of a toluene molecule and the mean plane of the porphinato plane is 12.0°. Figure 2 also displays the perpendicular distances between individual atoms of the toluene molecule and the mean plane of the core; the average distance is 3.34 Å. Figure 3 shows the specific orientation of the toluene solvate with respect to the metalloporphyrin; the C_{16} and C_{17} carbon atoms of the toluene make rather close contacts of 3.121 and 3.379 Å, respectively, with the zinc atom. The geometry and interplanar spacings observed in this crystal structure are quite similar to those observed in the isomorphous crystals of MnTPP and also to those observed in the toluene solvate of CrTPP.[7] The arrangement suggests the possibility of π-complex formation between the toluene and the metalloporphyrin; this matter is considered in the following paper.[7] Other than the close intermolecular contacts between toluene and ZnTPP, there are no significantly short intermolecular contacts.

Acknowledgment. We are grateful for support for this research from the National Institutes of Health (HL-15627).

Registry No. ZnTPP·2(toluene), 65150-26-7.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (25 pages). Ordering information is given on any current masthead page.

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Stereochemistry of the Toluene Solvate of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphinatochromium(II)

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Received October 21, 1977

The crystal and molecular structure of the toluene solvate of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatochromium(II) has been determined by x-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group $P2_1/c$. The unit cell constants are $a = 10.518\ (3)$ Å, $b = 15.778\ (4)$ Å, $c = 13.425\ (3)$ Å, $\beta = 101.02\ (3)°$, and $Z = 2$. Measurements of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} (2707 unique observed data) were examined. These data were employed for the determination of structure and least-squares refinement. The final values of the conventional and weighted discrepancy factors were 0.070 and 0.067. The CrTPP molecule has required C_i—$\bar{1}$ molecular symmetry. The average Cr–N bond distance is 2.033 (1) Å. The interplanar spacing between the porphyrin mean plane and a plane of the toluene solvate is 3.37 Å and the interplanar angle is 4.5°. The similarity in structure of the toluene solvates of CrTPP, ZnTPP, and MnTPP is discussed.

The preceding paper[3] has noted that the structural study of the first-row, divalent transition metal derivatives of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin provides a quantitative description of the structural changes resulting from the stepwise addition of d electrons. We report herein the molecular stereochemistry of the recently reported[4] $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatochromium(II), the earliest of the presently known derivatives. Derivatives of this chromium(II) porphyrin have been reported[4] to form, irreversibly, dioxygen complexes.

Crystals of two members of this series of first-row complexes, MnTPP[5] and ZnTPP,[3] were obtained as bis(toluene) solvates. Crystal structure determination showed an apparently specific interaction of the toluene molecules with both the central metal atom and the porphyrin moiety. The similar interaction of toluene and the metalloporphyrin in the manganese(II) and zinc(II) complexes is virtually demanded

0020-1669/78/1317-0710$01.00/0

by the isomorphous nature of the derivatives. However, crystals of CrTPP, also obtained as a bis(toluene) solvate, are not isomorphous with the earlier derivatives. Thus the study of the crystals of CrTPP allows examination of the specific interaction of the toluene molecules with the metalloporphyrin in a distinctly different crystalline environment. We find that, although there are differences in the metalloporphyrin–toluene interaction, there are substantial similarities in the three derivatives and these are discussed in this report.

Experimental Section

Crystals of CrTPP for diffraction studies were obtained by recrystallization from toluene solution. The very air-sensitive crystals were mounted in thin-walled glass capillaries in a nitrogen-filled drybox. Preliminary x-ray examination established a two-molecule monoclinic unit cell, with the systematic absences consistent with the choice of $P2_1/c$ as the space group. Least-squares refinement of the setting angles of 25 reflections, each collected at $\pm 2\theta$, gives the cell constants (λ 0.71069 Å) a = 10.518 (3) Å, b = 15.778 (4) Å, c = 13.425 (3) Å, and β = 101.02 (3)°. With a cell content of $2[CrN_4C_{44}H_{28}\cdot 2C_7H_8]$, the calculated density is 1.289 g/cm^3; an experimental density was not obtained owing to the air sensitivity of the compound.

X-ray intensity data were collected by θ–2θ scanning using graphite-monochromated Mo Kα radiation on a computer-controlled four-circle diffractometer. Variable 2θ scan rates were used according to the intensity of the reflection and ranged from 1.0 to 6.0°/min. The scan range was 1.2° on either side of the Kα_1, Kα_2 doublet. Background counts were estimated from an analysis of the reflection profiles using a local modification of a program described by Coppens et al.[6] The sample crystal was an irregular fragment with approximate dimensions of 0.3 × 0.25 × 0.3 mm. Four standard reflections, measured every 50 reflections during data collection, displayed no trend with exposure to the x-ray beam. With the cited dimensions of the crystal and a linear absorption coefficient of 0.297 mm^{-1}, the error in the intensities was seen to be negligible and no correction was applied. Intensity data were reduced and standard deviations calculated as described previously.[7] Data were retained as objectively observed if $F_o > 3\sigma(F_o)$, leading to 2707 unique observed data (54% of the theoretical number possible) in the range $(\sin\theta)/\lambda \le 0.648$ Å^{-1}.

With two molecules per unit cell and the space group $P2_1/c$, molecules of CrTPP must be located at inversion centers with chromium atom coordinates of 0, 0, 0 and 0, $^1/_2$, $^1/_2$. A series of Fourier syntheses,[8] originally phased on the chromium atom positions, led to the complete structure. The structure was refined by full-matrix least-squares techniques[9] using standard values for atom scattering factors.[10] In the later stages of refinement, two blocks were used because of computer storage limitations. A difference Fourier synthesis, calculated after isotropic refinement, yielded hydrogen atom positions; these positions were idealized (C–H = 0.95 Å, $B(H) = B(C) + 1.0$ Å^2) and included in the refinement as fixed contributors. Anisotropic refinement of all heavy atoms was carried to convergence with the chromium(II) atom positioned at the center of symmetry. The final values of the discrepancy indices were $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o| = 0.070$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2} = 0.067$. The estimated standard deviation of an observation of unit weight was 1.71. The largest shift/error in the final cycle was less than 0.10; the largest peak in the final difference Fourier map was 0.60 e/Å^3 and was in the region of the chromium atom. An examination of $\sum w(|F_o| - |F_c|)^2$ for various classes of reflections based on Miller indices, $|F_o|$, and setting angles showed no unusual trends.

Derived atomic coordinates are listed in Table I, the associated thermal parameters are listed in Table II. Listings of the observed and calculated structure factors are available.[11] Primed and unprimed symbols, C_i' and C_i, denote a pair of atoms related by the center of symmetry wherein the chromium(II) atom is positioned.

Results and Discussion

Figure 1 is an ORTEP plot[12] of the centrosymmetric CrTPP molecule. The upper right-hand side of Figure 1 shows the numbering scheme used to define the crystallographically unique atoms of the molecule. On the lower left-hand side of the figure, the atom symbols have been replaced by the value of the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the porphinato core. As is usual, the individual subunits of the ligand (pyrrole and phenyl rings) retain planarity to within 0.01 Å. The dihedral angles between the mean plane of the porphyrin and the two phenyl rings are 78.4 and 69.1°.

Individual bond lengths and angles in the CrTPP molecule are tabulated in Tables III and IV. Using C_a and C_b to denote

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type	Coordinates 10^4x	10^4y	10^4z
Cr	0	0	0
N_1	271 (3)	993 (2)	982 (2)
N_2	1313 (3)	500 (2)	−767 (2)
C_{a1}	−334 (3)	1120 (2)	1796 (3)
C_{a2}	1093 (3)	1665 (2)	969 (3)
C_{a3}	2004 (3)	1236 (2)	−539 (3)
C_{a4}	1677 (3)	175 (2)	−1627 (3)
C_{b1}	102 (4)	1916 (3)	2265 (3)
C_{b2}	996 (4)	2256 (3)	1777 (3)
C_{b3}	2826 (4)	1376 (3)	−1269 (3)
C_{b4}	2607 (4)	731 (3)	−1939 (3)
C_{m1}	1926 (3)	1777 (2)	278 (3)
C_{m2}	1221 (3)	−576 (2)	−2103 (3)
C_1	2822 (4)	2522 (2)	463 (3)
C_2	3917 (4)	2497 (3)	1212 (3)
C_3	4722 (4)	3190 (3)	1410 (3)
C_4	4458 (5)	3914 (3)	875 (4)
C_5	3392 (5)	3953 (3)	138 (4)
C_6	2585 (5)	3258 (3)	−86 (3)
C_7	1729 (4)	−834 (3)	−3036 (3)
C_8	922 (4)	−819 (3)	−3977 (3)
C_9	1342 (5)	−1085 (3)	−4839 (3)
C_{10}	2586 (5)	−1352 (3)	−4767 (3)
C_{11}	3410 (5)	−1365 (3)	−3854 (4)
C_{12}	2979 (4)	−1097 (3)	−2979 (3)
C_{13}	7888 (5)	3655 (4)	3621 (4)
C_{14}	8341 (5)	3992 (4)	2789 (5)
C_{15}	7814 (6)	4727 (4)	2347 (4)
C_{16}	6868 (6)	5115 (4)	2695 (4)
C_{17}	6392 (5)	4806 (4)	3495 (5)
C_{18}	6894 (5)	4069 (4)	3987 (4)
C_{19}	6411 (6)	3714 (5)	4873 (4)

[a] The number in parentheses following each datum is the estimated standard deviation in the least significant figure.

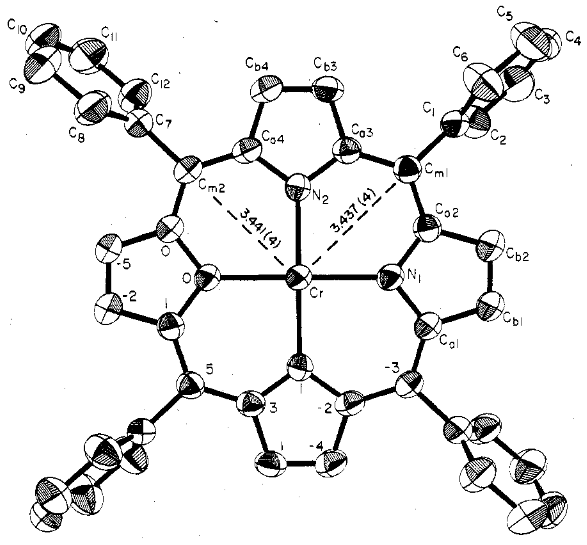

Figure 1. An ORTEP plot of the centrosymmetric CrTPP molecule. The atoms are represented by vibrational ellipsoids contoured to enclose 50% of the electron density. The labeling scheme for the atoms is shown on the upper right-hand side of the diagram. The perpendicular displacement of each atom in the porphinato core, in units of 0.01 Å, is displayed on the lower left-hand side of the figure. Also shown on the figure are the two unique Cr···C_m distances.

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å^2
Cr	3.35 (4)	3.42 (4)	2.59 (3)	−0.50 (4)	0.82 (3)	−0.23 (4)	3.03
N_1	3.3 (1)	3.6 (2)	2.5 (1)	−0.3 (1)	0.7 (1)	−0.2 (1)	3.1
N_2	3.4 (1)	3.3 (2)	2.7 (1)	−0.4 (1)	0.5 (1)	−0.3 (1)	3.1
C_{a1}	3.6 (2)	3.6 (2)	2.8 (2)	−0.0 (2)	0.9 (1)	−0.2 (1)	3.3
C_{a2}	3.1 (2)	3.6 (2)	3.0 (2)	−0.4 (1)	0.4 (1)	−0.2 (1)	3.2
C_{a3}	3.2 (2)	3.4 (2)	3.0 (2)	−0.2 (2)	0.6 (1)	0.2 (1)	3.2
C_{a4}	3.2 (2)	4.1 (2)	2.7 (2)	−0.0 (1)	0.9 (1)	0.2 (1)	3.2
C_{b1}	5.2 (2)	4.5 (2)	3.2 (2)	−0.9 (2)	1.6 (2)	−1.0 (2)	3.9
C_{b2}	4.8 (2)	4.3 (2)	3.4 (2)	−0.1 (2)	1.1 (2)	−0.8 (2)	4.0
C_{b3}	3.8 (2)	4.1 (2)	3.8 (2)	−0.9 (2)	1.1 (2)	0.3 (2)	3.7
C_{b4}	4.2 (2)	4.7 (2)	3.2 (2)	−0.1 (2)	1.4 (2)	0.2 (2)	3.8
C_{m1}	3.1 (2)	3.4 (2)	3.2 (2)	−0.3 (1)	0.4 (1)	−0.0 (2)	3.2
C_{m2}	3.6 (2)	3.8 (2)	2.6 (2)	0.1 (2)	0.9 (1)	−0.0 (1)	3.2
C_1	3.7 (2)	3.9 (2)	3.4 (2)	−0.8 (2)	1.1 (2)	−0.5 (2)	3.5
C_2	4.1 (2)	5.3 (2)	4.7 (2)	−0.7 (2)	−0.2 (2)	0.4 (2)	4.7
C_3	4.1 (2)	7.2 (3)	5.3 (3)	−1.5 (2)	0.1 (2)	−1.1 (2)	5.3
C_4	5.9 (3)	5.1 (3)	6.0 (3)	−2.6 (2)	2.5 (2)	−1.7 (2)	4.9
C_5	8.6 (4)	4.4 (3)	6.7 (3)	−1.9 (3)	0.8 (3)	0.7 (2)	6.1
C_6	5.9 (3)	4.5 (2)	5.5 (3)	−1.3 (2)	−0.6 (2)	0.8 (2)	5.2
C_7	4.1 (2)	4.0 (2)	3.6 (2)	−0.7 (2)	1.3 (2)	−0.6 (2)	3.7
C_8	5.2 (2)	6.5 (3)	3.9 (2)	−0.1 (2)	1.7 (2)	−0.3 (2)	4.9
C_9	7.4 (3)	7.9 (3)	3.5 (2)	−0.6 (3)	1.9 (2)	−0.7 (2)	5.6
C_{10}	8.9 (4)	6.2 (3)	4.4 (3)	−0.7 (3)	3.7 (3)	−1.0 (2)	5.4
C_{11}	5.7 (3)	7.3 (3)	7.5 (3)	0.4 (2)	3.7 (3)	−1.1 (3)	5.9
C_{12}	4.8 (2)	6.1 (3)	4.4 (2)	0.5 (2)	1.5 (2)	−0.7 (2)	4.9
C_{13}	6.7 (3)	7.3 (4)	7.6 (3)	−0.1 (3)	1.0 (3)	−1.5 (3)	7.1
C_{14}	6.1 (3)	8.3 (4)	8.7 (4)	−0.0 (3)	0.4 (3)	−2.0 (3)	7.5
C_{15}	7.6 (3)	8.6 (4)	6.6 (3)	−1.1 (3)	1.2 (3)	−1.6 (3)	7.4
C_{16}	8.4 (3)	7.9 (4)	7.2 (4)	−0.1 (3)	0.8 (3)	−2.0 (3)	7.7
C_{17}	6.3 (3)	8.4 (4)	7.8 (4)	0.9 (3)	−0.3 (3)	−2.9 (3)	7.2
C_{18}	6.4 (3)	9.7 (5)	6.3 (3)	−2.5 (3)	−0.1 (3)	−3.3 (3)	6.6
C_{19}	9.8 (4)	14.9 (6)	6.2 (3)	−4.4 (4)	2.2 (3)	−1.3 (4)	9.1

[a] The number following each datum is the estimated standard deviation in the least significant figure. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a^*_j$. [b] Isotropic thermal parameter calculated from $B = 4[V^2\det(\beta_{ij})]^{1/3}$.

Table III. Bond Lengths in the Coordination Group and Porphinato Skeleton[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
Cr–N_1	2.032 (3)	C_{a1}–C_{b1}	1.440 (5)	C_{a4}–C_{b4}	1.434 (5)
Cr–N_2	2.034 (3)	C_{a1}–C_{m2}'	1.388 (5)	C_{a4}–C_{m2}	1.387 (5)
N_1–C_{a1}	1.381 (4)	C_{a2}–C_{b2}	1.449 (5)	C_{b1}–C_{b2}	1.356 (5)
N_1–C_{a2}	1.370 (4)	C_{a2}–C_{m1}	1.404 (5)	C_{b3}–C_{b4}	1.349 (5)
N_2–C_{a3}	1.373 (5)	C_{a3}–C_{b3}	1.442 (5)	C_{m1}–C_1	1.497 (5)
N_2–C_{a4}	1.384 (4)	C_{a3}–C_{m1}	1.404 (5)	C_{m2}–C_7	1.507 (5)

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

the α- and β-carbon atoms of a pyrrole ring and C_m for the methine carbon atoms average, values for the chemically distinct bond parameters can be noted. The values for the bond distances in the core are N–C_a = 1.377 (7) Å, C_a–C_b = 1.441 (6) Å, C_b–C_b = 1.353 (5) Å, and C_a–C_m = 1.396 (10) Å. The number in parentheses in these and subsequent averaged values is the estimated standard deviation for the average. Averaged values for bond angles are C_aNC_a = 106.4 (1)°, NC_aC_m = 125.5 (2)°, NC_aC_b = 109.5 (9)°, $C_aC_bC_b$ = 107.2 (16)°, $C_aC_mC_a$ = 125.5 (4)°, and $C_mC_aC_b$ = 125.0 (10)°. The averaged bond parameters in CrTPP are in close agreement with those observed for ZnTPP.[3] Moreover, the bond parameters for both derivatives are consonant with the moderate expansion of the central hole of the macrocycle.[13]

The d^4 high-spin chromium(II) atom (S = 2) is centered in the porphinato plane with Cr–N = 2.033 (1) Å. This distance is comparable to the 2.027 (13) Å average chromium–porphinato nitrogen bond distance observed in low-spin (S = 1) bis(pyridine)-α,β,γ,δ-tetraphenylporphinatochromium(II).[14] It is to be expected[15] that this change in the spin state of the chromium(II) atom would not substantially effect the equatorial bond distances, although the M–N bond distances in porphinato derivatives generally show small increases with increasing coordination number. In what appears to be the only other chromium(II) complex available for comparison, the square-planar complex $Cr(N(Si(CH_3)_3)_2(THF))_2$ has Cr–N bond distances of 2.089 Å.[16] The 2.033-Å Cr–N bond

Table IV. Bond Angles in the Coordination Group and Porphinato Skeleton[a]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N_1CrN_2	90.2 (1)	$N_2C_{a3}C_{b3}$	109.7 (3)	$C_{a2}C_{m1}C_1$	116.2 (3)
$C_{a1}N_1C_{a2}$	106.5 (3)	$C_{m1}C_{a3}C_{b3}$	124.7 (3)	$C_{a3}C_{m1}C_1$	118.5 (3)
$C_{a3}N_2C_{a3}$	106.4 (3)	$N_2C_{a4}C_{m2}$	125.2 (3)	$C_{a4}C_{m2}C_{a1}'$	125.8 (3)
$N_1C_{a1}C_{m2}'$	125.7 (3)	$N_2C_{a4}C_{b4}$	109.2 (3)	$C_{a4}C_{m2}C_7$	117.9 (3)
$N_1C_{a1}C_{b1}$	108.5 (3)	$C_{m2}C_{a4}C_{b4}$	125.6 (3)	$C_{a1}'C_{m2}C_7$	116.4 (3)
$C_{m2}'C_{a1}C_{b1}$	125.9 (3)	$C_{a1}C_{b1}C_{b2}$	109.0 (3)	CrN_1C_{a1}	126.7 (2)
$N_1C_{a2}C_{m1}$	125.5 (3)	$C_{a2}C_{b2}C_{b1}$	105.2 (3)	CrN_1C_{a2}	126.8 (2)
$N_1C_{a2}C_{b2}$	110.7 (3)	$C_{a3}C_{b3}C_{b4}$	106.8 (3)	CrN_2C_{a3}	126.7 (2)
$C_{m1}C_{a2}C_{b2}$	123.8 (3)	$C_{a4}C_{b4}C_{b3}$	107.8 (3)	CnN_2C_{a4}	127.0 (2)
$N_2C_{a3}C_{m1}$	125.5 (3)	$C_{a2}C_{m1}C_{a3}$	125.2 (3)		

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

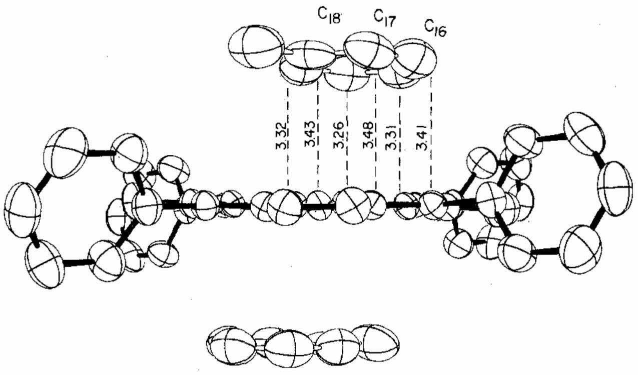

Figure 2. A plot showing the relationship between the two toluene molecules and the CrTPP molecule. The porphinato plane is approximately perpendicular to the plane of the paper. Perpendicular distances, in Å, between individual toluene atoms and the mean porphinato plane are displayed. Vibrational ellipsoids are shown at the 50% probability level.

distance in CrTPP is also short compared to the 2.06–2.09 Å range of Cr–N bond distances observed in several six-coordinate chromium(III) complexes with ammine and ethylenediamine ligands.[17]

Table V in the preceding paper has presented the average M–N bond distances for the known sequence of first-row metalloporphyrins. The Cr–N bond distance of 2.033 Å is seen to be one of the larger distances in the four-coordinate metalloporphyrins. However, the ≥0.05 Å difference in the M–N bond distances of the high-spin CrTPP and MnTPP derivatives clearly shows the effect of populating the $3d_{x^2-y^2}$ orbital. Table V also shows the required molecular symmetry of each derivative in its crystalline phase. The three derivatives with the longest M–N bond distances have nearly planar porphinato cores with required C_i-$\bar{1}$ molecular symmetry; the remaining derivatives have S_4-ruffled cores. Hoard[18] has shown that ruffling is conducive for forming shorter M–N bond distances in metalloporphyrins. The three derivatives with planar cores crystallize as toluene solvates in which the solvent molecule appears to interact with the metalloporphyrin; crystals of the other derivatives are unsolvated. Although Walker[19] has suggested 2:1 complex formation with toluene and Co(p-OCH_3)TPP at low temperatures, our attempts to crystallize CoTPP as a toluene solvate have been unsuccessful. This failure may reflect the greater stability of the unsolvated crystalline lattice compared to a solvated form.

Figures 2 and 3 display the relationship between the toluene molecules of solvation and the CrTPP molecule. The dihedral angle between the plane of the toluene molecule and the mean plane of the core is 4.5° (cf. Figure 2). The perpendicular distances between individual atoms of the toluene molecule and the mean plane of the porphinato core are displayed in Figure 2; the averaged value for the distance is 3.37 Å. Figure 3 shows the specific location and orientation of the toluene molecule with respect to the CrTPP molecule; the $C_{13}\cdots Cr$ separation is 3.361 Å.

The geometry and interplanar spacing observed in this solvated derivative and in the bis(toluene) solvates of ZnTPP[3] and MnTPP[5] suggest π-complex formation between the toluene molecule and the metalloporphyrin.[20] π complexes of porphyrins and metalloporphyrins have been known for some time[21] and have been the subject of a number of investigations.[22–26] Table V summarizes several features of the metalloporphyrin–toluene contacts in the three derivatives. Crystals of the ZnTPP and MnTPP species form an isomorphous set and hence the similarity in contacts is to be expected. CrTPP is not isomorphous with the other derivatives and, in principle, can display quite different interactions between the toluene and the metalloporphyrin. However, important similarities persist. In all derivatives, there is one toluene carbon atom which closely approaches the central metal atom and a bonded pair of toluene carbon atoms astraddle a pyrrole nitrogen (cf. Figure 3 in this and the preceding paper). Thus the interaction between the toluene and the metalloporphyrin apparently involves both the central metal atom and a pyrrole ring. In CrTPP, the toluene carbon atom that interacts with the metal atom is ortho to the methyl group, in ZnTPP and MnTPP the carbon atom is para to the toluene methyl group. Thus in all three derivatives an electron-rich carbon atom of the toluene interacts with the central metal atom, suggesting that the metal acts as a π acceptor. (Toluene is usually characterized as a π donor.[27]) In contrast to these results, the NMR studies of Fulton and LaMar[25] with strong π acceptors and cobalt(II) porphyrins suggest a complex in which only the porphyrin periphery is involved. Indeed, this appears to be a general pattern. Most structurally characterized molecular complexes in which one member is a metal complex have a π acceptor as the other member. In these cases, the π-acceptor–metal complex interation is at the periphery of the metal complex. Examples where the members are an uncharged metal complex and a π donor are limited. The perylene–bis[*cis*-(1,2-trifluoromethylethene-1,2-dithiolato)]nickel ($Ni(tfd)_2$) complex[28] has the π base interacting with the entire metal complex including, most probably, the metal atom. In the charged complex, (phenothiazine)$^+$–$(Ni(tfd)_2)^-$, the π base is shifted with respect to the nickel complex in a manner suggesting a specific π-base–metal interaction.[29]

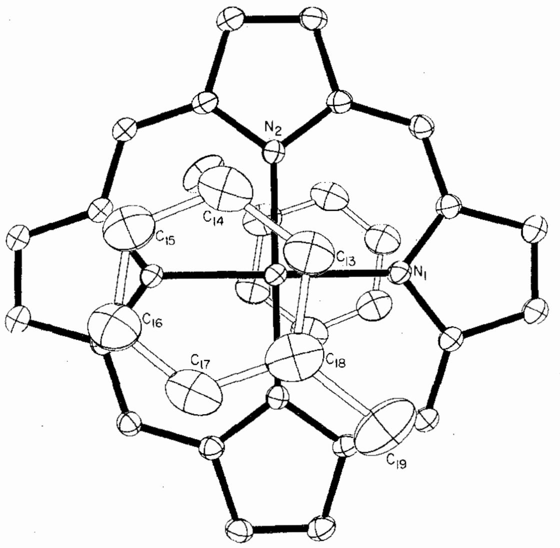

Figure 3. A second view of the CrTPP–toluene packing. The phenyl rings of CrTPP have been omitted. The vibrational ellipsoids are shown at the 20% probability level.

Table V. Summary of Metalloporphyrin–Toluene Contacts

Metalloporphyrin derivative	CrTPP	ZnTPP	MnTPP
Interplanar spacing, Å	3.37	3.34	3.30
Interplanar angle, deg	4.5	12.0	10.7
Closest $M\cdots C_{toluene}$ separation, Å	3.36	3.12	3.05
Carbon atom type	Ortho	Para	Para
Ref	*a*	*b*	*c*

[a] This work. [b] Reference 3. [c] Reference 5, data from −175 °C structure determination.

In CrTPP, there are no significantly short intermolecular contacts other than those involving the toluene and the CrTPP molecule.

Acknowledgment. We are grateful for support of this research from the Research Corporation, the National Institutes of Health, HL-15627 (W.R.S.), and the National Science Foundation, CHE-75-03648 (C.A.R.).

Registry No. CrTPP·2(toluene), 65150-27-8.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (13 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tetrameric Copper(I) Iodide–Piperidine, a Complex with a Tetrahedral Cu_4I_4 Core

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Received March 11, 1977

The tetrameric complex between copper(I) iodide and piperidine $[CuI\cdot C_5H_{11}N]_4$ crystallizes in the centrosymmetric tetragonal space group $P4_2/n$ (No. 86) with $a = 14.7715$ (2) Å, $c = 7.6073$ (2) Å, and $Z = 2$. The x-ray intensity data were measured with an Enraf-Nonius CAD-4 diffractometer complete to $\theta_{max} = 30°$ (Mo Kα radiation). The structure was solved by the 3-dimensional Patterson function and refined by full-matrix least-squares methods to $R = 0.042$ and $R_w = 0.047$ for 1159 independent reflections. The tetrameric molecules are centered on sites of $\bar{4}$ (S_4) symmetry. The compound consists of a tetrahedral Cu_4 cluster with short Cu–Cu distances (2.630 (2) and 2.671 (2) Å) surrounded by a concentric and opposed larger I_4 tetrahedron. The piperidine rings are connected to the clusters by coordination of nitrogen to copper. Adjacent molecules form chains which are probably linked together by means of weak hydrogen bonding between the hydrogen atom attached to nitrogen and an iodide ion in a neighboring cluster.

Introduction

The detailed x-ray crystal structure determination of the tetrameric complex between copper iodide and piperidine, $[CuI\cdot C_5H_{11}N]_4$, was undertaken as part of a study of the phenomena of "fluorescence thermochromism",[1-3] i.e., changing of fluorescence color from room temperature to liquid nitrogen temperature. The necessary precondition for the possibility of "fluorescence thermochromism" in complexes of copper iodide with organic ligands is the presence of an electron-donating bond from a ligand to copper. Unexpectedly the complex with piperidine does not show the phenomena of "fluorescence thermochromism" whereas most of the analogous complexes with other nitrogen bases do.[2] This unexpected physical property led to the following working hypothesis: A tetrameric complex between copper iodide and nitrogen bases does not show a marked phenomenon of "fluorescence thermochromism" if the point symmetry of its cluster molecule is at least of fourfold order, i.e., if the Cu–N bond lengths involved are equal by symmetry.[4] The results of the structure determination are given below and are discussed.

Experimental Section

The compound $[CuI\cdot C_5H_{11}N]_4$ was prepared as described in literature.[5] Suitable crystals for structure determination were obtained by recrystallization from acetonitrile under vacuum. The crystals were transparent, pale yellow needles with a prismatic habit of well-formed {100} and {110} faces. The measured angles between {100} and {110} were 45° within the accuracy of the goniometer suggesting a tetragonal crystal system. A needle of rectangular cross section (dominated by the {110} form) of 0.064 × 0.105 mm^2 was cut to a length of 0.159 mm to give a suitable sample for x-ray diffraction data collection.

The photographic study, using a Cu Kα oscillation around the needle axis (=*c* axis) and Mo Kα *hk*0, *hk*1, and *hhl* precession, revealed $4/m$ (C_{4h}) Laue symmetry for the diffraction pattern and showed the following conditions limiting possible reflections (1) (*hk*0) $h + k =$

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