

# Stereochemistry of Low-Spin Cobalt Porphyrins.

## IV. Molecular Stereochemistry of (1-Methylimidazole)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II)

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**Abstract:** (1-Methylimidazole)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II) crystallizes in the monoclinic system as the benzene solvate, space group  $P2_1/c$ . The unit cell has  $a = 10.633$  (7) Å,  $b = 18.827$  (12) Å,  $c = 21.750$  (6) Å, and  $\beta = 100.37$  (1)° and contains four molecules. The calculated and experimental densities are 1.290 and 1.27 g/cm<sup>3</sup>, respectively, at  $20 \pm 1^\circ$ . Measurement of diffracted intensities employed  $\omega$  scans and  $\theta$ - $2\theta$  scans with graphite-monochromated Mo  $K\alpha$  radiation on a four-circle diffractometer. All independent reflections for  $(\sin \theta/\lambda) \leq 0.602$  Å<sup>-1</sup> were scanned; 4065 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom technique and least-squares refinement of the 402 structural parameters. The final conventional and weighted discrepancy factors were 0.073 and 0.070, respectively. The square-pyramidal CoN<sub>5</sub> coordination group has equatorial bond lengths of 1.977 (3) Å; the axial Co-N<sub>b</sub> bond is 2.157 (3) Å. The cobalt is displaced 0.14 Å from the mean skeletal plane.

The genesis of our interest in the stereochemistry of the low-spin cobalt porphyrins has been adequately stressed in our earlier reports on the molecular stereochemistry of diamagnetic nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt<sup>1</sup> and paramagnetic ( $S = 1/2$ ) bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II).<sup>2</sup> We report herein the molecular stereochemistry of a low-spin ( $S = 1/2$ ) five-coordinate cobalt porphyrin, (1-methylimidazole)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II), written as MImCoTPP.

### Experimental Section

Crystals of MImCoTPP were obtained as the benzene solvate by the slow evaporation of benzene solutions containing 1.8–2.2 equiv of 1-methylimidazole per equivalent of CoTPP. Two crystalline modifications were obtained: a monoclinic form and a triclinic form. Preliminary X-ray photographic study of the triclinic form established a two-molecule unit cell. Approximate lattice constants are as follows:  $a = 13.25$ ,  $b = 17.86$ ,  $c = 9.67$  Å;  $\alpha = 90.21$ ,  $\beta = 97.68$ ,  $\gamma = 105.78^\circ$ ;  $V = 2177$  Å<sup>3</sup>. The triclinic form was not characterized further. Preliminary study of the monoclinic form established a four-molecule unit cell; the systematic absences suggest the unique choice of  $P2_1/c$  as the space group. Lattice constants,  $a = 10.633$  (7) Å,  $b = 18.827$  (12) Å,  $c = 21.750$  (6) Å, and  $\beta = 100.37$  (1)°, came from a least-squares refinement that utilized the setting angles of 26 reflections, each collected at  $\pm 2\theta$ . These constants led to a calculated density at  $20 \pm 1^\circ$  of 1.290 g/cm<sup>3</sup> for the crystal. The experimental density, measured by flotation, was 1.27 g/cm<sup>3</sup>.

Intensity data were measured on a Syntex P1 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation; the sample specimen had dimensions of  $0.25 \times 0.30 \times 0.35$  mm. The data were collected in concentric shells of increasing  $(\sin \theta)/\lambda$ , each such shell comprising one-tenth of the volume of the theoretical Cu  $K\alpha$  limiting sphere. Data in the first five such shells were collected using the "wandering"  $\omega$ -scan technique, the remainder with the  $\theta$ - $2\theta$  scan technique, and two separate scale factors were employed during the subsequent refinement of structure. The  $\omega$ -scan was performed in  $0.035^\circ$  increments of  $\omega$  and extended  $\pm 0.175^\circ$  from the calculated peak position. Background counts were taken at  $\pm 0.5^\circ$   $\omega$  displacement from the peak center for a duration of one-half the time required for the scan.

The remaining data, for which  $42.9^\circ < 2\theta < 50.7^\circ$ , were collected by  $\theta$ - $2\theta$  scanning. The range of each scan consisted of a base width of  $1.4^\circ$  at  $2\theta = 0$  and an increment to allow for spectral dis-

persion; background counts were taken at the extremes of the scan for a duration of 0.4 times the time required for the scan itself. Four standard reflections that were well distributed in reciprocal space were used for periodic checking (every 50 reflections) on the alignment and possible deterioration of the crystal; a decrease of  $\sim 10\%$  in the intensity of the standard reflections was observed during the course of the measurements. All independent data having  $(\sin \theta)/\lambda < 0.602$  Å<sup>-1</sup> were measured.

The net intensities were reduced directly to a set of relative squared amplitudes,  $|F_o|^2$ , by application of the standard Lorentz and polarization factor ( $Lp$ ) and a linear correction for decomposition. Standard deviations were calculated as described previously.<sup>2</sup> All data having  $F_o < 3\sigma(F_o)$  were taken to be unobserved, leaving 4065 independent observed data from  $\sim 7800$  independent observations. Only the observed data were used for the determination and refinement of structure. With the cited dimensions of the crystal and a linear absorption coefficient of only 0.47 mm<sup>-1</sup> for Mo  $K\alpha$  radiation, the maximum error in any intensity occasioned by the neglect of absorption corrections was seen to be 3%.

The structure was solved by the heavy-atom method.<sup>3</sup> The structure was refined by block-diagonal least-squares techniques.<sup>4</sup> Converging cycles of least-squares refinement of the 402 parameters describing the model with anisotropic thermal parameters for the porphinato core and the coordinated ligand and isotropic thermal parameters for the four phenyl groups and the benzene solvate led to a conventional  $R$  of 0.073 and a weighted  $R$  of 0.070 for the data-parameter ratio of 10.1.<sup>5</sup> The estimated standard deviation of an observation of unit weight was 1.34. A final difference Fourier was judged to be significantly free of features with no peaks greater than  $0.25$  e Å<sup>-3</sup>.

Atomic coordinates and the associated anisotropic and isotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II.

### Discussion

Figure 1 is a model<sup>6</sup> in perspective of the MImCoTPP

(3) The program ALFF was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL," IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

(4) The program REFINE written by J. J. Park at Cornell University was used. The function minimized was  $\sum w(|F_o| - s|F_c|)^2$  where  $w$  is the weight ( $= 1/\sigma^2$ ) and  $s$  is the scale factor. Atomic form factors were taken from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factor of the cobalt atom from D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(5) See paragraph at end of paper regarding supplementary material.

(6) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(1) W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8281 (1973).

(2) W. R. Scheidt, *J. Amer. Chem. Soc.*, **95**, 84 (1973).

**Table I.** Atomic Coordinates and Isotropic Thermal Parameters in the Unit Cell

Atom type	Coordinates <sup>a</sup>			$B_i^b$ Å <sup>2</sup>
	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z	
Co <sup>c</sup>	1851 (1)	2056 (0)	3924 (0)	3.05
N <sub>1</sub>	79 (4)	2061 (2)	3462 (2)	3.2
N <sub>2</sub>	2207 (4)	1194 (2)	3464 (2)	3.2
N <sub>3</sub>	3554 (4)	1972 (2)	4471 (2)	3.1
N <sub>4</sub>	1418 (4)	2834 (2)	4458 (2)	3.1
C <sub>a1</sub>	-887 (5)	2535 (3)	3521 (3)	3.5
C <sub>a2</sub>	-438 (5)	1634 (5)	2952 (3)	3.4
C <sub>a3</sub>	1432 (5)	877 (3)	2962 (3)	3.5
C <sub>a4</sub>	3346 (5)	825 (3)	3529 (3)	3.4
C <sub>a5</sub>	4518 (5)	1503 (3)	4405 (3)	3.3
C <sub>a6</sub>	4030 (5)	2353 (3)	5010 (2)	3.2
C <sub>a7</sub>	2172 (5)	3123 (3)	4988 (2)	3.2
C <sub>a8</sub>	296 (5)	3230 (3)	4379 (3)	3.1
C <sub>m1</sub>	193 (5)	1085 (3)	2711 (2)	3.3
C <sub>m2</sub>	4436 (5)	967 (3)	3962 (3)	3.2
C <sub>m3</sub>	3382 (5)	2888 (3)	5262 (2)	3.3
C <sub>m4</sub>	-789 (5)	3088 (3)	3945 (2)	3.1
N <sub>5</sub>	2424 (4)	2727 (2)	3220 (2)	3.4
N <sub>6</sub>	3597 (5)	3318 (3)	2647 (2)	5.1
C <sub>b1</sub>	-2007 (6)	2407 (3)	3049 (3)	4.1
C <sub>b2</sub>	-1734 (5)	1846 (3)	2700 (3)	4.2
C <sub>b3</sub>	2704 (6)	313 (3)	2715 (3)	4.1
C <sub>b4</sub>	3264 (6)	273 (3)	3064 (3)	3.8
C <sub>b5</sub>	5606 (5)	1595 (3)	4909 (3)	3.9
C <sub>b6</sub>	5289 (5)	2103 (3)	5282 (3)	3.9
C <sub>b7</sub>	1541 (6)	3720 (3)	5212 (3)	4.0
C <sub>b8</sub>	390 (5)	3783 (3)	4842 (3)	3.7
C <sub>2</sub>	1655 (6)	2963 (4)	2681 (2)	4.3
C <sub>1</sub>	3584 (6)	2947 (4)	3185 (3)	4.4
C <sub>3</sub>	2362 (6)	3327 (4)	2327 (3)	4.9
C <sub>4</sub>	4728 (7)	3634 (5)	2431 (4)	6.5
C <sub>11</sub>	-507 (5)	717 (3)	2129 (3)	3.8 (1)
C <sub>12</sub>	-703 (6)	1069 (4)	1565 (3)	5.4 (2)
C <sub>13</sub>	-1377 (7)	743 (4)	1023 (3)	6.4 (2)
C <sub>14</sub>	-1796 (7)	67 (4)	1061 (3)	5.9 (2)
C <sub>15</sub>	-1613 (7)	-298 (4)	1607 (3)	6.2 (2)
C <sub>16</sub>	-958 (6)	26 (4)	2160 (3)	5.3 (2)
C <sub>21</sub>	5588 (5)	502 (3)	3966 (3)	3.7 (1)
C <sub>22</sub>	6637 (6)	745 (3)	3736 (3)	4.4 (1)
C <sub>23</sub>	7700 (6)	299 (4)	3744 (3)	5.3 (2)
C <sub>24</sub>	7716 (6)	-367 (4)	3982 (3)	5.1 (2)
C <sub>25</sub>	6689 (6)	-624 (4)	4219 (3)	5.7 (2)
C <sub>26</sub>	5589 (6)	-182 (3)	4202 (3)	4.7 (1)
C <sub>31</sub>	3962 (5)	3194 (3)	5885 (3)	3.6 (1)
C <sub>32</sub>	5049 (6)	3613 (3)	5970 (3)	4.0 (1)
C <sub>33</sub>	5544 (6)	3899 (3)	6566 (3)	4.5 (1)
C <sub>34</sub>	4939 (6)	3768 (3)	7059 (3)	4.8 (1)
C <sub>35</sub>	3855 (6)	3369 (4)	6979 (3)	5.2 (2)
C <sub>36</sub>	3360 (6)	3065 (3)	6392 (3)	4.7 (1)
C <sub>41</sub>	-1944 (5)	3544 (3)	3971 (3)	3.3 (1)
C <sub>42</sub>	-2006 (6)	4233 (3)	3748 (3)	4.2 (1)
C <sub>43</sub>	-3062 (6)	4656 (4)	3795 (3)	5.3 (2)
C <sub>44</sub>	-4044 (6)	4389 (4)	4068 (3)	5.4 (2)
C <sub>45</sub>	-3977 (6)	3712 (4)	4291 (3)	5.1 (2)
C <sub>46</sub>	-2926 (6)	3276 (3)	4240 (3)	4.2 (1)
C <sub>51</sub>	9430 (9)	2993 (5)	619 (4)	9.5 (3)
C <sub>52</sub>	9030 (10)	3108 (6)	1180 (5)	11.8 (3)
C <sub>53</sub>	8631 (9)	3780 (5)	1305 (5)	10.2 (3)
C <sub>54</sub>	8621 (7)	4302 (4)	890 (4)	7.4 (2)
C <sub>55</sub>	8995 (7)	4190 (4)	324 (4)	7.4 (2)
C <sub>56</sub>	9425 (8)	3517 (5)	195 (4)	8.1 (2)

<sup>a</sup> Numbers in parentheses are the estimated standard deviations.

<sup>b</sup> Thermal parameters for which no estimated standard deviation is given were refined anisotropically. Isotropic thermal parameters are calculated from  $B = 4[V^2 \det \beta_{ij}]^{1/2}$ . <sup>c</sup> For Co  $10^4x = 18,512(7)$ ,  $10^4y = 20,556(4)$ ,  $10^4z = 39,244(4)$ .

molecule as it exists in the crystal. Also displayed in Figure 1 are the identifying labels assigned to the atoms and the crystallographically independent bond distances in the porphinato core, the coordination group, and the axial ligand. Individual bond lengths and

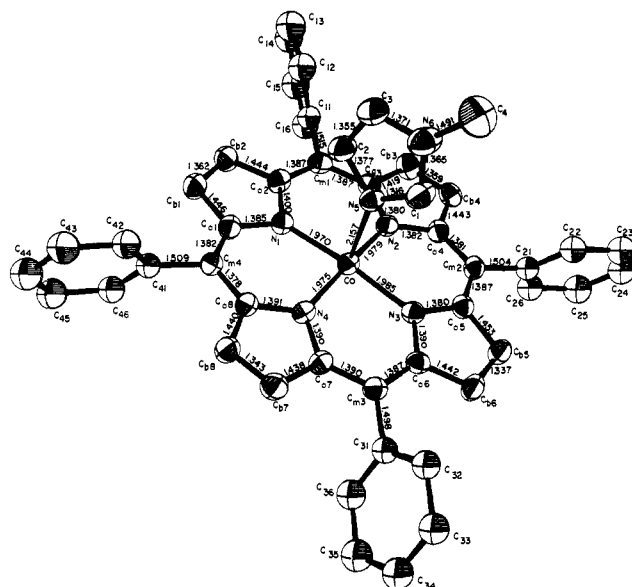


Figure 1. Computer-drawn model in perspective of the MIM-CoTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size required by the thermal parameters listed in Table II. Each atom is identified with the symbol used throughout the paper. Also displayed are the structurally independent bond distances of the porphinato core and the axial ligand.

bond angles<sup>7</sup> are listed in Tables III and IV, respectively; bond parameters for the peripheral phenyl groups and the benzene solvate are given in Table V.

Bond lengths in the porphinato skeleton depart immaterially from fourfold geometry. Using  $C_a$  and  $C_b$  to denote the respective  $\alpha$ - and  $\beta$ -carbon atoms of a pyrrole ring,  $C_m$  for methine carbon, and  $C_p$  for a phenyl carbon atom that is bonded to the core, the averaged values for bond lengths in the porphine skeleton are  $N-C_a = 1.387(5, 5)$ ,  $C_a-C_m = 1.385(3, 6)$ ,  $C_a-C_b = 1.441(6, 6)$ ,  $C_b-C_b = 1.350(10, 6)$ , and  $C_m-C_p = 1.506(6, 6)$  Å, wherein the first number in parentheses following each averaged length is the mean deviation in units of 0.001 Å and the second is the value of the estimated standard deviation for an individually determined length.<sup>8</sup> For comparison, the averaged bond lengths in the core of low-spin bis(piperidine)- $\alpha, \beta, \gamma, \delta$ -tetraphenylporphinatocobalt(II)<sup>2</sup> (Pip<sub>2</sub>CoTPP) can be cited:  $N-C_a = 1.380(2, 2)$ ,  $C_a-C_m = 1.392(2, 2)$ ,  $C_a-C_b = 1.444(3, 3)$ ,  $C_b-C_b = 1.344(3, 3)$ ,  $C_m-C_p = 1.498(3, 3)$  Å. The agreement in the bond angles of a given chemical type in the core is equally close with averaged values as follows:  $C_aNC_a = 104.6(1, 3)$ ,  $NC_aC_b = 110.7(2, 4)$ ,  $NC_aC_m = 125.4(2, 4)$ ,  $C_aC_bC_b = 107.0(3, 4)$ ,  $C_aC_mC_a = 123.5(2, 4)$ ,  $C_aC_mC_p = 118.2(7, 4)^\circ$ .

The departures of the carbon and nitrogen atoms in the porphine skeleton from the mean plane of the core are displayed in Figure 2, which is drawn in the same orientation as Figure 1. Each labeled atom of Figure 1 has been replaced by its out-of-plane displacement in units of 0.01 Å. The irregular ruffling of the core is much less pronounced than that which

(7) These calculations followed W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(8) This notation for reporting averaged values for both angles and bond lengths is used throughout the discussion.

**Table II.** Anisotropic Thermal Parameters<sup>a</sup>

Atom type	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co	3.05 (3)	3.06 (3)	3.03 (3)	-0.02 (3)	0.42 (3)	0.13 (2)
N <sub>1</sub>	3.1 (2)	3.0 (2)	3.4 (2)	-0.1 (2)	0.4 (2)	-0.4 (2)
N <sub>2</sub>	3.3 (2)	3.1 (2)	3.1 (2)	-0.1 (2)	0.6 (2)	-0.1 (2)
N <sub>3</sub>	3.5 (2)	2.8 (2)	3.0 (2)	0.1 (2)	0.7 (2)	-0.1 (2)
N <sub>4</sub>	3.2 (2)	3.3 (2)	2.9 (2)	0.1 (2)	0.2 (2)	0.2 (2)
C <sub>a1</sub>	3.2 (3)	3.5 (3)	3.7 (3)	0.2 (2)	0.6 (2)	0.3 (2)
C <sub>a2</sub>	3.1 (3)	3.5 (3)	3.7 (3)	-0.8 (2)	0.2 (2)	-0.1 (2)
C <sub>a3</sub>	3.8 (3)	3.3 (3)	3.4 (3)	-0.1 (2)	0.8 (2)	-0.2 (2)
C <sub>a4</sub>	3.3 (3)	3.3 (3)	3.8 (3)	0.4 (2)	0.9 (2)	0.8 (2)
C <sub>a5</sub>	3.2 (3)	3.3 (3)	3.7 (3)	0.3 (2)	0.8 (2)	0.3 (2)
C <sub>a6</sub>	3.6 (3)	3.4 (3)	2.8 (3)	-0.2 (2)	0.8 (2)	0.2 (2)
C <sub>a7</sub>	3.1 (2)	3.2 (3)	3.2 (3)	-0.2 (2)	0.3 (2)	0.0 (2)
C <sub>a8</sub>	3.2 (3)	3.1 (3)	3.2 (3)	0.4 (2)	0.5 (2)	0.2 (2)
C <sub>m1</sub>	4.1 (3)	3.1 (3)	3.0 (3)	-0.6 (2)	0.5 (2)	-0.6 (2)
C <sub>m2</sub>	3.1 (3)	3.0 (3)	3.7 (3)	0.6 (2)	0.8 (2)	0.3 (2)
C <sub>m3</sub>	3.4 (3)	3.5 (3)	3.0 (3)	-0.3 (2)	0.5 (2)	-0.1 (2)
C <sub>m4</sub>	3.2 (3)	3.1 (3)	3.1 (3)	0.3 (2)	0.5 (2)	0.1 (2)
N <sub>5</sub>	3.4 (2)	3.4 (2)	3.2 (2)	-0.3 (2)	0.3 (2)	0.0 (2)
N <sub>6</sub>	5.6 (3)	5.8 (3)	4.4 (3)	-0.9 (3)	0.2 (2)	1.3 (2)
C <sub>b1</sub>	3.3 (3)	4.9 (4)	4.2 (3)	0.1 (3)	0.2 (2)	-0.6 (3)
C <sub>b2</sub>	3.3 (3)	5.5 (4)	4.1 (3)	-0.4 (3)	0.5 (2)	-0.8 (3)
C <sub>b3</sub>	4.2 (3)	3.8 (3)	4.8 (3)	-0.4 (3)	1.3 (3)	-1.2 (3)
C <sub>b4</sub>	4.3 (3)	3.5 (3)	4.1 (3)	0.2 (3)	1.4 (3)	-0.8 (3)
C <sub>b5</sub>	3.4 (3)	4.2 (3)	3.9 (3)	0.4 (3)	0.0 (2)	0.2 (3)
C <sub>b6</sub>	3.1 (3)	4.6 (3)	4.2 (3)	0.6 (3)	-0.1 (2)	0.0 (3)
C <sub>b7</sub>	4.4 (3)	3.9 (3)	3.9 (3)	0.2 (3)	0.5 (3)	-0.7 (3)
C <sub>b8</sub>	3.7 (3)	3.7 (3)	3.8 (3)	0.5 (2)	0.2 (2)	-0.5 (3)
C <sub>2</sub>	4.2 (3)	5.4 (4)	3.7 (3)	-0.2 (3)	0.5 (2)	1.1 (3)
C <sub>1</sub>	4.1 (3)	5.2 (3)	4.1 (3)	-0.8 (3)	-0.1 (2)	0.8 (3)
C <sub>3</sub>	5.4 (4)	5.9 (4)	4.2 (3)	0.5 (3)	0.7 (3)	1.6 (3)
C <sub>4</sub>	5.4 (4)	14.4 (8)	9.1 (6)	-4.6 (5)	2.4 (4)	4.0 (5)

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the least significant figure.  $B_{ij}$  is related to the dimensionless  $\beta_{ij}$  employed during refinement as  $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ .

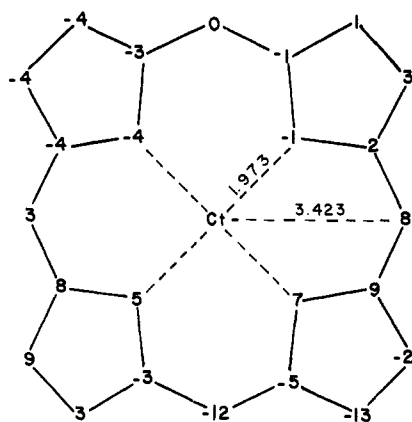


Figure 2. Formal diagram of the porphinato core with the same relative orientation as Figure 1. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. Also displayed are the values of two important structural radii,  $\text{Co} \cdots \text{N}$  and  $\text{Co} \cdots \text{C}_m$ .

characterizes the porphine skeleton in tetragonal crystals of tetraphenylporphine<sup>9</sup> and its Cu(II) and Pd(II) derivatives.<sup>10</sup> As is usual, local flatness is preserved (within 0.02 Å) in the trigonal carbon atoms of the inner 16-membered ring and in the pyrrole rings as well. The four nitrogen atoms of the porphine skeleton are coplanar; the cobalt atom is displaced 0.13 Å from the mean plane toward the nitrogen atom of the coordinated ligand. The mean planes defined respec-

(9) M. J. Hamor, J. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, **86**, 1938 (1964).

(10) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

**Table III.** Bond Lengths in the Coordination Group, Porphinato Skeleton, and Imidazole Ligand<sup>a</sup>

Type	Length, Å	Type	Length, Å	Type	Length, Å
Co-N <sub>1</sub>	1.970 (3)	C <sub>a1</sub> -C <sub>b1</sub>	1.446 (6)	C <sub>a8</sub> -C <sub>b8</sub>	1.440 (6)
Co-N <sub>2</sub>	1.979 (3)	C <sub>a2</sub> -C <sub>m1</sub>	1.387 (6)	C <sub>m1</sub> -C <sub>11</sub>	1.515 (6)
Co-N <sub>3</sub>	1.985 (3)	C <sub>a2</sub> -C <sub>b2</sub>	1.444 (6)	C <sub>m2</sub> -C <sub>21</sub>	1.504 (6)
Co-N <sub>4</sub>	1.975 (3)	C <sub>a3</sub> -C <sub>m1</sub>	1.387 (6)	C <sub>m3</sub> -C <sub>31</sub>	1.498 (6)
Co-N <sub>5</sub>	2.157 (3)	C <sub>a3</sub> -C <sub>b3</sub>	1.419 (6)	C <sub>m4</sub> -C <sub>41</sub>	1.509 (6)
N <sub>1</sub> -C <sub>a1</sub>	1.385 (5)	C <sub>a4</sub> -C <sub>m2</sub>	1.381 (6)	C <sub>b1</sub> -C <sub>b2</sub>	1.362 (6)
N <sub>1</sub> -C <sub>a2</sub>	1.400 (5)	C <sub>a4</sub> -C <sub>b4</sub>	1.443 (6)	C <sub>b3</sub> -C <sub>b4</sub>	1.359 (6)
N <sub>2</sub> -C <sub>a3</sub>	1.380 (5)	C <sub>a5</sub> -C <sub>m2</sub>	1.387 (6)	C <sub>b5</sub> -C <sub>b6</sub>	1.337 (6)
N <sub>2</sub> -C <sub>a4</sub>	1.382 (5)	C <sub>a5</sub> -C <sub>b5</sub>	1.453 (6)	C <sub>b7</sub> -C <sub>b8</sub>	1.343 (6)
N <sub>3</sub> -C <sub>a5</sub>	1.380 (5)	C <sub>a6</sub> -C <sub>m3</sub>	1.387 (6)	N <sub>5</sub> -C <sub>1</sub>	1.316 (6)
N <sub>3</sub> -C <sub>a6</sub>	1.390 (5)	C <sub>a6</sub> -C <sub>b6</sub>	1.442 (6)	N <sub>5</sub> -C <sub>2</sub>	1.377 (5)
N <sub>4</sub> -C <sub>a7</sub>	1.390 (5)	C <sub>a7</sub> -C <sub>m3</sub>	1.390 (6)	N <sub>5</sub> -C <sub>1</sub>	1.365 (6)
N <sub>4</sub> -C <sub>a8</sub>	1.391 (5)	C <sub>a7</sub> -C <sub>b7</sub>	1.438 (6)	N <sub>5</sub> -C <sub>3</sub>	1.371 (6)
C <sub>a1</sub> -C <sub>m4</sub>	1.382 (6)	C <sub>a8</sub> -C <sub>m4</sub>	1.378 (6)	N <sub>5</sub> -C <sub>4</sub>	1.491 (6)
				C <sub>2</sub> -C <sub>3</sub>	1.355 (7)

<sup>a</sup> The numbers in parentheses are the estimated standard deviations.

tively by the four nitrogen atoms and the entire porphine skeleton are separated by  $\sim 0.01$  Å; consequently, the cobalt atom is displaced by  $\sim 0.14$  Å from the mean skeletal plane.

The dihedral angles between the mean plane of the porphine skeleton and the planes of the four phenyl groups are 70.9, 76.6, 65.9, and 78.2°. The averaged value of the internal angles in the phenyl rings is 120.0 (5, 4)°. The sum of the angles subtended at  $C_p$  is 360.0°, corresponding to a planar trigonal carbon atom. The individually determined C-C bond distances of the four structurally independent phenyl rings are listed in Table V.

**Table IV.** Bond Angles in the Coordination Group, Porphinato Skeleton, and Imidazole Ring<sup>a</sup>

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N <sub>2</sub> CoN <sub>2</sub>	89.9 (1)	C <sub>a8</sub> C <sub>m4</sub> C <sub>41</sub>	116.8 (4)	C <sub>a1</sub> C <sub>b1</sub> C <sub>b2</sub>	107.1 (4)
N <sub>1</sub> CoN <sub>3</sub>	172.5 (2)	N <sub>1</sub> C <sub>a1</sub> C <sub>m4</sub>	125.4 (4)	C <sub>a2</sub> C <sub>b2</sub> C <sub>b1</sub>	106.7 (4)
N <sub>2</sub> CoN <sub>4</sub>	89.6 (1)	N <sub>1</sub> C <sub>a1</sub> C <sub>b1</sub>	110.9 (4)	C <sub>a3</sub> C <sub>b3</sub> C <sub>b4</sub>	107.3 (4)
N <sub>1</sub> CoN <sub>5</sub>	90.1 (1)	C <sub>m4</sub> C <sub>a1</sub> C <sub>b1</sub>	123.7 (4)	C <sub>a4</sub> C <sub>b4</sub> C <sub>b3</sub>	106.3 (4)
N <sub>2</sub> CoN <sub>3</sub>	90.1 (1)	N <sub>1</sub> C <sub>a2</sub> C <sub>m1</sub>	125.4 (4)	C <sub>a5</sub> C <sub>b5</sub> C <sub>b6</sub>	106.8 (4)
N <sub>2</sub> CoN <sub>4</sub>	172.8 (2)	N <sub>1</sub> C <sub>a2</sub> C <sub>b2</sub>	110.8 (4)	C <sub>a6</sub> C <sub>b6</sub> C <sub>b5</sub>	107.6 (4)
N <sub>2</sub> CoN <sub>5</sub>	91.0 (1)	C <sub>m1</sub> C <sub>a2</sub> C <sub>b2</sub>	123.8 (4)	C <sub>a7</sub> C <sub>b7</sub> C <sub>b8</sub>	107.2 (4)
N <sub>3</sub> CoN <sub>4</sub>	89.5 (1)	N <sub>2</sub> C <sub>a3</sub> C <sub>m1</sub>	125.4 (4)	C <sub>a8</sub> C <sub>b8</sub> C <sub>b7</sub>	107.2 (4)
N <sub>3</sub> CoN <sub>5</sub>	97.4 (1)	N <sub>2</sub> C <sub>a3</sub> C <sub>b3</sub>	111.2 (4)	C <sub>1</sub> N <sub>5</sub> C <sub>2</sub>	105.6 (3)
N <sub>4</sub> CoN <sub>5</sub>	96.2 (1)	C <sub>m1</sub> C <sub>a3</sub> C <sub>b3</sub>	123.3 (4)	N <sub>5</sub> C <sub>1</sub> N <sub>6</sub>	111.5 (4)
C <sub>a1</sub> N <sub>1</sub> C <sub>a2</sub>	104.6 (3)	N <sub>2</sub> C <sub>a4</sub> C <sub>m2</sub>	125.8 (4)	C <sub>1</sub> N <sub>6</sub> C <sub>3</sub>	106.5 (4)
C <sub>a3</sub> N <sub>2</sub> C <sub>a4</sub>	104.6 (3)	N <sub>2</sub> C <sub>a4</sub> C <sub>b4</sub>	110.6 (4)	C <sub>1</sub> N <sub>6</sub> C <sub>4</sub>	127.5 (4)
C <sub>a5</sub> N <sub>3</sub> C <sub>a6</sub>	104.7 (3)	C <sub>m2</sub> C <sub>a4</sub> C <sub>b4</sub>	123.6 (4)	C <sub>3</sub> N <sub>6</sub> C <sub>4</sub>	126.0 (4)
C <sub>a7</sub> N <sub>4</sub> C <sub>a8</sub>	104.3 (3)	N <sub>3</sub> C <sub>a5</sub> C <sub>m2</sub>	125.6 (4)	N <sub>5</sub> C <sub>2</sub> C <sub>3</sub>	110.0 (4)
C <sub>a2</sub> C <sub>m1</sub> C <sub>a3</sub>	123.4 (4)	N <sub>3</sub> C <sub>a5</sub> C <sub>b5</sub>	110.6 (4)	C <sub>2</sub> C <sub>3</sub> N <sub>6</sub>	106.5 (4)
C <sub>a4</sub> C <sub>m2</sub> C <sub>a5</sub>	123.7 (4)	C <sub>m2</sub> C <sub>a5</sub> C <sub>b5</sub>	123.5 (4)	CoN <sub>5</sub> C <sub>1</sub>	127.8 (3)
C <sub>a6</sub> C <sub>m3</sub> C <sub>a7</sub>	123.2 (4)	N <sub>3</sub> C <sub>a6</sub> C <sub>m3</sub>	125.3 (4)	CoN <sub>5</sub> C <sub>2</sub>	126.4 (3)
C <sub>a1</sub> C <sub>m4</sub> C <sub>a8</sub>	123.8 (4)	N <sub>3</sub> C <sub>a6</sub> C <sub>b6</sub>	110.3 (4)	CoN <sub>1</sub> C <sub>a1</sub>	127.8 (3)
C <sub>a2</sub> C <sub>m1</sub> C <sub>11</sub>	117.2 (4)	C <sub>m3</sub> C <sub>a6</sub> C <sub>b6</sub>	124.4 (4)	CoN <sub>1</sub> C <sub>a2</sub>	127.2 (3)
C <sub>a3</sub> C <sub>m1</sub> C <sub>11</sub>	119.3 (4)	N <sub>4</sub> C <sub>a7</sub> C <sub>m3</sub>	125.6 (4)	CoN <sub>2</sub> C <sub>a3</sub>	127.8 (3)
C <sub>a4</sub> C <sub>m2</sub> C <sub>21</sub>	118.2 (4)	N <sub>4</sub> C <sub>a7</sub> C <sub>b7</sub>	110.6 (3)	CoN <sub>2</sub> C <sub>a4</sub>	127.2 (3)
C <sub>a5</sub> C <sub>m2</sub> C <sub>21</sub>	118.1 (4)	C <sub>m3</sub> C <sub>a7</sub> C <sub>b7</sub>	123.7 (4)	CoN <sub>3</sub> C <sub>a5</sub>	127.1 (3)
C <sub>a6</sub> C <sub>m3</sub> C <sub>31</sub>	118.9 (4)	N <sub>4</sub> C <sub>a8</sub> C <sub>m4</sub>	125.1 (4)	CoN <sub>3</sub> C <sub>a6</sub>	128.2 (3)
C <sub>a7</sub> C <sub>m3</sub> C <sub>31</sub>	117.7 (4)	N <sub>4</sub> C <sub>a8</sub> C <sub>b8</sub>	110.5 (3)	CoN <sub>4</sub> C <sub>a7</sub>	128.1 (3)
C <sub>a1</sub> C <sub>m4</sub> C <sub>41</sub>	119.3 (4)	C <sub>m4</sub> C <sub>a8</sub> C <sub>b8</sub>	124.3 (4)	CoN <sub>4</sub> C <sub>a8</sub>	127.6 (3)

<sup>a</sup> The numbers in parentheses are the estimated standard deviations.

**Table V.** Bond Lengths in the Phenyl Groups and the Benzene Solute<sup>a</sup>

Type	Length, Å	Type	Length, Å	Type	Length, Å
C <sub>11</sub> -C <sub>12</sub>	1.377 (7)	C <sub>24</sub> -C <sub>25</sub>	1.377 (7)	C <sub>42</sub> -C <sub>43</sub>	1.396 (7)
C <sub>11</sub> -C <sub>16</sub>	1.392 (7)	C <sub>25</sub> -C <sub>26</sub>	1.431 (7)	C <sub>43</sub> -C <sub>44</sub>	1.384 (7)
C <sub>12</sub> -C <sub>13</sub>	1.407 (7)	C <sub>31</sub> -C <sub>32</sub>	1.385 (6)	C <sub>44</sub> -C <sub>45</sub>	1.362 (7)
C <sub>13</sub> -C <sub>14</sub>	1.357 (8)	C <sub>31</sub> -C <sub>36</sub>	1.391 (6)	C <sub>45</sub> -C <sub>46</sub>	1.406 (7)
C <sub>14</sub> -C <sub>15</sub>	1.357 (8)	C <sub>32</sub> -C <sub>33</sub>	1.414 (6)	C <sub>51</sub> -C <sub>56</sub>	1.35 (1)
C <sub>15</sub> -C <sub>16</sub>	1.415 (7)	C <sub>33</sub> -C <sub>34</sub>	1.368 (7)	C <sub>51</sub> -C <sub>52</sub>	1.38 (1)
C <sub>21</sub> -C <sub>22</sub>	1.380 (6)	C <sub>34</sub> -C <sub>35</sub>	1.360 (7)	C <sub>52</sub> -C <sub>53</sub>	1.38 (1)
C <sub>21</sub> -C <sub>26</sub>	1.387 (6)	C <sub>35</sub> -C <sub>36</sub>	1.412 (7)	C <sub>53</sub> -C <sub>54</sub>	1.33 (1)
C <sub>22</sub> -C <sub>23</sub>	1.406 (7)	C <sub>41</sub> -C <sub>42</sub>	1.381 (6)	C <sub>54</sub> -C <sub>55</sub>	1.38 (1)
C <sub>23</sub> -C <sub>24</sub>	1.355 (7)	C <sub>41</sub> -C <sub>46</sub>	1.382 (6)	C <sub>55</sub> -C <sub>56</sub>	1.39 (1)

<sup>a</sup> The figure in parentheses is the estimated standard deviation.

The equatorial Co-N lengths of the square-pyramidal CoN<sub>5</sub> coordination group average to 1.977 (5, 3) Å; the NCoN angles of the equatorial plane average to 89.8 (2, 1)°. The "radius of the central hole," Ct ··· N, is 1.973 Å, comparable to the 1.987 Å value that characterizes Pip<sub>2</sub>CoTPP<sup>2</sup> wherein Ct ··· N ≡ Co-N. These equatorial structural radii are also quite similar to those found for the cobalt(III) porphyrin,<sup>11</sup> Pip<sub>2</sub>CoTPP<sup>+</sup>, for which Ct ··· N ≡ Co-N = 1.978 Å. The slightly shorter radii for MImCoTPP can be attributed to the slightly greater ruffling of its porphine core.<sup>12</sup> Indeed, the effects of ruffling the porphine core, which are in large part required by the steric interactions between the axial ligand(s) and the core, would appear to have a greater influence on the Co-N and Ct ··· N distances in the cobalt(II) and -(III) porphyrins than the oxidation state of the central cobalt atom.

The Co-N<sub>b</sub> bond to the axial 1-methylimidazole ligand is 2.157 (3) Å, substantially shorter than the

2.436 Å distance in low-spin six-coordinate Pip<sub>2</sub>CoTPP;<sup>2</sup> the unpaired electron in both complexes has axial or nearly axial symmetry<sup>13</sup> and must be largely d<sub>z<sup>2</sup></sub> in character. The axial bond distance is significantly longer than the 2.114 Å Co-N bond distance in the *high-spin* complex Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>.<sup>14</sup> The Co-N<sub>b</sub> distance is also longer than the 2.10 Å Co-pyridine distance in *N,N'*-ethylenebis(salicylideneiminato)pyridinecobalt(II),<sup>15</sup> a five-coordinate cobalt(II) complex which has a sterically unconstrained axial ligand.

The axial Co-N<sub>b</sub> bond in MImCoTPP is tipped ~4° from the normal to the mean skeletal plane or the equatorial girdle; consequently, the coordination group deviates substantially from C<sub>4v</sub> or C<sub>2v</sub> geometry. The dihedral angles defined by the plane of the axial ligand and the four C<sub>m</sub>CoN<sub>5</sub> planes are ~45°; the dihedral angle between the mean skeletal plane and the ligand plane is 82.8°. The axial ligand is thus described as approximately lying in a plane tipped ~7° from the normal to the mean skeletal plane and containing N<sub>1</sub> and N<sub>3</sub>. The orientation of the planar imidazole ring with respect to rotation around the complexing axial bond is thus unfavorable for minimizing the steric interactions of the porphinato core with the neighboring pair of the hydrogen atoms of the imidazole (the hydrogen atoms bonded to C<sub>1</sub> (H<sub>c1</sub>) and C<sub>2</sub> (H<sub>c2</sub>); see Figure 1). Despite the unfavorable orientation of the imidazole ring, the H<sub>c2</sub> ··· N<sub>1</sub> distance is 2.62 Å and H<sub>c1</sub> ··· N<sub>3</sub> is 2.85 Å. The deviation of the coordination group from quasi-C<sub>4v</sub> geometry and the unfavorable orientation of the ligand are attributable to the packing relationships in the crystal. Of the 52 intermolecular contacts less than 4.0 Å and the 12 less than 3.7 Å, 22 and six,

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respectively, involve atoms of the axial ligand. No contacts, however, are less than 3.50 Å.

A thermodynamic study<sup>16</sup> of the formation of the five-coordinate cobalt complexes has been interpreted as indicating  $M \rightarrow L\pi^*$  back-bonding when the axial ligand is an aromatic amine. Furthermore, imidazoles were found to form more stable complexes than pyridines of the same  $\sigma$ -donor strength,<sup>16</sup> suggesting that imidazoles are better  $\pi$  acceptors than the pyridines. Possible  $\pi$  back-bonding for the imidazole complexes is also suggested by their reluctance to add a second ligand; the addition of a second imidazole would require substantially lengthened Co–N<sub>b</sub> bonds and, hence, decrease the  $\pi$ -accepting ability of the imidazole. The Co–N<sub>b</sub> bond length of MImCoTPP is compatible with  $\pi$  back-bonding but certainly cannot be regarded as compelling evidence for such bonding. Since imidazoles do not have significant  $\pi$  acceptor capacity in the low-spin bis(imidazole)ferrous and -ferric porphyrins,<sup>17</sup> the possible  $\pi$ -acceptor ability in the five-

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coordinate porphyrins must be related to the displacement of the cobalt out of the porphyrin plane.

**Acknowledgments.** I thank Professors J. L. Hoard and F. A. Walker for helpful discussions and Messrs. P. N. Dwyer, P. Hawley, and G. Rupprecht for preparing and purifying CoTPP. This investigation was sponsored by Biomedical Sciences Support Grant RR 07033-07 and HL-15627 from the National Institutes of Health whose support is gratefully acknowledged.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-90.

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## Kinetics and Mechanism of Alkylchromium Formation in the Reductive Cobalt–Carbon Bond Cleavage of Alkylcorrins by Chromium(II)<sup>1</sup>

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**Abstract:** The stoichiometry and kinetics of reactions of methyl and ethylcobalamin with Cr<sup>2+</sup> in aqueous perchloric acid have been examined. These reactions occur with a 1:1 stoichiometry, producing (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>3</sub><sup>2+</sup> and (H<sub>2</sub>O)<sub>5</sub>CrC<sub>2</sub>H<sub>5</sub><sup>2+</sup> (respectively), and B<sub>12r</sub>. The reactions follow second-order kinetics, the rate constants (298°K,  $\mu \sim 1 M$ ) being  $3.6 \pm 0.3 \times 10^2$  and  $4.4 \pm 0.4 M^{-1} \text{ sec}^{-1}$ . In the same medium B<sub>12a</sub> is reduced by Cr<sup>2+</sup> at a specific rate of  $14.3 \pm 1.0 M^{-1} \text{ sec}^{-1}$ . The reactions show no dependence upon pH in the range 0–2.3. Activation parameters were determined. Two plausible mechanisms are proposed, one of which is a direct bimolecular homolytic attack (SH<sub>2</sub>) at the saturated carbon center.

Treatment of organocobalt complexes with reducing agents under appropriate conditions results in cleavage of the Co–C bond. Thus Schrauzer and co-workers have realized the reductive cleavage of alkylcorrins and of related model compounds by thiols,<sup>2</sup> and by alkaline CO, S<sub>2</sub>O<sub>4</sub><sup>2-</sup>, and Sn(II).<sup>3</sup> These reactions result in the effective transfer of a carbanion, the products being the Co<sup>I</sup>(chelate) or a compound derived therefrom, and the alkane. Reactions with electrophilic reagents such as Hg<sup>2+</sup> and Tl<sup>3+</sup> also result in carbanion transfer but no reduction; HgR<sup>+</sup>, for example, is formed along with (H<sub>2</sub>O)<sub>2</sub>Co<sup>III</sup>(chelate).<sup>4–8</sup>

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Recently, two reactions were reported in which reductive cleavage of the Co–C bond resulted in transfer of an alkyl radical. The first of these was the reaction of a methylcobalt(III) (chelate) complex with a Co(II) derivative of a different chelate



where L and L' represent the two different planar, tetradentate, Schiff's base chelates.<sup>9</sup> The second reaction was that between alkylaquobis(dimethylglyoximate)cobalt(III) complexes (alkylcobaloximes) and Cr<sup>2+</sup> in aqueous solution<sup>10</sup>

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