

Stereochemistry of Cobalt Porphyrins. II. The  
 Characterization and Structure of  
*meso*-Tetraphenylporphinatobis(imidazole)cobalt(III)  
 Acetate Monohydrate Monochloroformate,  
 $[\text{Co}(\text{Im})_2(\text{TPP})][\text{OAc}] \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$

Joseph W. Lauher and James A. Ibers\*

*Contribution from the Department of Chemistry and Materials Research Center,  
 Northwestern University, Evanston, Illinois 60201. Received December 28, 1973*

**Abstract:** The six-coordinate Co(III) porphyrin,  $[\text{Co}(\text{Im})_2(\text{TPP})][\text{OAc}] \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$ , was prepared accidentally and has been characterized by a complete structural analysis. The material crystallizes with two formula units in space group  $C_2^1-P\bar{1}$  of the triclinic system in a cell of dimensions  $a = 13.055(8) \text{ \AA}$ ,  $b = 17.239(7) \text{ \AA}$ ,  $c = 11.807(8) \text{ \AA}$ ,  $\alpha = 105.94(3)^\circ$ ,  $\beta = 91.97(3)^\circ$ , and  $\gamma = 107.49(3)^\circ$ . The asymmetric unit consists of two half cations, so that there are two independent cations in the cell, each with a crystallographically imposed center of symmetry. The Co-N (of imidazole) axial bond length averages  $1.93(2) \text{ \AA}$ . Comparison of the present structure with that of the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion enables us to estimate a minimum approach distance of a histidine to the plane of the porphyrin ring. This minimal approach distance is an essential factor in estimating the movement of the proximal histidine group toward the mean plane of the porphyrin ring upon oxygenation of cobalt-substituted hemoglobin.

The reactions of molecular oxygen with cobalt porphyrins are of considerable interest. In a series of experiments<sup>1-3</sup> it has been shown that in non-aqueous solvents at low temperatures cobalt porphyrins in the presence of a base such as imidazole will reversibly combine with oxygen to form a 1:1 cobalt oxygen complex. Such complexes model the naturally occurring iron porphyrins and the synthetically prepared coboglobin<sup>4</sup> (hemoglobin with the iron replaced by cobalt), which is itself a model for the natural systems.

It has also been observed<sup>5</sup> that a second reaction may take place. Cobalt porphyrins will react with molecular oxygen at room temperature in the presence of a base, such as imidazole, in an irreversible manner in a 2:1 cobalt to oxygen ratio to give a product of unknown composition. Stynes, *et al.*,<sup>5</sup> have studied the kinetics of this reaction and have proposed that the product is either a Co(III) hydroxy complex or a  $\mu$ -peroxy dimer in which two cobalt porphyrins, each with one axial base, are bridged by a peroxy ligand forming a dimer analogous to those well characterized in simple Werner complexes.

In order to characterize fully this product an X-ray structure determination was undertaken. The porphyrin used was cobalt tetraphenylporphyrin, Co(TPP), and the base selected was imidazole. Crystals of what was originally thought to be the kinetic product were isolated, and the structure was determined. It was apparent that the compound prepared was actually the title compound. This compound was formed because of acetate impurities in the starting materials. In retrospect the product has nothing to do with the kinetic experiment which always involved pure starting materials prepared by an alternative method.

The structure reported here is that of a Co(III) porphyrin with axial imidazole bases. The cobalt-to-imidazole nitrogen bond lengths are of immediate interest because they are necessary for a detailed analysis of the trigger mechanism in coboglobin presented in the following paper.<sup>6</sup>

Note that the structure here models a recently reported cobalt(III) protoporphyrin IX complex of horse globin.<sup>7</sup> This complex experimentally resembles an internal ferrihemochrome in which the heme is attached to the globin by two metal protein bonds. The complex is probably a cobalt(III) porphyrin with both the proximal and distal histidine groups coordinated in the axial positions through their imidazole residues.

### Experimental Section

Following the procedure given by Falk<sup>8</sup> a sample of Co(TPP) was prepared from  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{TPP}$  in glacial acetic acid-chloroform solution. The product obtained was purified on an alumina column. A sample of Co(TPP) prepared in this manner was dissolved in refluxing chloroform and an excess of imidazole was added to the solution. Oxygen was bubbled through the solution and the reaction mixture was allowed to remain at  $-20^\circ$  for several days. The crystals that had formed were separated from the solution. These crystals were poorly shaped, but recrystallizations did not yield a better crystalline product. Subsequent preparations using the Co(TPP) from the same original preparation yielded crystals of similar quality. Subsequent reactions using a sample of Co(TPP) prepared in DMF solution yielded no crystalline product.

The crystals are diamagnetic, their visible spectrum when dissolved in chloroform is similar to those found for Co(III) porphyrins, and their ir spectrum contains bands characteristic of imidazole and porphyrin groups. Elemental analysis gave results which did not agree well with any expected formulation. *Anal.* Calcd for the title compound,  $\text{C}_{53}\text{H}_{42}\text{Cl}_3\text{CoN}_8\text{O}_3$ : C, 63.40; H, 4.18; N, 11.16. Found: C, 62.58; H, 4.48; N, 11.96.

X-Ray photographic studies of the crystals indicated a triclinic space group. The density was measured by flotation in aqueous  $\text{ZnCl}_2$  and was found to be  $1.30(1) \text{ g cm}^{-3}$ . (The final calculated

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(8) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 139.

**Table II.** Positional, Thermal, and Group Parameters for  $[\text{Co}(\text{Im})_2(\text{TPP})][\text{OAc}] \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co(1)	0.0000	0.0000	0.0000	0.0084 (4) <sup>b</sup>	0.0021 (2)	0.0096 (5)	0.0003 (2)	-0.0009 (4)	0.0023 (3)
Co(2)	0.5000	0.5000	0.5000	0.0067 (4)	0.0024 (2)	0.0115 (5)	-0.0003 (2)	-0.0006 (4)	0.0029 (3)
Cl(1)	-0.1023 (9)	0.2695 (7)	0.0886 (16)	0.0211 (12)	0.0133 (8)	0.0970 (43)	0.0033 (8)	0.0141 (19)	0.0105 (14)
Cl(2)	-0.1864 (13)	0.3982 (8)	0.1036 (14)	0.0626 (28)	0.0136 (9)	0.0577 (29)	0.0126 (13)	-0.0062 (22)	0.0096 (12)
Cl(3)	-0.1727 (13)	0.3439 (10)	0.3005 (13)	0.0462 (24)	0.0257 (14)	0.0379 (23)	0.0034 (15)	-0.0126 (19)	0.0014 (14)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
N(1)	-0.0033 (11)	-0.0670 (8)	0.1158 (12)	3.75 (35)	C(14)	0.7761 (17)	0.4405 (12)	0.6037 (17)	5.37 (51)
N(2)	0.1073 (11)	0.0998 (9)	0.1136 (13)	4.29 (37)	C(15)	0.8247 (16)	0.5108 (13)	0.5679 (17)	5.93 (54)
C(1)	-0.0629 (15)	-0.1530 (12)	0.0980 (17)	4.38 (48)	C(16)	0.7410 (16)	0.5389 (12)	0.5304 (16)	4.61 (48)
C(2)	-0.0322 (15)	-0.1771 (12)	0.1979 (17)	4.90 (50)	CD	0.7619 (14)	0.6074 (11)	0.4821 (15)	4.30 (47)
C(3)	0.0421 (15)	-0.1120 (12)	0.2735 (17)	4.90 (49)	IN(1)	-0.1167 (11)	0.0346 (8)	0.0622 (12)	3.44 (3)
C(4)	0.0597 (15)	-0.0412 (12)	0.2237 (17)	4.67 (48)	IC(1)	0.2025 (18)	-0.0399 (12)	-0.0033 (18)	5.77 (53)
CA	0.1317 (14)	0.0388 (12)	0.0012 (16)	4.16 (46)	IN(2)	-0.2701 (13)	0.0638 (9)	0.0736 (15)	5.47 (41)
C(5)	0.1548 (16)	0.1045 (13)	0.2222 (18)	4.09 (51)	IC(2)	-0.2325 (18)	0.0744 (13)	0.1865 (19)	6.12 (55)
C(6)	0.2332 (15)	0.1859 (12)	0.2746 (16)	4.46 (47)	IC(3)	-0.1386 (17)	0.0577 (12)	0.1783 (19)	5.36 (51)
C(7)	0.2322 (15)	0.2300 (12)	0.1971 (17)	4.74 (49)	IN(3)	0.4978 (11)	0.4312 (9)	0.3424 (14)	4.33 (37)
C(8)	0.1572 (15)	0.1796 (12)	0.0951 (18)	4.97 (49)	IC(4)	-0.4786 (15)	0.3596 (13)	0.3158 (19)	5.15 (51)
CB	0.1354 (15)	0.2032 (11)	-0.0021 (17)	4.26 (46)	IN(4)	-0.4832 (12)	0.3294 (9)	0.2008 (15)	5.32 (40)
N(3)	0.4266 (12)	0.3975 (9)	0.5508 (12)	4.18 (36)	IC(5)	0.4865 (15)	0.3826 (13)	0.1471 (18)	5.66 (52)
N(4)	0.6406 (12)	0.4910 (9)	0.5448 (12)	3.99 (36)	IC(6)	0.4751 (15)	0.4446 (13)	0.2382 (19)	5.38 (53)
C(9)	0.3159 (15)	0.3638 (11)	0.5524 (15)	4.16 (46)	AC(1)	-0.4790 (20)	0.1393 (16)	0.0053 (23)	7.83 (63)
C(10)	0.2975 (15)	0.2902 (11)	0.5974 (15)	4.13 (46)	AC(2)	-0.4301 (20)	-0.1535 (15)	0.0604 (22)	8.97 (68)
C(11)	0.3928 (15)	0.2803 (11)	0.6197 (16)	4.37 (47)	AO(1)	0.4416 (11)	-0.0835 (9)	0.0445 (13)	7.46 (41)
C(12)	0.4758 (17)	0.3486 (12)	0.5939 (16)	4.52 (49)	AO(2)	-0.4379 (11)	0.1871 (9)	0.1052 (14)	7.74 (40)
CC	0.5839 (17)	0.3603 (12)	0.6100 (16)	4.69 (48)	C(CHCl <sub>3</sub> )	-0.1927 (25)	0.3089 (19)	0.1494 (28)	11.13 (83)
C(13)	0.6645 (16)	0.4288 (12)	0.5884 (16)	4.60 (48)	O(H <sub>2</sub> O)	-0.4827 (13)	0.0600 (10)	0.2440 (14)	9.97 (48)

Group	<i>x</i> <sub>c</sub> <sup>c</sup>	<i>y</i> <sub>c</sub>	<i>z</i> <sub>c</sub>	$\delta$	$\epsilon$	$\eta$
Phenyl A	0.2496 (7)	0.0568 (4)	0.4970 (8)	-1.838 (9)	2.536 (9)	-1.742 (9)
Phenyl B	0.2458 (7)	0.3747 (6)	-0.0109 (8)	-2.208 (18)	2.146 (8)	0.183 (17)
Phenyl C	0.6474 (7)	0.2320 (7)	0.6846 (10)	-3.593 (31)	1.920 (11)	-0.898 (31)
Phenyl D	0.9771 (9)	0.6878 (7)	0.4342 (11)	-2.793 (10)	-2.838 (10)	0.332 (14)

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. <sup>c</sup> These group parameters have been defined previously. See, for example, S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

density is 1.298 g cm<sup>-3</sup>). The crystal selected for data collection was a small rounded needle with the approximate dimensions 0.56 × 0.07 × 0.05 mm. The crystal was mounted on a Picker four-circle diffractometer, and the lattice parameters were obtained as previously described.<sup>9</sup> Careful hand centering of 15 reflections with Cu K $\alpha_1$  radiation ( $\lambda$  1.540562 Å) in the range 15° < 2 $\theta$  < 35° yielded cell parameters  $a = 13.055$  (8) Å,  $b = 17.239$  (7) Å,  $c = 11.807$  (8) Å,  $\alpha = 105.94$  (3)°,  $\beta = 91.97$  (3)°, and  $\gamma = 107.49$  (3)°.

Data were collected in shells of 2 $\theta$  by the  $\theta$ -2 $\theta$  scan method using Cu K $\alpha$  radiation post filtered with Ni foil. The scan range in 2 $\theta$  was from 1° below the Cu K $\alpha_1$  peak to 1° above the Cu K $\alpha_2$  peak and the rate of scan was 1° per minute. The takeoff angle was 3.3° and the counter was positioned 31 cm from the crystal with an aperture 3.0 mm high by 6.0 mm wide. Data were collected in the range 3° ≤ 2 $\theta$  ≤ 80°. Backgrounds were measured for 10 sec in the range 3-42°, for 40 sec in the range 42-67°, and for 100 sec in the range 67-80°. The intensities of six standard reflections were monitored every 75 reflections. These intensities decreased in an anisotropic manner as data collection proceeded. Data collection was terminated at 80° in 2 $\theta$  because of the fall-off in intensities of the standards and because of low inherent intensity from the small crystal.

The data were processed in the usual manner<sup>9</sup> using a value of 0.04 for  $p$ . Of the 3208 reflections measured only those 1814 unique reflections with  $F^2 > 3\sigma(F^2)$  were used in subsequent refinements. Because of the small size and the poorly defined shape of the crystal no absorption correction was made ( $\mu = 48.4$  cm<sup>-1</sup>). Moreover, since the decrease in the standards was anisotropic and limited to about 12% in the extreme no correction for decomposition was made.

Since the data set was obviously of less than normal quality two additional data collections similar to the first were made using new

crystals. Each of these data collections was of lower quality because of excessive crystal decomposition. These data were not used further.

Normalized structure factors ( $|E|$ 's) scaled such that  $\langle E^2 \rangle = 1.0$  were calculated from the measured structure amplitudes.<sup>10</sup> The statistical distribution of the  $|E|$ 's suggested that the correct space group is  $P\bar{1}$ .

Using the quantities  $(E^2 - 1)$  a sharpened, origin-removed Patterson map was calculated. This map was characterized by an exceedingly strong peak at ( $1/2, 1/2, 1/2$ ). There followed a long and expensive series of attempts at solution and refinement. Involved were a series of direct-methods programs as well as the Patterson map. All attempts at solution of the structure failed.

Eventually a laboratory fire occurred which destroyed the results of all previous computing efforts. We thus began anew. A structure factor calculation was made with a Co porphyrin at the origin as found in the original Patterson map and a Co atom at ( $1/2, 1/2, 1/2$ ). A difference map revealed what appeared to be an imidazole group bound to the origin Co atom in the axial position relative to the porphyrin and in addition a few peaks around the second Co atom which could be construed to be part of a second porphyrin in a different orientation. We then proceeded with a long series of structure factor calculations and difference maps in which two independent Co(imd)<sub>2</sub>(TPP)<sup>+</sup> ions were located. In addition a molecule of CHCl<sub>3</sub> solvent was found in the asymmetric unit.

Two independent Co(imd)<sub>2</sub>(TPP)<sup>+</sup> ions were obviously inconsistent with our original formulation for the compound and required the presence of a pair of anions in the unit cell. A difference map revealed a molecule consisting of four atoms. The molecule was planar with three atoms bonded to a central atom. Two of the atoms were within hydrogen bonding distance of the imidazole groups of the two independent Co(imd)<sub>2</sub>(TPP)<sup>+</sup> ions. From this evidence and the method of preparation of the Co(TPP), the molecule was identified with reasonable certainty as an acetate ion.

(9) (a) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); (b) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(10) See R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, **96**, 4440 (1974), for a listing of computer programs and other technical details.

Table III. Derived Phenyl Carbon Parameters and Calculated Hydrogen Positions

Phenyl carbon	x	y	z	B, Å <sup>2</sup>	x <sub>H</sub> <sup>a</sup>	y <sub>H</sub>	z <sub>H</sub>
PA-C(1) <sup>b</sup>	0.1936 (11)	0.0513 (7)	0.3908 (9)	3.6 (4)			
C(2)	0.1439 (8)	0.0602 (8)	0.4941 (13)	5.2 (5)	0.067	0.061	0.492
C(3)	0.1999 (12)	0.0657 (8)	0.6003 (10)	5.9 (6)	0.166	0.071	0.676
C(4)	0.3056 (12)	0.0623 (8)	0.6032 (9)	5.8 (5)	0.348	0.067	0.682
C(5)	0.3552 (8)	0.0534 (8)	0.4999 (14)	5.8 (5)	0.430	0.052	0.504
C(6)	0.2992 (11)	0.0480 (8)	0.3937 (10)	5.4 (5)	0.331	0.043	0.319
PB-C(1)	0.1936 (10)	0.2923 (7)	-0.0056 (13)	4.2 (5)			
C(2)	0.1769 (10)	0.3607 (10)	0.0750 (11)	5.7 (5)	0.127	0.349	0.124
C(3)	0.2291 (12)	0.4431 (8)	0.0696 (11)	7.5 (6)	0.222	0.491	0.023
C(4)	0.2980 (11)	0.4571 (7)	-0.0163 (14)	6.5 (6)	0.342	0.518	0.157
C(5)	0.3147 (10)	0.3887 (10)	-0.0969 (11)	7.0 (6)	0.368	0.402	-0.145
C(6)	0.2625 (11)	0.3064 (8)	-0.0915 (11)	5.5 (5)	0.274	0.259	0.823
PC-C(1)	0.6202 (11)	0.2953 (9)	0.6485 (16)	5.3 (5)			
C(2)	0.6484 (13)	0.3058 (9)	0.7678 (14)	8.6 (7)	0.650	0.357	0.822
C(3)	0.6756 (13)	0.2426 (13)	0.8040 (11)	10.8 (8)	0.700	0.249	0.891
C(4)	0.6745 (12)	0.1687 (10)	0.7208 (18)	8.2 (7)	0.698	0.123	0.755
C(5)	0.6464 (13)	0.1582 (8)	0.6014 (15)	9.8 (7)	0.647	0.107	0.549
C(6)	0.6192 (12)	0.2214 (12)	0.5653 (10)	8.8 (7)	0.597	0.216	0.479
PD-C(1)	0.8730 (10)	0.6496 (11)	0.4388 (18)	6.5 (6)			
C(2)	0.9045 (14)	0.6209 (9)	0.3484 (15)	10.0 (8)	0.865	0.580	0.286
C(3)	0.0087 (17)	0.6591 (12)	0.3238 (13)	11.5 (8)	0.048	0.651	0.259
C(4)	0.0813 (10)	0.7261 (12)	0.4096 (20)	7.9 (7)	0.163	0.761	0.414
C(5)	0.0497 (15)	0.7548 (9)	0.5200 (16)	11.4 (9)	0.095	0.800	0.596
C(6)	0.9456 (11)	0.7165 (12)	p. 5446 (12)	10.4 (8)	0.912	0.729	0.623
Hydrogen	x	y	z	Hydrogen	x	y	z
H-IC(1)	-0.215	0.026	-0.092	H-C(6)	0.278	0.205	0.353
H-IN(2)	-0.342	0.072	0.045	H-C(7)	0.277	0.293	0.206
H-IC(2)	-0.270	0.092	0.266	H-C(10)	0.227	0.253	0.613
H-IC(3)	-0.085	0.062	0.254	H-C(11)	0.406	0.231	0.650
H-IC(4)	-0.458	0.330	0.381	H-C(14)	0.809	0.404	0.639
H-IN(4)	-0.465	0.277	0.162	H-C(15)	0.906	0.539	0.566
H-IC(5)	0.474	0.377	0.053	H(1)-AC(1)	-0.420	-0.210	0.023
H-IC(6)	0.451	0.498	0.228	H(2)-AC(2)	-0.361	-0.108	0.059
H-C(2)	-0.060	0.231	0.214	H(3)-AC(3)	-0.442	-0.155	0.144
H-C(3)	0.077	0.111	0.357	H(CHCl <sub>3</sub> )	-0.272	0.264	0.113

<sup>a</sup> Position calculated for hydrogen of given phenyl carbon atom. <sup>b</sup> PA-C(1) is bound to CA of the porphyrin macrocycle; other carbon atoms are numbered in succession so that PA-C(4) is para to PA-C(1).

The structure was refined by full-matrix least-squares techniques.<sup>10</sup> The phenyl groups were treated as rigid groups of  $D_{6h}$  symmetry,  $d(C-C) = 1.397$  Å, in all refinements. Three cycles of refinement of all group and nongroup atoms with isotropic temperature factors assigned to each led to values of 0.18 and 0.21 for  $R$  and  $R_w$ . A difference map calculated at this point revealed the presence of a water molecule hydrogen bonded to the acetate anion. In the next cycle of refinement the Co atoms and the Cl atoms were allowed to vibrate anisotropically while the light atoms were restricted to isotropic vibration. This calculation reduced  $R$  and  $R_w$  to 0.14 and 0.14. Hydrogen positions were calculated for the 37 porphyrin, imidazole, and  $CHCl_3$  hydrogen atoms. The hydrogen atoms ( $C-H = 1.0$  Å,  $B(H) = B(C)$ ) of the acetate methyl group could be found in a difference map and were idealized ( $C-H = 1.0$  Å;  $\angle$ 's =  $109.5^\circ$ ,  $B(H) = B(C)$ ). The hydrogen atoms of the water molecule could not be found.

The final cycles with the hydrogen atoms added as fixed contributions reduced the agreement indices to 0.098 and 0.12 for  $R$  and  $R_w$ . Refinement was terminated at this point because the poor quality and limited number of data do not, in our opinion, justify a more elaborate vibration model.

An analysis of  $\sum w(|F_o| - |F_c|)^2$  as a function of setting angles, magnitude of  $|F_o|$ , and Miller indices shows a minor trend toward larger errors as the magnitude of  $|F_o|$  increased. The standard deviation of an observation of unit weight is 3.50 electrons.

A final difference map shows residual electron density with a magnitude of about 0.4 e/Å, about 20% the height of the O atom of the  $H_2O$ . A structure factor calculation for the 964 reflections having  $F_o^2 < 3\sigma(F_o^2)$ , which were omitted from the refinement, shows 78 reflections having  $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$ . Table I presents the values of  $10|F_o|$  and  $10|F_c|$  for reflections used in the refinement.<sup>11</sup> Table II lists the final atomic parameters. Table III lists the positions of the C atoms of the phenyl groups, derivable from the data of Table II, as well as the positions of the H atoms. The rms ampli-

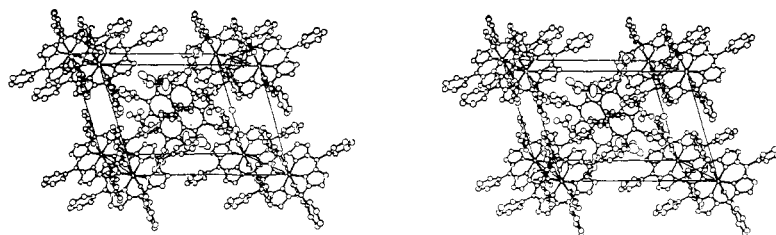
tudes of vibration for Co(1), Co(2), Cl(1), Cl(2), and Cl(3) are 0.144 (6), 0.227 (6), 0.292 (7); 0.143 (6), 0.230 (6), 0.297 (6); 0.367 (20), 0.442 (22), 0.809 (32); 0.368 (21), 0.576 (25), 0.744 (28); and 0.413 (23), 0.622 (27), 0.688 (29) Å, respectively. The principal axes of Co(1) and Co(2) make angles of 2 and  $12^\circ$ , respectively, with the normal to the porphyrin plane.

## Discussion

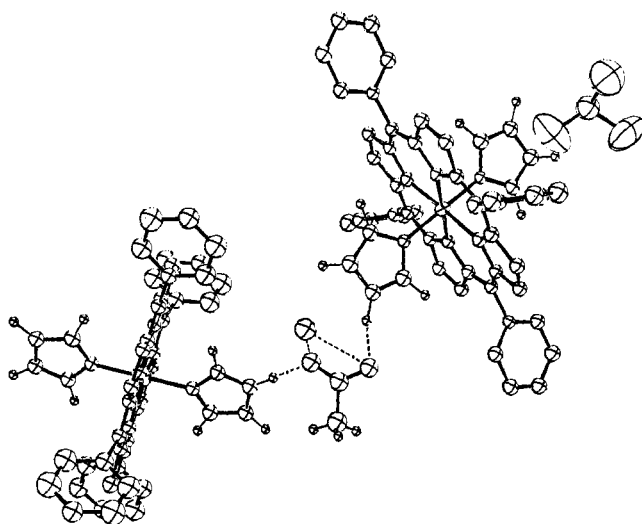
The structure consists of two independent  $Co(imd)_2(TPP)^+$  ions each with a crystallographically imposed center of symmetry. These two molecules are bridged together by acetate anions which hydrogen bond to the hydrogen atoms of the coordinated imidazole ligands. A molecule of water is also hydrogen bonded to each acetate anion although the hydrogen atoms have not been located. In addition there are two  $CHCl_3$  molecules in the unit cell. The molecules and ions are well separated in the unit cell and except for the hydrogen bonds show no unusual intermolecular distances. The molecular packing is illustrated in Figure 1.

Figure 2 shows the two independent porphyrin molecules with the acetate anion that bridges them. Also shown are the  $H_2O$  and  $CHCl_3$  molecules of solvation. Values for important bond distances and angles are listed in Tables IV and V. Figure 3 shows a representation of the imidazole groups along with important distances and angles. The bond lengths and angles in the acetate ions are reasonable and the two C-O bonds are equivalent. The acetate anion forms hydrogen bonds with the hydrogen atoms of the imidazole nitrogen atoms. Distances are 2.74 (2) Å for AO(1)-

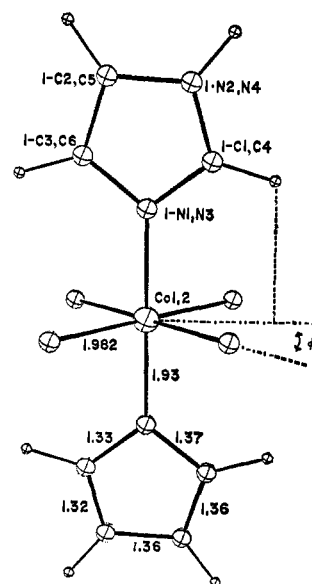
(11) See paragraph at end of paper regarding supplementary material.



**Figure 1.** A stereoscopic view of a unit cell of  $[\text{Co}(\text{Im})_2(\text{TPP})][\text{OAc}] \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$ . The view is down the  $x$  axis, the  $y$  axis is horizontal, and the  $z$  axis is vertical. The H atoms are omitted for the sake of clarity.



**Figure 2.** A perspective drawing showing the two independent centrosymmetric  $\text{Co}(\text{Im})_2(\text{TPP})^+$  ions, the acetate anion which bridges them, and the two solvent molecules,  $\text{H}_2\text{O}$  and  $\text{CHCl}_3$ . The dotted lines represent hydrogen bonds between the acetate anion and the hydrogens of the imidazole nitrogens and between the acetate and the  $\text{H}_2\text{O}$  molecule. Non-hydrogen atoms are drawn at their 35% probability ellipsoids. Hydrogen atoms have been drawn artificially small. Porphyrin hydrogens have been omitted for clarity.



**Figure 3.** A representation of the imidazole portion of the  $\text{Co}(\text{imd})_2(\text{TPP})^+$  ions. Only the nitrogen atoms of the porphyrins are represented. The upper portion of the figure shows the labeling schemes for the two independent imidazoles, the first label for imidazole 1 and the second for imidazole 2. The lower portion of the figure shows the mean bond distances for the two ions. The angle  $\varphi$  is shown and described in the text.

**Table IV.** Selected Bond Lengths (Å) and Bond Angles in (deg)

Co(1)–IN(1)	1.906 (15)	Co(1)–IN(1)–IC(1)	128.0 (14)
Co(2)–IN(2)	1.945 (15)	Co(2)–IN(3)–IC(4)	125.9 (14)
IN(1)–IC(1)	1.34 (2)	Co(1)–IN(1)–IC(3)	130.4 (13)
IN(3)–IC(4)	1.33 (2)	Co(2)–IN(3)–IC(6)	129.2 (14)
IC(1)–IN(2)	1.32 (2)	IC(3)–IN(1)–IC(1)	102 (2)
IC(4)–IN(4)	1.33 (2)	IC(6)–IN(3)–IC(4)	105 (2)
IN(2)–IC(2)	1.36 (2)	IN(1)–IC(1)–IN(2)	112 (2)
IN(4)–IC(5)	1.37 (2)	IN(3)–IC(4)–IN(4)	112 (2)
IC(2)–IC(3)	1.34 (2)	IC(1)–IN(2)–IC(2)	109 (2)
IC(5)–IC(6)	1.37 (2)	IC(4)–IN(4)–IC(5)	108 (2)
IC(3)–IN(1)	1.40 (2)	IN(2)–IC(2)–IC(3)	104 (2)
IC(6)–IN(3)	1.34 (2)	IN(4)–IC(5)–IC(6)	104 (2)
		IC(2)–IC(3)–IC(6)	113 (2)
		IC(5)–IC(6)–IN(3)	111 (2)
AC(1)–AC(2)	1.51 (3)	AO(1)–AC(1)–AO(2)	121 (2)
AC(1)–AO(1)	1.24 (2)	AO(1)–AC(1)–AC(2)	119 (2)
AC(1)–AO(2)	1.26 (2)	AO(2)–AC(1)–AC(2)	120 (2)
C–Cl(1)	1.64 (3)	Cl(1)–C–Cl(2)	108 (2)
C–Cl(2)	1.73 (3)	Cl(1)–C–Cl(3)	116 (2)
C–Cl(3)	1.72 (3)	Cl(2)–C–Cl(3)	104 (2)

IN(2) and 2.69 (2) Å for AO(2)–IN(4). The water molecule is also hydrogen bonded to the acetate ion; distances are 2.86 (2) Å for AO(1)–O( $\text{H}_2\text{O}$ ) and 2.97 (2) Å for AO(2)–O( $\text{H}_2\text{O}$ ). The chloroform molecule of solvent is ordered but does exhibit large thermal motion. The slow decomposition of the crystals may

**Table V.** Mean Bond Lengths (Å) and Bond Angles (deg) for the Chemically Equivalent Bonds in the Porphyrin Macrocycles<sup>a</sup>

	Mean <sup>b</sup>	Min <sup>c</sup>	Max <sup>c</sup>	No. <sup>d</sup>
Co–N	1.982 (11)	1.953 (14)	2.009 (15)	4
N–Ca	1.390 (6)	1.365 (19)	1.412 (19)	8
Ca–Cb	1.433 (5)	1.408 (23)	1.449 (22)	8
Cb–Cb'	1.340 (8)	1.325 (21)	1.361 (23)	4
Cb–Cm	1.378 (8)	1.346 (21)	1.408 (22)	8
Co–N–Ca	127.3 (5)	125.7 (12)	129.3 (13)	8
Ca–N–Ca	105.3 (14)	101.6 (16)	107.9 (16)	4
N–Ca–Cb	109.7 (9)	106.5 (16)	113.1 (18)	8
Cb–Ca–Cm	124.6 (7)	122.2 (19)	127.2 (19)	8
Ca–Cm–Ca	123.9 (6)	122.9 (18)	125.5 (18)	4

<sup>a</sup> The atom labels used in this table refer to general positions and have been defined previously.<sup>12</sup> <sup>b</sup> Mean value of bond length or angle with standard deviation in parentheses. <sup>c</sup> Min and Max refer to minimum and maximum individual values observed for each bond length or angle. <sup>d</sup> No. is the number of chemical equivalent bonds lengths or angles which occur.

result from loss of  $\text{CHCl}_3$ . This structure thus has two solvent molecules, a  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  molecule, and is a relatively rare example of a substance containing two molecules of solvation of such different character.

The porphyrin cores of the two molecules are essentially planar with all atoms within 0.07 Å of a calculated

least-squares plane of each porphyrin core. Overall the porphyrins retain the pseudo- $D_{4h}$  symmetry expected for metalloporphyrins.<sup>12</sup> Although individual bond lengths have rather large standard deviations (0.02 Å) the values found are in agreement with those for similar systems (Table IV).<sup>12</sup> The phenyl rings were treated as rigid groups in the refinement and the dihedral angles they make with their respective porphyrin plane are 66, 74, 86, and 88°. Values of less than 60° would be difficult to achieve because of steric interactions between the phenyl hydrogen atoms and the porphyrin pyrrole rings.

The equatorial cobalt to porphyrin nitrogen bond lengths average 1.98 (2) Å and are fixed by the rigidity of the porphyrin skeleton. The imidazole ligands occupy the axial positions of the cobalt porphyrins and these axial Co-N<sub>imd</sub> bond lengths are of immediate interest. Most Co(III) amine complexes have bond distances in the range of 1.94–1.97 Å.<sup>13</sup> In the simple hexaammine cobalt complex, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, a Co-NH<sub>3</sub> bond distance of 1.936 (15) Å was found.<sup>14</sup> Since the N atom of the NH<sub>3</sub> ligand is tetrahedrally coordinated while the N atom of the imidazole ligand is trigonal, we would expect the Co-N bond formed by the imidazole to be shorter than the Co-N bond distances observed in the various amine complexes. A comparison of the sp<sup>2</sup>-sp<sup>3</sup> radii of nitrogen<sup>15</sup> suggests that the shortening should be about 0.05–0.06 Å, and thus we would predict a Co-N<sub>imd</sub> bond length of 1.90 Å or less. The observed bond distances for the imidazole nitrogen atoms are 1.906 (15) Å for Co(1)-N(1) and 1.945 (15) Å for Co(2)-N(3) yielding an average value of 1.93 (2) Å. An examination of the intramolecular nonbonded distances between the imidazole groups and their respective porphyrin leads to a reasonable explanation for the slightly longer than expected distance.

In their analysis of the structure of the Fe(imd)<sub>2</sub>(TPP)<sup>+</sup> ion Collins, *et al.*,<sup>13</sup> have used an idealized model in which the complexing bond to the imidazole nitrogen is taken to be a dimensionally exact twofold axis. A dihedral angle ( $\varphi$ ) is defined between the imidazole plane and a second plane passing through the twofold axis and one of the porphyrin nitrogen atoms. (See Figure 3.) If  $\varphi$  is 0 or 90° there will be maximum steric interaction between the nitrogen atoms of the porphyrin ring and the hydrogen atoms of the imidazole ligand. At a  $\varphi$  value of 45° these steric interactions are minimized and the imidazole hydrogen atoms will point toward the methine carbon atoms. We now examine a series of cobalt and iron porphyrins with axial bases, listed in Table VI. Scheidt, *et al.*,<sup>16</sup> have found in the structure of the Co(pip)<sub>2</sub>(TPP)<sup>+</sup> ion a Co(III)-N<sub>pip</sub> bond length of 2.060 (3) Å. Steric interactions between the hydrogen atoms of the nonplanar piperidine ligand and the atoms of the porphyrin ring are severe and result in a Co-N<sub>pip</sub> bond that is about 0.1 Å longer than the Co(III)-N bond distances of 1.94–1.97 Å normally found in complexes with saturated amine bases. Takenaka, *et al.*,<sup>17</sup> have reported

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(15) See Table VIII of ref 10.

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**Table VI.** Axial Bond Distances and Angle  $\varphi$  for Selected Metalloporphyrins

	M-N <sub>b</sub> (Å)	$\varphi^a$ (deg)	Ref
Co(pip) <sub>2</sub> (TPP) <sup>+</sup>	2.060 (3)		<i>b</i>
Fe(imd) <sub>2</sub> (OEP) <sup>+</sup>	2.01	7	<i>c</i>
Fe(imd) <sub>2</sub> (TPP) <sup>+</sup>	1.997 (5)	18	<i>d</i>
	1.957 (4)	39	
Co(imd) <sub>2</sub> (TPP) <sup>+</sup>	1.945 (15)	43	<i>e</i>
	1.909 (15)	42	

<sup>a</sup> Defined in text. <sup>b</sup> Reference 16. <sup>c</sup> Reference 17. <sup>d</sup> Reference 13. <sup>e</sup> This work.

the structure of the bis(imidazole)octaethylporphyrinato-iron(III) ion (Fe(imd)<sub>2</sub>(OEP)<sup>+</sup>). In this structure the dihedral angle  $\varphi$  is 7°, steric interactions are severe, and a long Fe-N<sub>imd</sub> bond length of 2.01 Å is found. In the Fe(imd)<sub>2</sub>(TPP)<sup>+</sup> structure<sup>13</sup> there are two independent Fe-N<sub>imd</sub> bonds. The first imidazole has a  $\varphi$  value of 18° and a correspondingly long bond distance of 1.997 Å for Fe-N<sub>imd</sub>. The second imidazole has a  $\varphi$  value of 39° and a shorter bond of 1.957 Å. The shortest nonbonded intramolecular contact distances are 2.56–2.58 Å for the first imidazole and about 2.7 Å for the second.

In the present Co(imd)<sub>2</sub>(TPP)<sup>+</sup>  $\varphi$  is nearly 45° and shorter bond lengths are found. The closest nonbonded contact is 2.57 Å between the hydrogen atom of the imidazole carbon, IC(3), and a porphyrin C atom; all other short contacts are greater than 2.6 Å. If  $\varphi$  were 0° the hydrogen atoms of the imidazole ligands would directly eclipse the nitrogen atoms of the porphyrins and there would be close contacts of less than 2.4 Å. We believe that the close contacts that do exist prevent the imidazole group from coming closer to the porphyrin plane as would be predicted for a nonsterically hindered imidazole cobalt(III) complex. We thus believe that 1.93 Å represents the closest approach of an imidazole group to a porphyrin plane and we shall employ this value in our discussion<sup>8</sup> that follows on the trigger mechanism for the oxygenation of cobalt substituted hemoglobin. This correspondence between metal-nitrogen bond lengths and imidazole orientation seems to be real and may have a role in natural systems. Whenever an axial ligand of a metalloporphyrin shortens its bond length to the central metal, a corresponding twist of that ligand may be needed to relieve steric interactions.

Since the crystals isolated were thought to be of a different composition than was found, the presence of acetate anions was not expected. The identification of the anion as an acetate is consistent with the source of the Co(TPP) starting material, prepared in acetic acid-chloroform solution from Co(Ac)<sub>2</sub>·6H<sub>2</sub>O and H<sub>2</sub>TPP by the method of Falk. The presence of acetate in the starting material points out the difficulties of purification in porphyrin systems. Presumably, reaction of acetic acid with either a Co(III) hydroxy complex or a  $\mu$ -peroxy dimer in the presence of excess imidazole yielded the present compound.

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**Supplementary Material Available.** A listing of structure 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, 24 × 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. 200036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche referring to code number JACS-74-4447.

## Stereochemistry of Cobalt Porphyrins. III. The Structure of 2,3,7,8,12,13,17,18-Octaethylporphinato(1-methylimidazole)-cobalt(II). A Model for Deoxycoboglobin

Robert G. Little and James A. Ibers\*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received December 28, 1973

**Abstract:** The five-coordinate Co(II) porphyrin, Co(1-Me-Im)(OEP), has been prepared and its structure determined from three-dimensional X-ray diffraction data. The complex crystallizes with four formula units in the monoclinic space group  $C_{2h}^5-P2_1/n$  with  $a = 14.049(4) \text{ \AA}$ ,  $b = 17.587(8) \text{ \AA}$ ,  $c = 14.331(5) \text{ \AA}$ , and  $\beta = 95.20(1)^\circ$ . The cobalt atom is  $0.16(1) \text{ \AA}$  out of the mean plane of the porphyrin toward the imidazole ligand. The averaged Co-N(imidazole) and Co-N(porphyrin) bond lengths are  $2.15(1)$  and  $1.96(1) \text{ \AA}$ , respectively. The porphyrin itself is significantly nonplanar. Some of the  $\beta$ -C atoms of the ethyl groups are disordered. The structure suggests that the out-of-plane displacement of the cobalt atom in deoxycoboglobin is small compared with the displacement of the iron atom in hemoglobin and comparable with that in methemoglobin. In view of the fact that CoHb and met-Hb have differing quaternary structures, we conclude that structure of deoxy-CoHb is inconsistent with both the trigger mechanism of Perutz and the linear energy distribution model of Hopfield.

In an impressive series of papers<sup>1,2a</sup> Hoard and his co-workers have demonstrated that the porphyrin macrocycle is a remarkably flexible ligand<sup>3-5</sup> and that the chelated metal atom can be displaced considerably from the plane of the porphyrin.<sup>6-7</sup> Hoard concluded<sup>1,6</sup> that the displacement of the metal atom is related to its effective radius, since the size of the central "hole" in the porphyrin is relatively constant. On this basis he predicted<sup>2</sup> that the high-spin ferrous ion in deoxy-Hb<sup>10</sup> and Mb is five-coordinate and is displaced

from the porphyrin plane toward the proximal histidine by 0.5–0.8 Å. Upon binding an oxygen molecule, the iron atom becomes six-coordinate and low spin, and moves back into the plane of the porphyrin. An alternative description of this process suggests that oxy-Hb can be formally described as Fe(III)-O<sub>2</sub><sup>-</sup>.<sup>1,2</sup> The oxy to deoxy transition would then involve a change from high-spin Fe(II) to low-spin Fe(III) with a concomitant decrease in the radius of the iron atom.

Williams<sup>13</sup> and Hoard<sup>2b</sup> have suggested that the movement of the iron atom causes a change in the position of the imidazole group of the proximal histidine and that this leads to movements in the protein framework. On the basis of his structural studies of oxy-(met) and deoxy-Hb Perutz<sup>14,15</sup> has proposed that this is indeed the case and that this movement triggers conformational changes in the protein which result in an increased oxygen affinity—the so-called cooperative effect.<sup>16</sup> The large effective radius of a high-spin,  $t_{2g}^4 e_g^2$ , ferrous ion results mainly from the presence of electrons in the  $e_g$  orbitals. The d<sup>7</sup>-cobaltous ion also has an unpaired electron in the  $e_g$

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(10) The following abbreviations are used throughout: Hb, ferrous hemoglobin; Mb, ferrous myoglobin; CoHb, Co(II)-reconstituted Hb; met-Hb, ferric hemoglobin. 1-Me-Im, 1-methylimidazole; Im, imidazole; py, pyridine; 3-pic, 3-methylpyridine; pip, piperidine; TPP, meso-tetraphenylporphyrin dianion; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion;<sup>11</sup> PP-IX, 2,7,12,18-tetramethyl-3,8-divinylporphine-13,17-dipropionic acid dianion; MP-IX, 2,7,12,18-tetramethyl-3,8-diethylporphine-13,17-dipropionic acid dianion; MP-IX DME, dimethyl ester of MP-IX. DMG, dimethylglyoxime dianion; salen, N,N'-ethylenebis(salicylidene) dianion; py-salen,  $\alpha,\alpha'$ -{2-(2-

pyridyl)ethyl}ethylenebis(salicylidene) dianion; bae, N,N'-ethylenebis(benzoylacetoneimine) dianion; acacen, N,N'-ethylenebis(acetylacetoneimine) dianion; acac, acetylacetone anion; OAc, acetate anion.

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