that as one goes to the higher "capped" porphyrins, especially to the $C_4$ system, the cavity is potentially large enough to accommodate a solvent molecule. Then the binding of a small molecule is not a simple addition process but is a solvent displacement reaction and a different equilibrium is involved.

The understanding of structure–function relationships in these model systems awaits not only more structural information but also more thermodynamic and kinetic measurements. The structural work has just begun: we still have no structures of a $C_4$-cap or of any system with a small molecule or ligand under a cap. In general we possess insufficient information on the relative contributions of enthalpy and entropy to the free energy of binding and on the dynamic processes involved. But many of these measurements appear to be feasible, as does the growing of single crystals. With increased understanding of these model systems will come a complementary understanding of some aspects of the natural systems.

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**Supplementary Material Available:** Table SI, positional and equivalent isotropic thermal parameters; Table SII, anisotropic thermal parameters; Table SIII, hydrogen-atom positions (4 pages); Table SIV, structure amplitudes (33 pages). Ordering information is given on any current masthead page.