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## Preparation and Molecular Stereochemistry of Metalloporphyrin Complexes with Cyano Ligands. Cyano(pyridine)(*meso*-tetraphenylporphinato)iron(III) Hydrate and Cyano(*meso*-tetraphenylporphinato)manganese(III) Chloroform Solvate

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The synthesis and structural characterization of two metalloporphyrin complexes with cyanide ligands are reported. The compounds are a low-spin six-coordinate iron(III) complex, cyano(pyridine)(*meso*-tetraphenylporphinato)iron(III), [Fe(TPP)(CN)(py)], and a high-spin five-coordinate manganese(III) complex, cyano(*meso*-tetraphenylporphinato)manganese(III), [Mn(TPP)(CN)]. The two stability quotients for the stepwise coordination of cyanide to manganese(III) porphyrinate were measured and are  $7.0 \times 10^2$  and  $5.3 \text{ M}^{-1}$ , significantly different from those reported for the iron(III) system. The small binding constant for the addition of the second cyanide allows the isolation of the five-coordinate monocyanomanganese(III) species. Despite considerable effort, we have been unable to prepare the analogous iron(III) species. The structure of [Mn(TPP)(CN)] is quite similar to those of related five-coordinate Mn(III) derivatives. The Mn(III) atom is displaced 0.25 Å from the porphinato plane; the Mn–N<sub>p</sub> bond distance of 2.008 (8) Å is a normal value. The axial Mn–C(CN) bond distance is exceptionally long at 2.166 (6) Å. There is a significant distortion from ideality for the axial Mn–C–N group, which is both bent and tilted with respect to the normal to the porphinato plane. The structure of [Fe(TPP)(CN)(py)] is that expected for a low-spin (porphinato)iron(III) species with an average Fe–N<sub>p</sub> bond distance of 1.970 (14) Å and axial distances of Fe–C = 1.908 (4) Å and Fe–N = 2.075 (3) Å. Crystal data for [Fe(TPP)(CN)(py)]:  $a = 13.227$  (2) Å,  $b = 23.575$  (4) Å,  $c = 14.065$  (3) Å,  $\beta = 102.64$  (1)°,  $Z = 4$ , space group  $P2_1/n$ , 6307 unique observed reflections ( $F_o > 3\sigma(F_o)$ ) used in the structure analysis,  $R_1 = 0.071$ ,  $R_2 = 0.076$ . Crystal data for [Mn(TPP)(CN)]:  $a = 12.433$  (2) Å,  $b = 22.023$  (3) Å,  $c = 14.460$  (2) Å,  $\beta = 102.01$  (1)°,  $Z = 4$ , space group  $P2_1/n$ , 3866 reflections,  $R_1 = 0.061$ ,  $R_2 = 0.068$ .

### Introduction

Cyanide ion is frequently used as a ligand for ferric hemoproteins and (porphinato)iron(III) species in order to prepare low-spin iron(III) complexes. Such species have been studied by a number of physical and chemical methods.<sup>4,5</sup> Surprisingly however, almost all such work has utilized only solution species; the characterization of compounds in the solid state is generally wanting. In part, the lack of isolated compounds results from synthetic difficulties (unfavorable equilibria and the greater stability of unwanted side products), which renders their isolation difficult. Recently, we have been able to isolate and characterize<sup>6</sup> dicyanoiron(III) porphyrinates. In addition to their intrinsic interest, these species also provide a starting point for the preparation of mixed-ligand species having cyanide ion and neutral nitrogen donors as the axial ligands. We report the preparation and structural characterization of one such species, cyano(pyridine)(*meso*-tetraphenylporphinato)iron(III), [Fe(TPP)(CN)(py)].<sup>7</sup> This complex is, to our knowledge, the first mixed-ligand cyanoiron(III) porphyrinate to be isolated and definitively characterized.

We have also investigated the reaction of cyanide with (porphinato)manganese(III) species. In this system, the two binding constants of cyanide ion are significantly different,

in distinct contrast to the iron(III) system where  $K_1 \approx K_2$ . This has allowed the isolation of the monocyanide derivative cyano(*meso*-tetraphenylporphinato)manganese(III), written as [Mn(TPP)(CN)]. We also describe the molecular structure of [Mn(TPP)(CN)], which is a high-spin  $d^4$  species. An interesting feature of this molecule is the distortion of the MnCN group from its ideal linear geometry.

### Experimental Section

**Synthesis of [Fe(TPP)(CN)(py)].** K[Fe(TPP)(CN)<sub>2</sub>]·2CH<sub>3</sub>CO·CH<sub>3</sub><sup>8</sup> (100 mg) was dissolved in 1 mL of pyridine and 3 mL of CHCl<sub>3</sub>. The solution was allowed to stand for 24 h and was then filtered through a cotton-wool plug. *n*-Hexane was then allowed to diffuse slowly into the solution. Air-stable single crystals of [Fe(TPP)(CN)(py)] as the monohydrate (yield 70 mg) were then obtained. The infrared spectrum (KBr pellet) has a cyanide stretch at 2130 cm<sup>-1</sup>, at slightly higher frequency than that observed (2120 cm<sup>-1</sup>) for K[Fe(TPP)(CN)<sub>2</sub>].  $\mu_{\text{eff}} = 2.6 \mu_B$  (solid state, 25 °C). Solid-state susceptibilities were measured as described previously.<sup>8</sup> Solution-state susceptibilities were measured by using the Evans NMR technique<sup>9</sup> on a JEOL FX-100 spectrometer. The related 1-methylimidazole complex, [Fe(TPP)(CN)(1-MeIm)], was prepared in an analogous fashion; however, crystals adequate for an X-ray structure determination could not be prepared.  $\mu_{\text{eff}} = 2.5 \mu_B$  (solid state).

**Preparation of [Mn(TPP)(CN)].** "Mn(TPP)(OH)"<sup>10</sup> was prepared by reaction of H<sub>2</sub>TPP with Mn(CH<sub>3</sub>COO)<sub>2</sub> in DMF, precipitation with NaOH/H<sub>2</sub>O, and recrystallization from CH<sub>3</sub>OH/H<sub>2</sub>O. To a green solution of Mn(TPP)(OH) (95 mg) in hot ethanol (19 mL) was added KCN (300 mg) in water (1 mL). The resulting hot solution was filtered quickly through a cotton plug and allowed to cool slowly (2 days). The crystalline compound (63 mg) was collected on a glass frit and redissolved in chloroform (5 mL). Single crystals of [Mn(TPP)(CN)] as the chloroform solvate were obtained by slowly diffusing *n*-pentane into the solution: IR (CN) 2120 cm<sup>-1</sup> (very weak);  $\mu_{\text{eff}} = 4.9 \mu_B$  (chloroform solution) and  $4.8 \mu_B$  (solid state). UV spectra were recorded on a Shimadzu Model 200S spectrophotometer, and IR

(1) University of Notre Dame.

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(4) Wang, J.-T.; Yeh, H. J. C.; Johnson, D. F. *J. Am. Chem. Soc.* **1978**, *100*, 2400–2405. Goff, H.; Morgan, L. O. *Inorg. Chem.* **1976**, *15*, 2069–2076 and references cited therein.

(5) Traylor, T. G.; Berzins, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 2844–2846. Wüthrich, K.; Baumann, R. *Helv. Chim. Acta* **1974**, *57*, 336–350. La Mar, G. N.; Viscio, D. B.; Smith, K. M.; Caughey, W. S.; Smith, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 8085–8092 and following papers.

(6) Scheidt, W. R.; Haller, K. J.; Hatano, K. *J. Am. Chem. Soc.* **1980**, *102*, 3017–3021.

(7) Abbreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; OEP, the dianion of octaethylporphyrin; py, pyridine; 1-MeIm, 1-methylimidazole; 3-Cl(py), 3-chloropyridine; N<sub>p</sub>, porphinato nitrogen atom.

(8) Adams, K. M.; Rasmussen, P. G.; Scheidt, W. R.; Hatano, K. *Inorg. Chem.* **1979**, *18*, 1892–1899.

(9) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(10) Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 6729–6735.

**Table I.** Summary of Crystal Data and Intensity Collection Parameters for Fe(TPP)(CN)(py)·H<sub>2</sub>O and Mn(TPP)(CN)·CHCl<sub>3</sub>

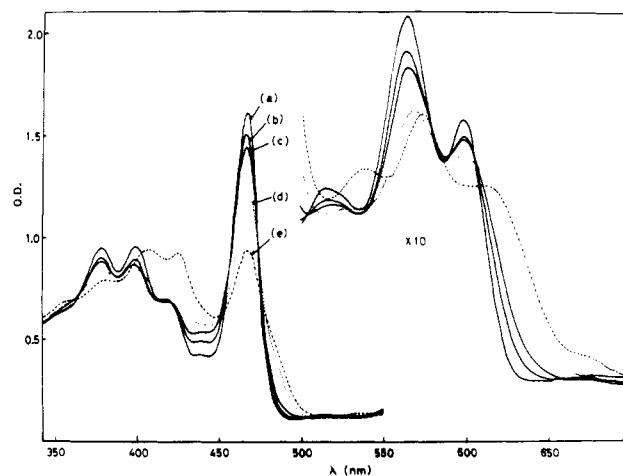
| compd                                 | Fe(TPP)(CN)(py)·H <sub>2</sub> O                           | Mn(TPP)(CN)·CHCl <sub>3</sub>                                    |
|---------------------------------------|------------------------------------------------------------|------------------------------------------------------------------|
| formula                               | FeON <sub>6</sub> C <sub>50</sub> H <sub>35</sub>          | MnCl <sub>3</sub> N <sub>5</sub> C <sub>46</sub> H <sub>29</sub> |
| fw                                    | 791.72                                                     | 813.07                                                           |
| space group                           | P2 <sub>1</sub> /n                                         | P2 <sub>1</sub> /n                                               |
| a, Å                                  | 13.227 (2)                                                 | 12.433 (2)                                                       |
| b, Å                                  | 23.575 (4)                                                 | 22.023 (3)                                                       |
| c, Å                                  | 14.065 (3)                                                 | 14.460 (2)                                                       |
| β, deg                                | 102.64 (1)                                                 | 102.01 (1)                                                       |
| V, Å <sup>3</sup>                     | 4279.5                                                     | 3872.7                                                           |
| temp, °C                              | 20                                                         | 20                                                               |
| no. of reflns used for cell constants | 60                                                         | 60                                                               |
| Z                                     | 4                                                          | 4                                                                |
| d(calcd), g/cm <sup>3</sup>           | 1.23                                                       | 1.39                                                             |
| d(obsd), g/cm <sup>3</sup>            | 1.24                                                       | 1.38                                                             |
| cryst dimens, mm                      | 0.3 × 0.4 × 0.6                                            | 0.2 × 0.2 × 0.5                                                  |
| radiation                             | graphite-monochromated Mo Kα (λ = 0.710 73 Å)              |                                                                  |
| scan technique                        | θ-2θ                                                       | θ-2θ                                                             |
| scan range                            | 0.80° below Kα <sub>1</sub> to 0.80° above Kα <sub>2</sub> | 0.60° below Kα <sub>1</sub> to 0.60° above Kα <sub>2</sub>       |
| scan rate, deg/min                    | 2-24                                                       | 2-24                                                             |
| bkgd                                  | 0.5 times scan time at extremes of scan                    |                                                                  |
| 2θ limits                             | 3.5-54.9                                                   | 3.5-54.9                                                         |
| criterion for observn                 | F <sub>o</sub> > 3σ(F <sub>o</sub> )                       |                                                                  |
| unique obsd data                      | 6307                                                       | 3866                                                             |
| μ, mm <sup>-1</sup>                   | 0.354                                                      | 0.534                                                            |
| R <sub>1</sub>                        | 0.071                                                      | 0.061                                                            |
| R <sub>2</sub>                        | 0.076                                                      | 0.068                                                            |
| GOF                                   | 1.957                                                      | 1.571                                                            |

spectra were obtained as KBr pellets on a JASCO IRA-2 spectrometer.

**X-ray Structure Determinations.** Both crystals were subjected to preliminary examination on a Nicolet P1 diffractometer. Least-squares refinement of the setting angles for the several reflections, collected at ±2θ and in the range 26 ≤ 2θ < 35, gave the cell constants reported in Table I. All measurements utilized graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Details of the intensity collection parameters are summarized in Table I. Data were reduced as described previously.<sup>11</sup> Both structures were solved by heavy-atom methods. Standard values for the atomic scattering factors including corrections for anomalous dispersion<sup>12</sup> were employed in the structure analysis.

After preliminary refinement of [Fe(TPP)(CN)(py)], the position of the solvent water molecule was determined. Subsequent difference Fourier syntheses gave evidence of electron density appropriately located for all hydrogen atoms except those of the water molecule. The position of all located hydrogen atoms were idealized (C-H = 0.95 Å, B(H) = B(C) + 1.0 Å<sup>2</sup>) and were included in subsequent refinement cycles as fixed contributors. The refinement was carried to convergence by using anisotropic temperature factors for all heavy atoms.<sup>13</sup> A final difference Fourier synthesis was judged to have no significant features; the largest difference peaks (<0.8 e/Å<sup>3</sup>, ~15% of a typical carbon atom) are near the iron atom. A listing of the final observed and calculated structure amplitudes is available as

- (11) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84-89.  
 (12) Programs used in this study included local modifications of Jacobson's ALFF and ALLS, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP. Atomic form factors were from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321-323. Real and imaginary corrections for anomalous dispersion in the form factor of the iron, manganese, and chlorine atoms were from: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891-1898. Scattering factors for hydrogen were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175-3187.  
 (13) The temperature factors of the water molecule were rather large, suggesting either partial occupancy or some small positional disorder. At this point, R<sub>1</sub> = 0.071 and R<sub>2</sub> = 0.077. The occupancy factor of this atom was then varied, yielding an occupancy factor of 0.822 (11) and smaller temperature factors. Changes in other parameters were insignificant. Parameters from this refinement are reported herein.



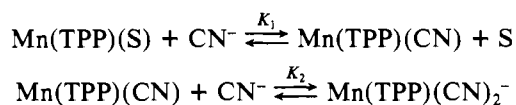
**Figure 1.** Spectral changes upon addition of KCN to Mn(TPP)(OH) ( $1.4 \times 10^{-5}$  M) in methanol. KCN concentration (M): (a) none; (b)  $1.90 \times 10^{-3}$ ; (c)  $6.34 \times 10^{-3}$ ; (d)  $6.34 \times 10^{-2}$  (dotted line); (e)  $2.54 \times 10^{-1}$  (broken line).

supplementary material. Atomic coordinates in the asymmetric unit of structure are tabulated in Table II. Table III (supplementary material) lists the associated anisotropic temperature factors.

After preliminary refinement of the structure for [Mn(TPP)(CN)], the chloroform molecule of crystallization was found to be disordered with three distinct orientations. The three orientations used a carbon atom at a common center with one chlorine atom position common to two orientations. There were thus eight individual chlorine atom positions; the final refined occupancy of the chloroform molecule was essentially unity, 0.98. In subsequent cycles of least-squares refinement, the three chlorine atoms of the major orientation were allowed anisotropic temperature factors and the remaining chlorine atoms were restricted to isotropic temperature factors. As before, hydrogen atoms were idealized and included as fixed contributors in subsequent refinement cycles. The refinement was then taken to convergence by using anisotropic temperature factors. A final difference Fourier synthesis had all its largest peaks (<0.5 e/Å<sup>3</sup>) in the region of the disordered chloroform molecule. The final observed and calculated structure amplitudes for [Mn(TPP)(CN)] are available as supplementary material. Atomic coordinates are listed in Table IV. Anisotropic temperature factors are given in Table V (supplementary material).

## Results and Discussion

**Solution Equilibria.** The reaction of Mn(TPP)(OH) with CN<sup>-</sup> appears to proceed in two steps. Figure 1 shows the spectral changes observed upon addition of KCN to a methanol solution of Mn(TPP)(OH). The solid lines are the spectral changes at low concentrations of CN<sup>-</sup> ([CN<sup>-</sup>] range 0-6.34) × 10<sup>-3</sup> M). When the concentration of CN<sup>-</sup> is increased above 10<sup>-2</sup> M, the spectrum begins to shift from the isosbestic points observed at low concentrations of CN<sup>-</sup>. These are shown in Figure 1 as (d) and (e). Since the concentration of CN<sup>-</sup> at (e) is almost saturated, (e) is not the ultimate spectrum observed at high cyanide concentration. These data are consistent with the stepwise equilibria



where S is either solvent or original anion. The apparent equilibrium quotients for the first and second steps were determined graphically from the change in absorbance at 467 nm following the method of Rossotti and Rossotti.<sup>14</sup> K<sub>1</sub> was

- (14) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961; p 277. For a use of this procedure in evaluating the binding constants of water to a manganese(III) porphyrinate, see: Neya, S.; Morishima, I.; Yonezawa, T. *Biochemistry* **1981**, *20*, 2610-2614.

determined by assuming S as solvent and using the relationship

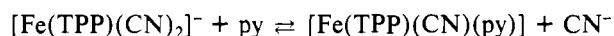
$$\frac{1}{A - A_0} = \frac{1}{K_1(A_1 - A_0)} \frac{1}{[\text{KCN}]} + \frac{1}{A_1 - A_0}$$

where  $A_0$  and  $A_1$  are the absorbances of  $\text{Mn}(\text{TPP})(\text{OH})$  and  $\text{Mn}(\text{TPP})(\text{CN})$  and  $A$  is the observed absorbance. The plot of  $1/(A - A_0)$  vs.  $1/[\text{KCN}]$  is shown in Figure 2A. From the values of  $K_1$  and  $A_1$  so determined,  $K_2$  and  $A_2$  were determined following Rossotti and Rossotti<sup>14</sup> by using the relationship

$$\frac{A - A_0}{A[\text{KCN}]^2} + \frac{(A - A_1)K_1}{A[\text{KCN}]} = K_1K_2A_2\left(\frac{1}{A}\right) - K_1K_2$$

The graphical solution is shown in Figure 2B. The values are  $K_1 = 7.0 \times 10^2 \text{ M}^{-1}$  and  $K_2 = 5.3 \text{ M}^{-1}$ . Since  $K_1 \gg K_2$ ,  $\text{Mn}(\text{TPP})(\text{CN})$  can be obtained. This is in distinct contrast to the iron(III) case, where  $K_1 \approx K_2$  and where the binding constants for  $\text{CN}^-$  are much larger.<sup>4</sup> It may also be noted that the stability constants<sup>15</sup> for the binding of two nitrogen ligands to  $\text{Mn}(\text{III})$  and  $\text{Fe}(\text{III})$  also favor iron(III).

Attempts to quantitatively determine the equilibrium constant for the reaction

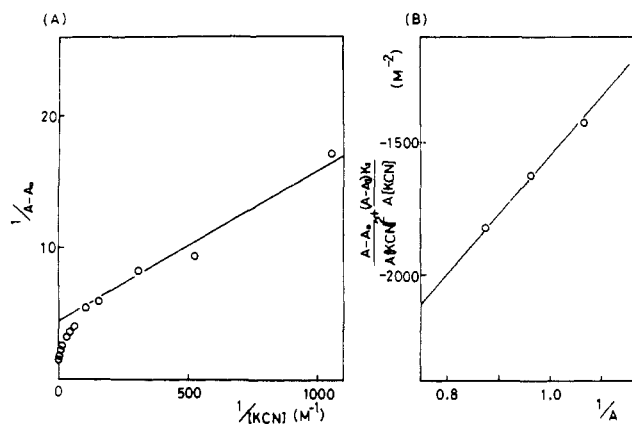


were unsuccessful, at least in part because of competing equilibria with the polar solvents (e.g., methanol) required to dissolve  $[\text{Fe}(\text{TPP})(\text{CN})_2]$ .

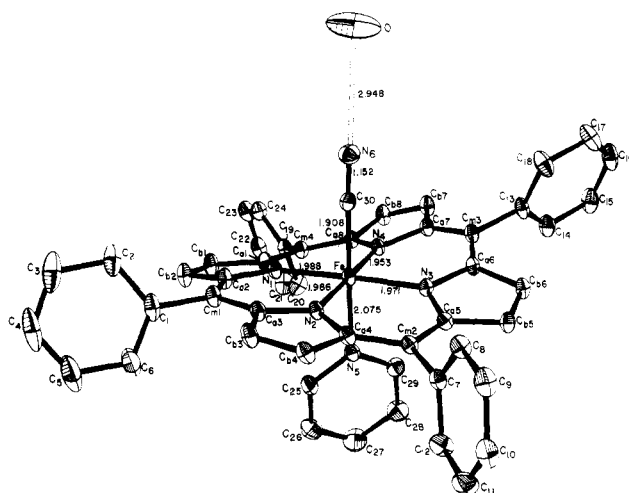
**Structure of  $[\text{Fe}(\text{TPP})(\text{CN})(\text{py})]$ .** Figure 3 presents a perspective view of the molecule as it exists in the crystal. Figure 3 illustrates the labeling scheme used for all atoms and bond distances in the coordination group and axial cyanide ligand. Individual bond distances and bond angles are listed in Table VI. Averaged values<sup>16</sup> of the bond distances and angles for the various chemical classes in the porphinato core are given in Figure 4. These bond distances and angles are normal. The average value of the  $\text{C}_m\text{-C}_p$  bond distance is 1.493 (12) Å, and the average C-C distance in the peripheral phenyl groups is 1.372 (24) Å.

Figure 4 is a formal diagram of a porphinato core illustrating the displacement of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core. Atoms with negative displacements are toward the cyanide side of the plane. The core in  $[\text{Fe}(\text{TPP})(\text{CN})(\text{py})]$  has a pronounced quasi- $S_4$  ruffling. The magnitude of the ruffling is not exceptional for porphinato derivatives,<sup>17,18</sup> although it is somewhat larger than usually observed for low-spin iron(III) derivatives. The  $\alpha$ -carbon atoms of the pyridine ligand are almost directly below (within 5°) the line defined by the  $\text{C}_{m1}$  and  $\text{C}_{m3}$  methine carbon atoms. These methine carbon atoms are displaced away from the pyridine ligand atoms (cf. Figure 3). The pyridine plane is not quite perpendicular to the porphinato plane, forming a dihedral angle of 80.8° between the two planes. Dihedral angles between the peripheral phenyl groups and the 24-atom core are within the normal range with values of 62.3, 80.1, 68.1, and 73.2°.

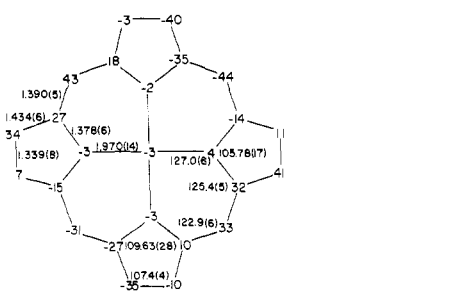
The nitrogen atom of the cyanide ligand is within hydrogen-bonding distance (2.948 (7) Å) of the oxygen of the water molecule. A second water molecule is related to the first by an inversion center, and the two oxygen atoms are separated by 3.043 (14) Å. Hence, in crystals of  $\text{Fe}(\text{TPP})(\text{CN})(\text{py}) \cdot \text{H}_2\text{O}$ , there is a small hydrogen-bonding network connecting



**Figure 2.** (A) Relation between the absorbance and KCN concentration. The absorbance is measured at 467 nm;  $A$  is absorbance with KCN present and  $A_0$  is the absorbance in the absence of KCN. (B) Analysis of the absorption data at high KCN concentrations.  $A_1$  is the absorbance of  $[\text{Mn}(\text{TPP})(\text{CN})]$  obtained from (A). All measurements in Figures 1 and 2 were made at  $25 \pm 1^\circ\text{C}$ .



**Figure 3.** ORTEP plot of the  $[\text{Fe}(\text{TPP})(\text{CN})(\text{py})]$  molecule and the water molecule hydrogen bonded to the cyano ligand. The atomic labels assigned to each atom are displayed as are the bond distances in the coordination group.



**Figure 4.** Formal diagram of the porphinato core in  $[\text{Fe}(\text{TPP})(\text{CN})(\text{py})]$ . The core in the diagram has the same orientation as that in Figure 3. The perpendicular displacements of each atom (in units of 0.01 Å) from the mean plane of the 24-atom core are displayed. Negative values for the displacement indicate a displacement on the cyano side of the plane. Also shown are the averaged bond parameters for the chemically equivalent types. The estimated standard deviations (in parentheses) are calculated on the assumption that all values are drawn from the same population.

two  $[\text{Fe}(\text{TPP})(\text{CN})(\text{py})]$  molecules via a hydrogen-bonded pair of water molecules.

Other structural features are in accord with the low-spin state of the molecule. The average  $\text{Fe-N}_p$  bond distance of 1.970 (14) Å is at the low end of the range of values observed<sup>19</sup>

(15) Kadish, K. M.; Bottomley, L. A. *Inorg. Chem.* **1980**, *19*, 832-836. Kelly, S. L.; Kadish, K. M. *Ibid.* **1982**, *21*, 2631-2639.

(16) The numbers in parentheses for these and other averaged values are the estimated standard deviations calculated on the assumption that the individual values are all drawn from the same population.

(17) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 317-380.

(18) Scheidt, W. R. *Porphyrins* **1978**, *3*, 463-511.

Table II. Fractional Monoclinic Coordinates for Fe(TPP)(CN)(py)·H<sub>2</sub>O<sup>a</sup>

| atom            | x             | y            | z             | atom            | x            | y            | z             |
|-----------------|---------------|--------------|---------------|-----------------|--------------|--------------|---------------|
| Fe              | 0.16130 (4)   | 0.30134 (2)  | -0.11662 (4)  | C <sub>3</sub>  | -0.3677 (4)  | 0.21460 (27) | -0.1962 (7)   |
| N <sub>1</sub>  | 0.07400 (21)  | 0.23622 (12) | -0.17504 (22) | C <sub>4</sub>  | -0.3872 (6)  | 0.1976 (3)   | -0.1094 (9)   |
| N <sub>2</sub>  | 0.05335 (21)  | 0.32345 (12) | -0.04743 (22) | C <sub>5</sub>  | -0.3138 (7)  | 0.1982 (4)   | -0.0308 (7)   |
| N <sub>3</sub>  | 0.25036 (20)  | 0.36424 (11) | -0.05528 (21) | C <sub>6</sub>  | -0.2153 (5)  | 0.21690 (29) | -0.0333 (5)   |
| N <sub>4</sub>  | 0.26859 (20)  | 0.27918 (12) | -0.18511 (20) | C <sub>7</sub>  | 0.13941 (27) | 0.44023 (16) | 0.13696 (28)  |
| N <sub>5</sub>  | 0.23045 (24)  | 0.24798 (13) | -0.00375 (22) | C <sub>8</sub>  | 0.1068 (3)   | 0.49519 (17) | 0.1132 (3)    |
| C <sub>30</sub> | 0.10519 (27)  | 0.34941 (17) | -0.2244 (3)   | C <sub>9</sub>  | 0.0887 (3)   | 0.53209 (18) | 0.1844 (4)    |
| C <sub>a1</sub> | 0.10721 (28)  | 0.18984 (15) | -0.2198 (3)   | C <sub>10</sub> | 0.1062 (4)   | 0.51488 (21) | 0.2789 (4)    |
| C <sub>a2</sub> | -0.02570 (28) | 0.22398 (17) | -0.1680 (3)   | C <sub>11</sub> | 0.1418 (4)   | 0.46161 (23) | 0.3042 (3)    |
| C <sub>a3</sub> | -0.04703 (27) | 0.30373 (16) | -0.06317 (28) | C <sub>12</sub> | 0.1591 (4)   | 0.42408 (18) | 0.2328 (3)    |
| C <sub>a4</sub> | 0.06070 (27)  | 0.36621 (15) | 0.02135 (27)  | C <sub>13</sub> | 0.4694 (3)   | 0.39428 (17) | -0.1811 (3)   |
| C <sub>a5</sub> | 0.23734 (27)  | 0.39697 (14) | 0.02298 (26)  | C <sub>14</sub> | 0.5699 (3)   | 0.37509 (20) | -0.1594 (3)   |
| C <sub>a6</sub> | 0.33960 (26)  | 0.38373 (15) | -0.07902 (27) | C <sub>15</sub> | 0.6479 (4)   | 0.40412 (26) | -0.1890 (4)   |
| C <sub>a7</sub> | 0.34882 (27)  | 0.31212 (15) | -0.20178 (28) | C <sub>16</sub> | 0.6257 (4)   | 0.45259 (25) | -0.2411 (5)   |
| C <sub>a8</sub> | 0.27394 (26)  | 0.22951 (15) | -0.23426 (28) | C <sub>17</sub> | 0.5301 (5)   | 0.47372 (22) | -0.2607 (5)   |
| C <sub>b1</sub> | 0.0268 (3)    | 0.14848 (17) | -0.2412 (4)   | C <sub>18</sub> | 0.4494 (4)   | 0.44483 (21) | -0.2302 (4)   |
| C <sub>b2</sub> | -0.0558 (3)   | 0.16918 (18) | -0.2108 (4)   | C <sub>19</sub> | 0.2318 (3)   | 0.12966 (17) | -0.2844 (3)   |
| C <sub>b3</sub> | -0.1041 (3)   | 0.33625 (17) | -0.0059 (3)   | C <sub>20</sub> | 0.3036 (4)   | 0.09532 (20) | -0.2256 (4)   |
| C <sub>b4</sub> | -0.0383 (3)   | 0.37331 (15) | 0.0466 (3)    | C <sub>21</sub> | 0.3313 (4)   | 0.04336 (21) | -0.2603 (5)   |
| C <sub>b5</sub> | 0.32450 (28)  | 0.43407 (15) | 0.05213 (28)  | C <sub>22</sub> | 0.2867 (4)   | 0.02726 (20) | -0.3528 (5)   |
| C <sub>b6</sub> | 0.38590 (27)  | 0.42642 (15) | -0.0107 (3)   | C <sub>23</sub> | 0.2173 (4)   | 0.06121 (20) | -0.4124 (4)   |
| C <sub>b7</sub> | 0.4014 (3)    | 0.28278 (18) | -0.2656 (3)   | C <sub>24</sub> | 0.1894 (3)   | 0.11245 (18) | -0.3775 (3)   |
| C <sub>b8</sub> | 0.3583 (3)    | 0.23167 (17) | -0.2827 (3)   | C <sub>25</sub> | 0.1770 (4)   | 0.20786 (19) | 0.0312 (4)    |
| C <sub>m1</sub> | -0.08588 (29) | 0.25647 (16) | -0.1179 (3)   | C <sub>26</sub> | 0.2260 (6)   | 0.16794 (23) | 0.0970 (4)    |
| C <sub>m2</sub> | 0.14816 (27)  | 0.39866 (14) | 0.05883 (26)  | C <sub>27</sub> | 0.3305 (5)   | 0.16946 (26) | 0.1296 (5)    |
| C <sub>m3</sub> | 0.38211 (27)  | 0.36267 (15) | -0.15367 (28) | C <sub>28</sub> | 0.3849 (4)   | 0.21083 (24) | 0.0976 (4)    |
| C <sub>m4</sub> | 0.20305 (28)  | 0.18521 (15) | -0.24447 (28) | C <sub>29</sub> | 0.3336 (3)   | 0.24876 (18) | 0.0303 (3)    |
| C <sub>1</sub>  | -0.1908 (3)   | 0.23592 (19) | -0.1159 (4)   | N <sub>6</sub>  | 0.07580 (28) | 0.37854 (16) | -0.29041 (29) |
| C <sub>2</sub>  | -0.2695 (4)   | 0.23531 (21) | -0.2008 (5)   | O <sup>b</sup>  | 0.0237 (8)   | 0.4375 (3)   | -0.4797 (5)   |

<sup>a</sup> The estimated standard deviations of the least significant digits are given in parentheses. <sup>b</sup> The refined occupancy factor for the water oxygen atom is 0.824 (11).

Table IV. Fractional Monoclinic Coordinates for Mn(TPP)(CN)·CHCl<sub>3</sub><sup>a</sup>

| atom            | x           | y             | z             | atom                         | x            | y             | z            |
|-----------------|-------------|---------------|---------------|------------------------------|--------------|---------------|--------------|
| Mn              | 0.08409 (7) | 0.11768 (4)   | 0.06817 (5)   | C <sub>4</sub>               | 0.3399 (6)   | -0.18982 (28) | 0.2448 (5)   |
| N <sub>1</sub>  | 0.0716 (3)  | 0.06407 (18)  | 0.17768 (26)  | C <sub>5</sub>               | 0.2294 (5)   | -0.18289 (26) | 0.2397 (4)   |
| N <sub>2</sub>  | 0.1434 (3)  | 0.04669 (18)  | 0.00660 (26)  | C <sub>6</sub>               | 0.1770 (4)   | -0.12959 (24) | 0.2073 (4)   |
| N <sub>3</sub>  | 0.0678 (3)  | 0.16275 (19)  | -0.05387 (27) | C <sub>7</sub>               | 0.1901 (5)   | 0.08237 (24)  | -0.2393 (4)  |
| N <sub>4</sub>  | -0.0175 (3) | 0.17762 (18)  | 0.11180 (28)  | C <sub>8</sub>               | 0.2962 (5)   | 0.06493 (29)  | -0.2410 (4)  |
| N <sub>5</sub>  | 0.3145 (4)  | 0.19216 (24)  | 0.1468 (4)    | C <sub>9</sub>               | 0.3302 (6)   | 0.0580 (3)    | -0.3261 (5)  |
| C <sub>25</sub> | 0.2366 (4)  | 0.16431 (25)  | 0.1261 (4)    | C <sub>10</sub>              | 0.2569 (6)   | 0.0689 (3)    | -0.4093 (4)  |
| C <sub>a1</sub> | 0.0289 (4)  | 0.07973 (24)  | 0.2550 (3)    | C <sub>11</sub>              | 0.1527 (6)   | 0.0858 (3)    | -0.4085 (4)  |
| C <sub>a2</sub> | 0.1297 (4)  | 0.01112 (23)  | 0.2018 (3)    | C <sub>12</sub>              | 0.1178 (5)   | 0.09293 (27)  | -0.3248 (4)  |
| C <sub>a3</sub> | 0.1765 (4)  | -0.00837 (22) | 0.0484 (3)    | C <sub>13</sub>              | -0.0517 (5)  | 0.31927 (26)  | -0.0415 (4)  |
| C <sub>a4</sub> | 0.1618 (4)  | 0.04280 (23)  | -0.0848 (3)   | C <sub>14</sub>              | -0.1430 (7)  | 0.3326 (3)    | -0.1080 (5)  |
| C <sub>a5</sub> | 0.1146 (4)  | 0.14820 (24)  | -0.1301 (3)   | C <sub>15</sub>              | -0.1634 (8)  | 0.3914 (4)    | -0.1429 (5)  |
| C <sub>a6</sub> | 0.0360 (4)  | 0.22280 (24)  | -0.0670 (4)   | C <sub>16</sub>              | -0.0918 (7)  | 0.4337 (4)    | -0.1108 (5)  |
| C <sub>a7</sub> | -0.0536 (4) | 0.23208 (24)  | 0.0682 (4)    | C <sub>17</sub>              | -0.0020 (6)  | 0.4238 (4)    | -0.0390 (8)  |
| C <sub>a8</sub> | -0.0610 (4) | 0.17482 (24)  | 0.1918 (4)    | C <sub>18</sub>              | 0.0169 (6)   | 0.3656 (3)    | -0.0059 (6)  |
| C <sub>b1</sub> | 0.0623 (5)  | 0.03584 (25)  | 0.3287 (4)    | C <sub>19</sub>              | -0.0834 (5)  | 0.13733 (26)  | 0.3497 (4)   |
| C <sub>b2</sub> | 0.1250 (5)  | -0.00525 (24) | 0.2966 (4)    | C <sub>20</sub>              | -0.0555 (5)  | 0.18793 (28)  | 0.4078 (4)   |
| C <sub>b3</sub> | 0.2085 (5)  | -0.04759 (24) | -0.0194 (4)   | C <sub>21</sub>              | -0.0999 (6)  | 0.1948 (3)    | 0.4877 (4)   |
| C <sub>b4</sub> | 0.1988 (5)  | -0.01671 (24) | -0.1003 (3)   | C <sub>22</sub>              | -0.1695 (6)  | 0.1516 (4)    | 0.5098 (4)   |
| C <sub>b5</sub> | 0.1140 (5)  | 0.20034 (26)  | -0.1880 (4)   | C <sub>23</sub>              | -0.1960 (6)  | 0.1020 (3)    | 0.4543 (5)   |
| C <sub>b6</sub> | 0.0666 (6)  | 0.24587 (26)  | -0.1501 (4)   | C <sub>24</sub>              | -0.1526 (5)  | 0.09443 (29)  | 0.3746 (4)   |
| C <sub>b7</sub> | -0.1229 (5) | 0.26270 (26)  | 0.1213 (4)    | C <sub>26</sub>              | 0.0142 (6)   | 0.3720 (4)    | 0.6086 (6)   |
| C <sub>b8</sub> | -0.1279 (5) | 0.22700 (26)  | 0.1952 (4)    | Cl <sub>1</sub> <sup>b</sup> | 0.1138 (3)   | 0.38716 (20)  | 0.70894 (27) |
| C <sub>m1</sub> | 0.1782 (4)  | -0.02366 (22) | 0.1421 (4)    | Cl <sub>2</sub> <sup>c</sup> | -0.0275 (5)  | 0.43520 (26)  | 0.5391 (4)   |
| C <sub>m2</sub> | 0.1531 (4)  | 0.09095 (24)  | -0.1476 (3)   | Cl <sub>3</sub> <sup>c</sup> | 0.0983 (4)   | 0.32421 (24)  | 0.5481 (4)   |
| C <sub>m3</sub> | -0.0218 (5) | 0.25556 (25)  | -0.0111 (4)   | Cl <sub>4</sub> <sup>d</sup> | 0.1273 (7)   | 0.3328 (4)    | 0.6152 (6)   |
| C <sub>m4</sub> | -0.0374 (4) | 0.13061 (24)  | 0.2617 (4)    | Cl <sub>5</sub> <sup>d</sup> | -0.0368 (10) | 0.3894 (5)    | 0.4906 (9)   |
| C <sub>1</sub>  | 0.2353 (4)  | -0.08171 (23) | 0.1786 (4)    | Cl <sub>6</sub> <sup>d</sup> | 0.0397 (10)  | 0.4326 (6)    | 0.6793 (8)   |
| C <sub>2</sub>  | 0.3465 (5)  | -0.08944 (27) | 0.1850 (5)    | Cl <sub>7</sub> <sup>e</sup> | 0.0371 (10)  | 0.3500 (6)    | 0.4964 (8)   |
| C <sub>3</sub>  | 0.3990 (5)  | -0.1427 (3)   | 0.2182 (5)    | Cl <sub>8</sub> <sup>e</sup> | -0.0369 (8)  | 0.4480 (4)    | 0.5923 (6)   |

<sup>a</sup> The estimated standard deviations of the least significant digits are given in parentheses. <sup>b</sup> The occupancy factor for the chlorine atom is 0.69 (2). <sup>c</sup> The occupancy factor is 0.44 (2). <sup>d</sup> The occupancy factor is 0.29 (2). <sup>e</sup> The occupancy factor is 0.25 (2).

for low-spin iron(III) porphyrinates. The decrease from the average value, 1.990 Å, observed for these species can be

attributed<sup>20</sup> to the ruffling of the porphyrinato core. The iron(III) atom is displaced only slightly, 0.03 Å, out of the porphyrinato plane toward the cyano ligand. The Fe-N<sub>py</sub> bond distance of 2.075 (3) Å is comparable to values observed for

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Table VI. Selected Interatomic Distances (Å) and Angles (deg) for Fe(TPP)(CN)(py)·H<sub>2</sub>O<sup>a</sup>

|                                  |           | Distances                        |           |                                  |            |                                  |            |
|----------------------------------|-----------|----------------------------------|-----------|----------------------------------|------------|----------------------------------|------------|
| Fe-N <sub>1</sub>                | 1.988 (3) | C <sub>a3</sub> -C <sub>b3</sub> | 1.440 (5) | C <sub>1</sub> -C <sub>6</sub>   | 1.349 (7)  | C <sub>17</sub> -C <sub>18</sub> | 1.411 (6)  |
| Fe-N <sub>2</sub>                | 1.966 (3) | C <sub>a3</sub> -C <sub>m1</sub> | 1.388 (5) | C <sub>2</sub> -C <sub>3</sub>   | 1.402 (7)  | C <sub>m4</sub> -C <sub>19</sub> | 1.506 (5)  |
| Fe-N <sub>3</sub>                | 1.971 (3) | C <sub>a4</sub> -C <sub>b4</sub> | 1.439 (5) | C <sub>3</sub> -C <sub>4</sub>   | 1.363 (12) | C <sub>19</sub> -C <sub>20</sub> | 1.377 (6)  |
| Fe-N <sub>4</sub>                | 1.953 (3) | C <sub>a4</sub> -C <sub>m2</sub> | 1.391 (5) | C <sub>4</sub> -C <sub>5</sub>   | 1.302 (12) | C <sub>19</sub> -C <sub>24</sub> | 1.369 (6)  |
| Fe-N <sub>5</sub>                | 2.075 (3) | C <sub>a5</sub> -C <sub>b5</sub> | 1.434 (5) | C <sub>5</sub> -C <sub>6</sub>   | 1.383 (8)  | C <sub>20</sub> -C <sub>21</sub> | 1.397 (6)  |
| Fe-C <sub>30</sub>               | 1.908 (4) | C <sub>a5</sub> -C <sub>m2</sub> | 1.381 (4) | C <sub>m2</sub> -C <sub>7</sub>  | 1.496 (5)  | C <sub>21</sub> -C <sub>22</sub> | 1.360 (7)  |
| N <sub>1</sub> -C <sub>a1</sub>  | 1.381 (4) | C <sub>a6</sub> -C <sub>b6</sub> | 1.433 (5) | C <sub>7</sub> -C <sub>8</sub>   | 1.383 (5)  | C <sub>22</sub> -C <sub>23</sub> | 1.360 (7)  |
| N <sub>1</sub> -C <sub>a2</sub>  | 1.374 (4) | C <sub>a6</sub> -C <sub>m3</sub> | 1.387 (5) | C <sub>7</sub> -C <sub>12</sub>  | 1.370 (6)  | C <sub>23</sub> -C <sub>24</sub> | 1.384 (6)  |
| N <sub>2</sub> -C <sub>a3</sub>  | 1.378 (4) | C <sub>a7</sub> -C <sub>b7</sub> | 1.429 (5) | C <sub>8</sub> -C <sub>9</sub>   | 1.386 (6)  | N <sub>5</sub> -C <sub>25</sub>  | 1.337 (5)  |
| N <sub>2</sub> -C <sub>a4</sub>  | 1.386 (4) | C <sub>a7</sub> -C <sub>m3</sub> | 1.394 (5) | C <sub>9</sub> -C <sub>10</sub>  | 1.360 (6)  | N <sub>5</sub> -C <sub>29</sub>  | 1.344 (5)  |
| N <sub>3</sub> -C <sub>a5</sub>  | 1.386 (4) | C <sub>a8</sub> -C <sub>b8</sub> | 1.430 (5) | C <sub>10</sub> -C <sub>11</sub> | 1.361 (7)  | C <sub>25</sub> -C <sub>26</sub> | 1.378 (7)  |
| N <sub>3</sub> -C <sub>a6</sub>  | 1.374 (4) | C <sub>a8</sub> -C <sub>m4</sub> | 1.390 (5) | C <sub>11</sub> -C <sub>12</sub> | 1.394 (6)  | C <sub>26</sub> -C <sub>27</sub> | 1.359 (8)  |
| N <sub>4</sub> -C <sub>a7</sub>  | 1.376 (4) | C <sub>b1</sub> -C <sub>b2</sub> | 1.350 (6) | C <sub>m3</sub> -C <sub>13</sub> | 1.494 (5)  | C <sub>27</sub> -C <sub>28</sub> | 1.346 (8)  |
| N <sub>4</sub> -C <sub>a8</sub>  | 1.369 (4) | C <sub>b3</sub> -C <sub>b4</sub> | 1.336 (5) | C <sub>13</sub> -C <sub>14</sub> | 1.374 (6)  | C <sub>28</sub> -C <sub>29</sub> | 1.369 (6)  |
| C <sub>a1</sub> -C <sub>b1</sub> | 1.425 (5) | C <sub>b5</sub> -C <sub>b6</sub> | 1.336 (5) | C <sub>13</sub> -C <sub>18</sub> | 1.373 (6)  | C <sub>30</sub> -N <sub>6</sub>  | 1.152 (4)  |
| C <sub>a1</sub> -C <sub>m4</sub> | 1.390 (4) | C <sub>b7</sub> -C <sub>b8</sub> | 1.332 (5) | C <sub>14</sub> -C <sub>15</sub> | 1.376 (6)  | N <sub>6</sub> ···O              | 2.948 (7)  |
| C <sub>a2</sub> -C <sub>b2</sub> | 1.444 (5) | C <sub>m1</sub> -C <sub>1</sub>  | 1.477 (5) | C <sub>15</sub> -C <sub>16</sub> | 1.354 (7)  | O···O'                           | 3.043 (14) |
| C <sub>a2</sub> -C <sub>m1</sub> | 1.400 (5) | C <sub>1</sub> -C <sub>2</sub>   | 1.401 (7) | C <sub>16</sub> -C <sub>17</sub> | 1.331 (7)  |                                  |            |

|                                                |             | Angles                                          |             |                                                 |           |                                                 |             |
|------------------------------------------------|-------------|-------------------------------------------------|-------------|-------------------------------------------------|-----------|-------------------------------------------------|-------------|
| N <sub>1</sub> FeN <sub>2</sub>                | 89.44 (11)  | C <sub>m4</sub> C <sub>a1</sub> C <sub>b1</sub> | 124.9 (3)   | C <sub>m4</sub> C <sub>a8</sub> C <sub>b8</sub> | 123.8 (3) | C <sub>a8</sub> C <sub>b8</sub> C <sub>b7</sub> | 107.1 (3)   |
| N <sub>1</sub> FeN <sub>3</sub>                | 178.10 (12) | N <sub>1</sub> C <sub>a2</sub> C <sub>m1</sub>  | 125.5 (3)   | C <sub>a2</sub> C <sub>m1</sub> C <sub>a3</sub> | 122.4 (3) | C <sub>25</sub> N <sub>5</sub> C <sub>29</sub>  | 117.1 (4)   |
| N <sub>1</sub> FeN <sub>4</sub>                | 90.49 (11)  | N <sub>1</sub> C <sub>a2</sub> C <sub>b2</sub>  | 109.8 (3)   | C <sub>a2</sub> C <sub>m1</sub> C <sub>1</sub>  | 118.1 (4) | N <sub>5</sub> C <sub>25</sub> C <sub>26</sub>  | 121.4 (4)   |
| N <sub>1</sub> FeN <sub>5</sub>                | 88.11 (12)  | C <sub>m1</sub> C <sub>a2</sub> C <sub>b2</sub> | 124.3 (3)   | C <sub>a3</sub> C <sub>m1</sub> C <sub>1</sub>  | 119.2 (3) | C <sub>25</sub> C <sub>26</sub> C <sub>27</sub> | 120.2 (5)   |
| N <sub>1</sub> FeC <sub>30</sub>               | 92.33 (14)  | N <sub>2</sub> C <sub>a3</sub> C <sub>m1</sub>  | 125.9 (3)   | C <sub>a4</sub> C <sub>m2</sub> C <sub>a5</sub> | 123.5 (3) | C <sub>26</sub> C <sub>27</sub> C <sub>28</sub> | 119.0 (5)   |
| N <sub>2</sub> FeN <sub>3</sub>                | 90.75 (11)  | N <sub>2</sub> C <sub>a3</sub> C <sub>b3</sub>  | 109.6 (3)   | C <sub>a4</sub> C <sub>m2</sub> C <sub>7</sub>  | 116.6 (3) | C <sub>27</sub> C <sub>28</sub> C <sub>29</sub> | 119.0 (5)   |
| N <sub>2</sub> FeN <sub>4</sub>                | 179.83 (12) | C <sub>m1</sub> C <sub>a3</sub> C <sub>b3</sub> | 124.2 (3)   | C <sub>a5</sub> C <sub>m2</sub> C <sub>7</sub>  | 119.8 (3) | C <sub>28</sub> C <sub>29</sub> N <sub>5</sub>  | 123.2 (4)   |
| N <sub>2</sub> FeN <sub>5</sub>                | 91.62 (12)  | N <sub>2</sub> C <sub>a4</sub> C <sub>m2</sub>  | 126.2 (3)   | C <sub>a5</sub> C <sub>m3</sub> C <sub>a7</sub> | 122.4 (3) | FeN <sub>1</sub> C <sub>a1</sub>                | 125.89 (24) |
| N <sub>2</sub> FeC <sub>30</sub>               | 92.14 (14)  | N <sub>2</sub> C <sub>a4</sub> C <sub>b4</sub>  | 109.1 (3)   | C <sub>a6</sub> C <sub>m3</sub> C <sub>13</sub> | 118.8 (3) | FeN <sub>1</sub> C <sub>a2</sub>                | 127.74 (25) |
| N <sub>3</sub> FeN <sub>4</sub>                | 89.31 (11)  | C <sub>m2</sub> C <sub>a4</sub> C <sub>b4</sub> | 124.7 (3)   | C <sub>a7</sub> C <sub>m3</sub> C <sub>13</sub> | 118.7 (3) | FeN <sub>2</sub> C <sub>a3</sub>                | 127.55 (24) |
| N <sub>3</sub> FeN <sub>5</sub>                | 90.00 (12)  | N <sub>3</sub> C <sub>a5</sub> C <sub>m2</sub>  | 124.8 (3)   | C <sub>a1</sub> C <sub>m4</sub> C <sub>a8</sub> | 123.2 (3) | FeN <sub>2</sub> C <sub>a4</sub>                | 126.21 (23) |
| N <sub>3</sub> FeC <sub>30</sub>               | 89.55 (14)  | N <sub>3</sub> C <sub>a5</sub> C <sub>b5</sub>  | 109.57 (29) | C <sub>a1</sub> C <sub>m4</sub> C <sub>19</sub> | 118.7 (3) | FeN <sub>3</sub> C <sub>a5</sub>                | 126.90 (22) |
| N <sub>4</sub> FeN <sub>5</sub>                | 88.22 (12)  | C <sub>m2</sub> C <sub>a5</sub> C <sub>b5</sub> | 125.2 (3)   | C <sub>a8</sub> C <sub>m4</sub> C <sub>19</sub> | 118.2 (3) | FeN <sub>3</sub> C <sub>a6</sub>                | 127.44 (23) |
| N <sub>4</sub> FeC <sub>30</sub>               | 88.02 (14)  | N <sub>3</sub> C <sub>a6</sub> C <sub>m3</sub>  | 125.2 (3)   | C <sub>a1</sub> C <sub>b1</sub> C <sub>b2</sub> | 107.7 (3) | FeN <sub>4</sub> C <sub>a7</sub>                | 127.15 (24) |
| N <sub>5</sub> FeC <sub>30</sub>               | 176.22 (14) | N <sub>3</sub> C <sub>a6</sub> C <sub>b6</sub>  | 109.6 (3)   | C <sub>a2</sub> C <sub>b2</sub> C <sub>b1</sub> | 106.7 (3) | FeN <sub>4</sub> C <sub>a8</sub>                | 126.95 (23) |
| C <sub>a1</sub> N <sub>1</sub> C <sub>a2</sub> | 105.83 (29) | C <sub>m3</sub> C <sub>a6</sub> C <sub>b6</sub> | 125.1 (3)   | C <sub>a3</sub> C <sub>b3</sub> C <sub>b4</sub> | 107.4 (3) | FeN <sub>5</sub> C <sub>25</sub>                | 122.02 (28) |
| C <sub>a3</sub> N <sub>2</sub> C <sub>a4</sub> | 106.00 (28) | N <sub>4</sub> C <sub>a7</sub> C <sub>m3</sub>  | 125.0 (3)   | C <sub>a4</sub> C <sub>b4</sub> C <sub>b3</sub> | 107.8 (3) | FeN <sub>5</sub> C <sub>29</sub>                | 120.51 (27) |
| C <sub>a5</sub> N <sub>3</sub> C <sub>a6</sub> | 105.63 (28) | N <sub>4</sub> C <sub>a7</sub> C <sub>b7</sub>  | 109.5 (3)   | C <sub>a5</sub> C <sub>b5</sub> C <sub>b6</sub> | 107.2 (3) | FeC <sub>30</sub> N <sub>6</sub>                | 176.8 (3)   |
| C <sub>a7</sub> N <sub>4</sub> C <sub>a8</sub> | 105.65 (28) | C <sub>m3</sub> C <sub>a7</sub> C <sub>b7</sub> | 125.0 (3)   | C <sub>a6</sub> C <sub>b6</sub> C <sub>b5</sub> | 107.8 (3) | C <sub>30</sub> N <sub>6</sub> O                | 168.5 (3)   |
| N <sub>1</sub> C <sub>a1</sub> C <sub>m4</sub> | 125.1 (3)   | N <sub>4</sub> C <sub>a8</sub> C <sub>m4</sub>  | 125.9 (3)   | C <sub>a7</sub> C <sub>b7</sub> C <sub>b8</sub> | 107.6 (3) | O'ON <sub>6</sub>                               | 128.6 (4)   |
| N <sub>1</sub> C <sub>a1</sub> C <sub>b1</sub> | 109.9 (3)   | N <sub>4</sub> C <sub>a8</sub> C <sub>b8</sub>  | 110.0 (3)   |                                                 |           |                                                 |             |

<sup>a</sup> The primed atom is related to the tabulated atomic coordinates by the transformation  $-x, 1.0 - y, -1.0 - z$ . The estimated standard deviations of the least significant digits are given in parentheses.

other low-spin iron(III) complexes: 2.082 (3) Å in Fe(TPP)(NCS)(py),<sup>21</sup> 2.089 (6) Å in Fe(TPP)(N<sub>3</sub>)(py),<sup>8</sup> and the 2.031 (2) Å value in the low-spin form of [Fe(OEP)(3-Cl(py))<sub>2</sub>]<sup>+</sup>.<sup>22</sup> All of these distances are considerably smaller than the 2.316 (5) Å value for Fe-N<sub>py</sub> in the high-spin form<sup>22</sup> of [Fe(OEP)(3-Cl(py))<sub>2</sub>]<sup>+</sup>.

The Fe-C(CN) bond distance of 1.908 (4) Å is in the normal range of Fe-C bond distances observed for a number of simple cyanoiron(III) complexes.<sup>23</sup> This is notable since the Fe-C bond distances in K[Fe(TPP)(CN)<sub>2</sub>] were found<sup>6</sup> to be exceptionally long, 1.975 (2) Å. These long Fe-C distances in K[Fe(TPP)(CN)<sub>2</sub>] were attributed to diminished  $\pi$  bonding of the axial CN<sup>-</sup> ligands as a result of competition between the porphinato ligand and the two axial cyanide ligands for iron  $\pi$  density.<sup>24</sup> With the weaker  $\pi$ -bonding ligand pyridine trans to CN<sup>-</sup>, the cyanide ion is apparently able to form a normal Fe-C(CN) bond. Other features of the axial-ligand geometry are normal. The angle between the two axial-ligand atoms is nearly linear with N<sub>3</sub>FeC<sub>30</sub> = 176.22 (14)°. The Fe-C<sub>CN</sub> vector is tipped by ~3.2° from the heme normal, and the Fe-C-N angle is 176.8 (3)°.

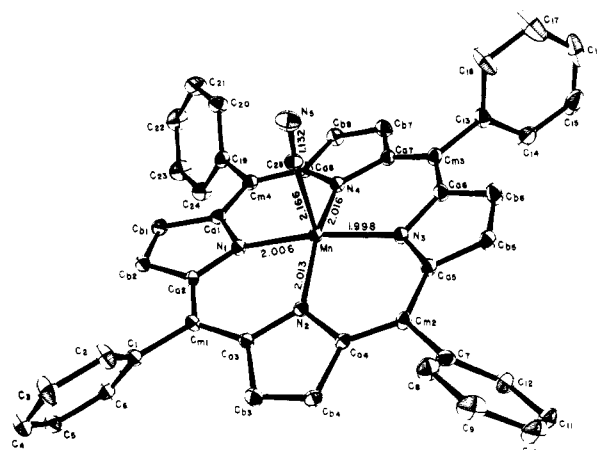


Figure 5. Computer-drawn model, in perspective, of the [Mn(TPP)(CN)] molecule showing the atom labels and bond distances in the coordination group.

**Structure of [Mn(TPP)(CN)].** A computer-drawn model of the molecule is given in Figure 5. This figure illustrates the labeling scheme used for the atoms and describes the bond distances in the coordination group. Values for individual bond distances and angles in the molecule are listed in Table VII. Figure 6 gives the averaged values for bond parameters in the core of [Mn(TPP)(CN)]. The average value for the C<sub>m</sub>-C<sub>p</sub> bonds is 1.502 (6) Å, and the C-C distance in the peripheral phenyl groups is 1.372 (18) Å.

(21) Scheidt, W. R.; Lee, Y. J.; Geiger, D. K.; Taylor, K.; Hatano, K. *J. Am. Chem. Soc.* **1982**, *104*, 3367-3374.

(22) Scheidt, W. R.; Haller, K. J.; Geiger, D. K. *J. Am. Chem. Soc.* **1982**, *104*, 495-499.

(23) Typical Fe-C distances are 1.91-1.93 Å. See Table V of ref. 6.

(24) A similar effect has been observed in a bis(isocyanide)iron(II) porphyrinate: Jameson, G. B.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 1200-1208.

Table VII. Selected Interatomic Distances (Å) and Angles (deg) for Mn(TPP)(CN)·CHCl<sub>3</sub><sup>a</sup>

|                                                 |             | Distances                                       |           |                                                 |            |                                                 |            |
|-------------------------------------------------|-------------|-------------------------------------------------|-----------|-------------------------------------------------|------------|-------------------------------------------------|------------|
| Mn-N <sub>1</sub>                               | 2.006 (4)   | C <sub>a3</sub> -C <sub>b3</sub>                | 1.424 (6) | C <sub>1</sub> -C <sub>6</sub>                  | 1.392 (7)  | C <sub>16</sub> -C <sub>17</sub>                | 1.374 (12) |
| Mn-N <sub>2</sub>                               | 2.013 (4)   | C <sub>a3</sub> -C <sub>m1</sub>                | 1.392 (6) | C <sub>2</sub> -C <sub>3</sub>                  | 1.379 (8)  | C <sub>17</sub> -C <sub>18</sub>                | 1.369 (9)  |
| Mn-N <sub>3</sub>                               | 1.998 (4)   | C <sub>a4</sub> -C <sub>b4</sub>                | 1.422 (6) | C <sub>3</sub> -C <sub>4</sub>                  | 1.370 (8)  | C <sub>m4</sub> -C <sub>19</sub>                | 1.507 (6)  |
| Mn-N <sub>4</sub>                               | 2.016 (4)   | C <sub>a4</sub> -C <sub>m2</sub>                | 1.385 (6) | C <sub>4</sub> -C <sub>5</sub>                  | 1.370 (8)  | C <sub>19</sub> -C <sub>20</sub>                | 1.395 (7)  |
| Mn-C <sub>25</sub>                              | 2.166 (6)   | C <sub>a5</sub> -C <sub>b5</sub>                | 1.419 (7) | C <sub>5</sub> -C <sub>6</sub>                  | 1.377 (7)  | C <sub>19</sub> -C <sub>24</sub>                | 1.376 (7)  |
| N <sub>1</sub> -C <sub>a1</sub>                 | 1.377 (5)   | C <sub>a5</sub> -C <sub>m2</sub>                | 1.390 (6) | C <sub>m2</sub> -C <sub>7</sub>                 | 1.505 (6)  | C <sub>20</sub> -C <sub>21</sub>                | 1.387 (7)  |
| N <sub>1</sub> -C <sub>a2</sub>                 | 1.379 (6)   | C <sub>a6</sub> -C <sub>b6</sub>                | 1.426 (6) | C <sub>7</sub> -C <sub>8</sub>                  | 1.379 (7)  | C <sub>21</sub> -C <sub>22</sub>                | 1.367 (9)  |
| N <sub>2</sub> -C <sub>a3</sub>                 | 1.379 (6)   | C <sub>a6</sub> -C <sub>m3</sub>                | 1.390 (6) | C <sub>7</sub> -C <sub>12</sub>                 | 1.387 (7)  | C <sub>22</sub> -C <sub>23</sub>                | 1.357 (9)  |
| N <sub>2</sub> -C <sub>a4</sub>                 | 1.391 (5)   | C <sub>a7</sub> -C <sub>b7</sub>                | 1.437 (6) | C <sub>8</sub> -C <sub>9</sub>                  | 1.391 (7)  | C <sub>23</sub> -C <sub>24</sub>                | 1.379 (7)  |
| N <sub>3</sub> -C <sub>a5</sub>                 | 1.388 (6)   | C <sub>a7</sub> -C <sub>m3</sub>                | 1.388 (6) | C <sub>9</sub> -C <sub>10</sub>                 | 1.368 (9)  | C <sub>26</sub> -Cl <sub>1</sub>                | 1.732 (8)  |
| N <sub>3</sub> -C <sub>a6</sub>                 | 1.382 (6)   | C <sub>a8</sub> -C <sub>b8</sub>                | 1.426 (7) | C <sub>10</sub> -C <sub>11</sub>                | 1.352 (9)  | C <sub>26</sub> -Cl <sub>2</sub>                | 1.730 (9)  |
| N <sub>4</sub> -C <sub>a7</sub>                 | 1.386 (6)   | C <sub>a8</sub> -C <sub>m4</sub>                | 1.391 (6) | C <sub>11</sub> -C <sub>12</sub>                | 1.377 (7)  | C <sub>26</sub> -Cl <sub>3</sub>                | 1.833 (9)  |
| N <sub>4</sub> -C <sub>a8</sub>                 | 1.376 (6)   | C <sub>b1</sub> -C <sub>b2</sub>                | 1.338 (7) | C <sub>m3</sub> -C <sub>13</sub>                | 1.494 (7)  | C <sub>26</sub> -Cl <sub>4</sub>                | 1.641 (10) |
| N <sub>5</sub> -C <sub>25</sub>                 | 1.132 (6)   | C <sub>b3</sub> -C <sub>b4</sub>                | 1.338 (7) | C <sub>13</sub> -C <sub>14</sub>                | 1.359 (8)  | C <sub>26</sub> -Cl <sub>5</sub>                | 1.739 (14) |
| C <sub>a1</sub> -C <sub>b1</sub>                | 1.435 (7)   | C <sub>b5</sub> -C <sub>b6</sub>                | 1.337 (7) | C <sub>13</sub> -C <sub>18</sub>                | 1.361 (8)  | C <sub>26</sub> -Cl <sub>6</sub>                | 1.664 (14) |
| C <sub>a1</sub> -C <sub>m4</sub>                | 1.407 (7)   | C <sub>b7</sub> -C <sub>b8</sub>                | 1.338 (7) | C <sub>14</sub> -C <sub>15</sub>                | 1.390 (10) | C <sub>26</sub> -Cl <sub>7</sub>                | 1.777 (14) |
| C <sub>a2</sub> -C <sub>b2</sub>                | 1.430 (6)   | C <sub>m1</sub> -C <sub>1</sub>                 | 1.504 (6) | C <sub>15</sub> -C <sub>16</sub>                | 1.306 (12) | C <sub>26</sub> -Cl <sub>8</sub>                | 1.781 (12) |
| C <sub>a2</sub> -C <sub>m1</sub>                | 1.383 (6)   | C <sub>1</sub> -C <sub>2</sub>                  | 1.377 (7) |                                                 |            |                                                 |            |
|                                                 |             | Angles                                          |           |                                                 |            |                                                 |            |
| N <sub>1</sub> MnN <sub>2</sub>                 | 89.29 (15)  | C <sub>m1</sub> C <sub>a2</sub> C <sub>b2</sub> | 124.7 (4) | C <sub>a2</sub> C <sub>m1</sub> C <sub>a3</sub> | 123.6 (4)  | C <sub>a7</sub> C <sub>b7</sub> C <sub>b8</sub> | 106.5 (5)  |
| N <sub>1</sub> MnN <sub>3</sub>                 | 168.20 (17) | N <sub>2</sub> C <sub>a3</sub> C <sub>m1</sub>  | 125.6 (4) | C <sub>a2</sub> C <sub>m1</sub> C <sub>1</sub>  | 119.1 (4)  | C <sub>a8</sub> C <sub>b8</sub> C <sub>b7</sub> | 108.7 (4)  |
| N <sub>1</sub> MnN <sub>4</sub>                 | 88.95 (15)  | N <sub>2</sub> C <sub>a3</sub> C <sub>b3</sub>  | 109.5 (4) | C <sub>a3</sub> C <sub>m1</sub> C <sub>1</sub>  | 117.2 (4)  | MnN <sub>1</sub> C <sub>a1</sub>                | 126.8 (3)  |
| N <sub>1</sub> MnN <sub>5</sub>                 | 100.33 (18) | C <sub>m1</sub> C <sub>a3</sub> C <sub>b3</sub> | 125.0 (4) | C <sub>a4</sub> C <sub>m2</sub> C <sub>a5</sub> | 124.0 (4)  | MnN <sub>1</sub> C <sub>a2</sub>                | 125.1 (3)  |
| N <sub>2</sub> MnN <sub>3</sub>                 | 88.53 (15)  | N <sub>2</sub> C <sub>a4</sub> C <sub>m2</sub>  | 124.7 (4) | C <sub>a4</sub> C <sub>m2</sub> C <sub>7</sub>  | 119.0 (4)  | MnN <sub>2</sub> C <sub>a3</sub>                | 126.4 (3)  |
| N <sub>2</sub> MnN <sub>4</sub>                 | 163.22 (16) | N <sub>2</sub> C <sub>a4</sub> C <sub>b4</sub>  | 109.2 (4) | C <sub>a5</sub> C <sub>m2</sub> C <sub>7</sub>  | 116.9 (4)  | MnN <sub>2</sub> C <sub>a4</sub>                | 128.0 (3)  |
| N <sub>2</sub> MnN <sub>5</sub>                 | 99.65 (17)  | C <sub>m2</sub> C <sub>a4</sub> C <sub>b4</sub> | 125.9 (4) | C <sub>a6</sub> C <sub>m3</sub> C <sub>a7</sub> | 123.9 (5)  | MnN <sub>2</sub> C <sub>a5</sub>                | 127.2 (3)  |
| N <sub>3</sub> MnN <sub>4</sub>                 | 89.79 (16)  | N <sub>3</sub> C <sub>a5</sub> C <sub>m2</sub>  | 124.7 (4) | C <sub>a6</sub> C <sub>m3</sub> C <sub>13</sub> | 116.3 (4)  | MnN <sub>3</sub> C <sub>a6</sub>                | 124.8 (3)  |
| N <sub>3</sub> MnN <sub>5</sub>                 | 91.47 (18)  | N <sub>3</sub> C <sub>a5</sub> C <sub>b5</sub>  | 109.2 (4) | C <sub>a7</sub> C <sub>m3</sub> C <sub>13</sub> | 119.8 (4)  | MnN <sub>3</sub> C <sub>a7</sub>                | 126.1 (3)  |
| N <sub>4</sub> MnN <sub>5</sub>                 | 97.09 (18)  | C <sub>m2</sub> C <sub>a5</sub> C <sub>b5</sub> | 126.0 (4) | C <sub>a1</sub> C <sub>m4</sub> C <sub>a8</sub> | 123.0 (4)  | MnN <sub>4</sub> C <sub>a8</sub>                | 127.9 (3)  |
| C <sub>a1</sub> N <sub>1</sub> C <sub>a2</sub>  | 106.0 (4)   | N <sub>3</sub> C <sub>a6</sub> C <sub>m3</sub>  | 125.8 (4) | C <sub>a1</sub> C <sub>m4</sub> C <sub>19</sub> | 117.9 (4)  | MnN <sub>4</sub> N <sub>5</sub>                 | 172.1 (5)  |
| C <sub>a3</sub> N <sub>2</sub> C <sub>a4</sub>  | 105.6 (4)   | N <sub>3</sub> C <sub>a6</sub> C <sub>b6</sub>  | 109.7 (4) | C <sub>a8</sub> C <sub>m4</sub> C <sub>19</sub> | 119.1 (4)  | Cl <sub>1</sub> C <sub>26</sub> Cl <sub>2</sub> | 114.1 (5)  |
| C <sub>a5</sub> N <sub>3</sub> C <sub>a6</sub>  | 105.5 (4)   | C <sub>m3</sub> C <sub>a6</sub> C <sub>b6</sub> | 124.4 (5) | C <sub>a1</sub> C <sub>b1</sub> C <sub>b2</sub> | 107.3 (4)  | Cl <sub>1</sub> C <sub>26</sub> Cl <sub>3</sub> | 97.4 (5)   |
| C <sub>a7</sub> N <sub>4</sub> C <sub>a8</sub>  | 105.9 (4)   | N <sub>4</sub> C <sub>a7</sub> C <sub>m3</sub>  | 125.2 (4) | C <sub>a2</sub> C <sub>b2</sub> C <sub>b1</sub> | 107.8 (4)  | Cl <sub>2</sub> C <sub>26</sub> Cl <sub>3</sub> | 108.5 (5)  |
| N <sub>1</sub> C <sub>a1</sub> C <sub>m4</sub>  | 125.9 (4)   | N <sub>4</sub> C <sub>a7</sub> C <sub>b7</sub>  | 109.6 (4) | C <sub>a3</sub> C <sub>b2</sub> C <sub>b1</sub> | 107.8 (4)  | Cl <sub>4</sub> C <sub>26</sub> Cl <sub>5</sub> | 107.6 (7)  |
| N <sub>1</sub> C <sub>a1</sub> C <sub>b1</sub>  | 109.5 (4)   | C <sub>m3</sub> C <sub>a7</sub> C <sub>b7</sub> | 125.0 (5) | C <sub>a4</sub> C <sub>b2</sub> C <sub>b1</sub> | 107.7 (4)  | Cl <sub>4</sub> C <sub>26</sub> Cl <sub>6</sub> | 109.5 (7)  |
| C <sub>m4</sub> C <sub>a1</sub> C <sub>b1</sub> | 124.6 (4)   | N <sub>4</sub> C <sub>a8</sub> C <sub>m4</sub>  | 125.6 (4) | C <sub>a5</sub> C <sub>b2</sub> C <sub>b1</sub> | 108.3 (4)  | Cl <sub>5</sub> C <sub>26</sub> Cl <sub>6</sub> | 114.5 (8)  |
| N <sub>1</sub> C <sub>a2</sub> C <sub>m1</sub>  | 125.7 (4)   | N <sub>4</sub> C <sub>a8</sub> C <sub>b8</sub>  | 109.1 (4) | C <sub>a6</sub> C <sub>b2</sub> C <sub>b1</sub> | 107.2 (5)  | Cl <sub>7</sub> C <sub>26</sub> C <sub>8</sub>  | 105.1 (7)  |
| N <sub>1</sub> C <sub>a2</sub> C <sub>b2</sub>  | 109.4 (4)   | C <sub>m4</sub> C <sub>a8</sub> C <sub>b8</sub> | 125.0 (4) |                                                 |            |                                                 |            |

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

Figure 6 also illustrates the conformation of the porphinato core and displays the displacement of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core. The core in [Mn(TPP)(CN)] is again quite ruffled. The dihedral angles between the peripheral phenyl groups and the mean plane of the core are smaller than generally observed with values of 57.1, 50.8, 80.4, and 54.4°.

The structural features of much of the coordination group of [Mn(TPP)(CN)] are typical of those previously observed for five-coordinate high-spin manganese(III) porphyrates. The 0.25-Å displacement of the Mn(III) atom from the porphinato plane is comparable to the 0.23-Å displacement seen in Mn(TPP)(N<sub>3</sub>)-C<sub>6</sub>H<sub>6</sub>,<sup>25</sup> the 0.27-Å displacement in Mn(TPP)(Cl)-CH<sub>3</sub>COCH<sub>3</sub>,<sup>26</sup> and the 0.26 Å displacement in Mn(TPP)(Cl)-CHCl<sub>3</sub>.<sup>27</sup> Similarly, the 2.008 (8) Å average Mn-N<sub>p</sub> bond distance is comparable to the values observed for the three derivatives above: 2.005 (3), 2.008 (15), and 2.01 Å, respectively.

There are other features of the axial-ligand geometry that command interest. The Mn-C(CN) bond distance of 2.166 (6) Å is substantially longer than the distances of 1.976–2.025 Å observed<sup>28</sup> in hexacyanomanganese(III) salts. This difference in the Mn-C<sub>CN</sub> bond distance can be attributed to a spin-state effect;<sup>29</sup> [Mn(TPP)(CN)] is a high-spin complex

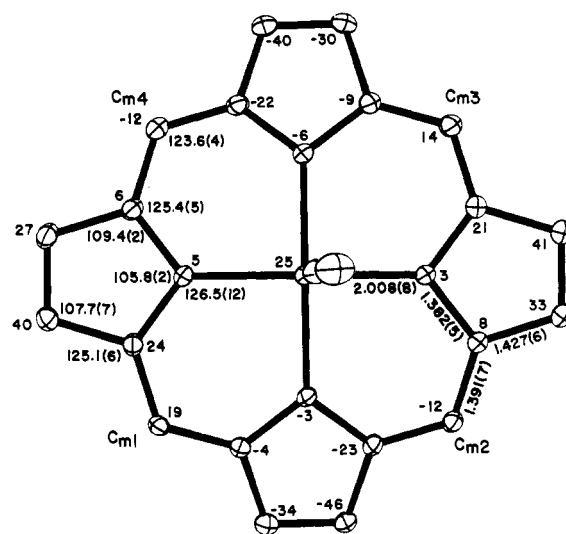


Figure 6. Diagram of the porphinato core in [Mn(TPP)(CN)]. The core has the same orientation as that shown in Figure 5 and displays the same information as given in Figure 4. Positive values of the displacements are toward the cyano ligand. The drawing also illustrates the distortion of the axial ligand group from an ideal linear arrangement. The normal to the porphinato plane is perpendicular to the plane of the paper.

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(d<sub>z<sup>2</sup></sub> populated) while the hexacyano species are low-spin complexes. Interestingly, this feature is in distinct contrast to that displayed by the analogous high-spin five-coordinate iron(III) porphyrates. In the high-spin five-coordinate iron species (but not the six-coordinate species), the axial-ligand-

iron bond distance is as short as those of low-spin complexes.<sup>30</sup>

Deviations from ideal linear geometry of the Mn-C-N group, illustrated in Figure 6, are of interest in view of the nonideality in the Fe-C-N group in cyanoheмоproteins.<sup>31</sup> The hemoprotein derivatives have apparent nonlinear Fe-C-N angles. Protein crystallographic studies show that the nitrogen atom is clearly displaced off the heme normal, but the poorly defined carbon atom position does not allow a clean distinction between a bent FeCN unit or a linear FeCN group tilted with respect to the N<sub>4</sub> plane. These nonideal geometries of the coordinated cyano ligand are presumed to result from constraints of the size and shape of the ligand-binding pocket. Similar deviations from ideality are seen in (carbon monoxide)hemoproteins.<sup>32</sup>

The Mn-C-N group in [Mn(TPP)(CN)] is distorted from ideal geometry by both bending and tilting. The Mn-C-N angle is 172.1 (5)°, but this bent group is further tilted off the normal to the porphyrin plane. The Mn-C<sub>25</sub> vector is tilted by 5.75° from a vector perpendicular to the porphyrin plane. Thus the C<sub>25</sub> atom is displaced 0.22 Å from the normal and N<sub>5</sub> is displaced by 0.47 Å. (This displacement would be 0.33 Å if the MnCN group was linear.)<sup>33</sup> However, the manganese

atom is located directly above the center of the porphyrin hole. The distortion apparently results from packing interactions involving the nitrogen atom but not the carbon atom of cyanide. The most significant contact is between N<sub>5</sub> and the carbon atom of the chloroform solvate at 3.01 Å. The fact that both bending and tilting of the MnCN group are observed attests to the stiffness of the Mn-C bond. In [Mn(TPP)(C-N)], where the Mn-C bond is unusually long and π bonding presumably somewhat weakened, the bending force constant apparently remains high. The bending force constant must be larger for a Fe-C<sub>CN</sub> bond. This suggests that a bending distortion in the FeCN group will be difficult and that the distortion in the FeCN group of hemoproteins must predominantly result from a tilting mechanism as suggested by Deatherage et al.<sup>31a</sup>

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**Registry No.** [Fe(TPP)(CN)(py)]·H<sub>2</sub>O, 85135-21-3; [Mn(TPP)(CN)]·CHCl<sub>3</sub>, 85135-22-4; Fe(TPP)(CN)(1-MeIm), 85135-23-5; K[Fe(TPP)(CN)<sub>2</sub>], 73946-20-0; Mn(TPP)(OH), 85136-24-6.

**Supplementary Material Available:** Table III, anisotropic temperature factors for [Fe(TPP)(CN)(py)], Table V, anisotropic temperature factors for [Mn(TPP)(CN)], Table VIII, idealized hydrogen atom positions for [Fe(TPP)(CN)(py)], Table IX, idealized hydrogen atom positions for [Mn(TPP)(CN)], and listings of observed and calculated structure amplitudes (×10) for [Fe(TPP)(CN)(py)] and [Mn(TPP)(CN)] (57 pages). Ordering information is given on any current masthead page.

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## Crystal and Molecular Structure of the Bis(pyridine) Adduct of a Dinuclear Rhodium(II) Complex with Trifluoroacetamido Bridging Ligands

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Trifluoroacetamide reacts with Rh<sub>2</sub>(OOCCH<sub>3</sub>)<sub>4</sub> to produce the amidato-bridged complex Rh<sub>2</sub>(ONHCCF<sub>3</sub>)<sub>4</sub>. The product is a mixture of four complexes that can be separated by liquid chromatography, with the distribution of complexes in the mixture being approximately 4% (band 1), 94% (band 2), 2% (band 3), and less than 1% (band 4). The complex in band 4 was not collected in this study because of the small amount present in the mixture. The molecular weights of the complexes in bands 1, 2, and 3 were determined by mass spectrometry and were all found to be the same, indicating they are three of the four possible geometric isomers. The visible spectra of all three isomers are similar, showing two bands shifted to higher energy relative to those of the corresponding dirhodium(II) carboxylate adducts. The <sup>19</sup>F NMR spectrum of the complex in band 1 shows three CF<sub>3</sub> resonances, suggesting this complex is the isomer with three N atoms and one O atom bonded to one rhodium and the reverse combination bonded to the other rhodium. The crystal structure of the bis(pyridine) adduct of the complex from band 2, Rh<sub>2</sub>(ONHCCF<sub>3</sub>)<sub>4</sub>(py)<sub>2</sub>, has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pnma* with four formula weights in the unit cell of dimensions *a* = 15.523 (4) Å, *b* = 16.613 (6) Å, and *c* = 10.407 (6) Å. The structure was solved by the Patterson method and refined to a final *R* value of 7.2%. This complex has two N and two O atoms on each rhodium cis to their own kind. A Rh-Rh bond distance 2.472 (3) Å was found, which is much longer than that in the corresponding carboxylato-bridged complex. The pyridine planes are coplanar, set 45° from the bridging ligand planes and bent slightly away from the NH groups. The average Rh-N<sub>py</sub> distance of 2.29 Å is also significantly longer than that reported for the tetraacetato-bridged complex.

### Introduction

The structure and chemical reactivity of dinuclear rhodium(II) complexes have been investigated extensively in recent years. Interest in these complexes stems from earlier controversy regarding the nature of the metal-metal interaction<sup>1-4</sup>

and the interpretation of σ and π components of the rhodium-axial ligand bond.<sup>5-11</sup> The questionable nature of the

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