

# Stereochemistry of Low-Spin Cobalt Porphyrins. II. The Bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(III) Cation in a Crystalline Solvated Salt<sup>1</sup>

W. Robert Scheidt,<sup>2a</sup> James A. Cunningham,<sup>2b</sup> and J. L. Hoard\*<sup>2b</sup>

Contribution from the Departments of Chemistry, Cornell University, Ithaca, New York 14850, and the University of Notre Dame, Notre Dame, Indiana 46656. Received May 10, 1973

**Abstract:** Abbreviating the dianion of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine as TPP<sup>2-</sup> and piperidine as Pip, the content of the triclinic unit cell of the solvated salt for which structure determination is reported may be written as [Pip<sub>2</sub>-CoTPP]<sup>+</sup>[NO<sub>3</sub>,HCO<sub>3</sub>]<sup>-</sup>·2Pip. Pertinent crystal data are: space group *P* $\bar{1}$ ;  $a = 12.049$ ,  $b = 12.911$ , and  $c = 10.405$  Å;  $\alpha = 102.73$ ,  $\beta = 92.04$ , and  $\gamma = 65.24^\circ$ ;  $Z = 1$ ;  $\rho_{\text{calcd}} = 1.247$  and  $\rho_{\text{exptl}} = 1.241$  g/cm<sup>3</sup> at  $20 \pm 1^\circ$ . Intensity data for 8415 independent reflections having  $(\sin \theta)/\lambda < 0.743$  Å<sup>-1</sup>, recorded with Zr-filtered Mo K $\alpha$  radiation on a Picker FACS-I diffractometer, were employed for the determination and least-squares refinement of the 367 variable parameters of the structure. All bond parameters in the Pip<sub>2</sub>CoTPP<sup>+</sup> ion are sharply defined and, excepting the metal–nitrogen bond distances, are very similar to those reported for the isoelectronic Pip<sub>2</sub>FeTPP molecule. Averaged equatorial bond lengths of Co(III)–N = 1.978 Å and Fe(II)–N = 2.004 Å, along with axial bond lengths of Co(III)–N = 2.060 Å and Fe(II)–N = 2.127 Å, reflect the difference in nuclear charge of the metal atoms. Statistical half-occupancy of the positions assigned to the trigonal anions gives rise to a loose disordered packing with the piperidine solvate molecules and, consequently, to bond parameters for both species that are only semiquantitative. Neither the X-ray data nor the elemental analyses afford a convincing basis for a definite choice between NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> as the counterion.

Interesting crystals containing the bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(III) cation (written hereinafter as Pip<sub>2</sub>CoTPP<sup>+</sup>) for which we report an X-ray structural analysis are preparable by the chemically mysterious procedure set forth in the Experimental Section. The contents of the triclinic unit cell are a single centrosymmetric Pip<sub>2</sub>CoTPP<sup>+</sup> ion, two additional uncomplexed molecules of piperidine (NC<sub>5</sub>H<sub>11</sub>), and just one trigonal or quasi-trigonal anion, nitrate or bicarbonate. Because this single anion may occupy either of two equivalent positions in the unit cell, the resulting crystalline arrangement is characterized by statistical disorder in association with very loose packing of the anions and the piperidine solvate molecules. Inasmuch as neither the X-ray data nor the chemical analyses lead to the unambiguous identification of the anionic species, the formulation, [Pip<sub>2</sub>CoTPP]<sup>+</sup>[NO<sub>3</sub>,NCO<sub>3</sub>]<sup>-</sup>·2NC<sub>5</sub>H<sub>11</sub>, allows for the maximum variation in the composition of the crystalline salt. This regrettable ambiguity notwithstanding, all stereochemical parameters of the Pip<sub>2</sub>CoTPP<sup>+</sup> ion are quite precisely defined in the crystalline arrangement. Comparison of these parameters with those in the analogous iron(II) and cobalt(II) species, Pip<sub>2</sub>FeTPP<sup>3</sup> and Pip<sub>2</sub>CoTPP,<sup>4</sup> are particularly illuminating (see Discussion).

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(2) (a) University of Notre Dame; (b) Cornell University. The study reported was initiated and largely developed at Cornell University. Subsequent papers will cover studies carried out at the University of Notre Dame.

(3) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972).

(4) W. R. Scheidt, *ibid.*, in press.

## Experimental Section

A few dark blue crystals of the new compound were first observed in the tar-like residue from the slow isothermal evaporation of a chloroform–piperidine solution (1:1 by volume) of nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II)<sup>5</sup> (ONCoTPP) which had been used in a pmr experiment. Following their mechanical separation from the residue, these crystals were washed with a small amount of cold methanol. One excellent specimen having the approximate dimensions, 0.22 × 0.27 × 0.29 mm, was immediately subjected to preliminary X-ray study by photographic methods and was subsequently employed for the measurement of diffracted intensities on a Picker FACS-I diffractometer. Structure determination had progressed to an advanced stage before we succeeded in preparing the compound in sufficient quantity for elemental analyses, for the determination of its essentially diamagnetic character, and for the recording of its infrared spectrum—which displayed no absorption band attributable to a nitrosyl stretching frequency. The desired compound was obtained by duplicating in essence the conditions in which the first crystals appeared; extending the period of isothermal evaporation over a period of 3 or more weeks was the key to success. X-Ray single-crystal photographic techniques were employed to verify isomorphism of the successful preparations.

Preliminary X-ray study of the crystal by photographic methods together with the experimentally measured density, 1.241 (6) g/cm<sup>3</sup> by flotation at  $20 \pm 1^\circ$ , led to a triclinic unit of structure with a cell content consistent with any of the formulations listed in Table I. Lattice constants ( $\lambda$  0.70926 Å) of  $a = 12.049$  (3),  $b = 12.911$  (3), and  $c = 10.405$  (5) Å;  $\cos \alpha = -0.2203$  (4),  $\cos \beta = -0.0356$  (4), and  $\cos \gamma = 0.4188$  (1); or  $\alpha = 102.73$ ,  $\beta = 92.04$ , and  $\gamma = 65.24^\circ$  came from a least-squares refinement<sup>6</sup> which utilized the setting angles of 38 reflections in the range,  $40^\circ < 2\theta < 52^\circ$ , as given by the automatic centering routine supplied with the FACS-I diffractometer. The noncentrosymmetric space group *P*1<sup>7</sup> was seen to be required for an ordered structure based upon any one of the formulations listed in Table I.

Intensity data were measured on the Picker FACS-I diffractometer using the  $\theta$ – $2\theta$  scanning technique with Zr-filtered Mo K $\alpha$  radiation at a takeoff angle of  $\sim 2^\circ$ . The range of each scan, taken

(5) W. R. Scheidt and J. L. Hoard, *ibid.*, **95**, 8281 (1973).

(6) The program PICK II, a modification of W. C. Hamilton's MODE I program was used.

(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 74.

**Table I.** Formulations Considered for the Content of the Unit Cell

Formulation <sup>a</sup>	Density (calcd), g/cm <sup>3</sup>
I ONCo(Pip)TPP · CHCl <sub>3</sub> · 2Pip	1.249
II ONCo(Pip)TPP · 2CHCl <sub>3</sub> · Pip	1.289
III [Pip <sub>2</sub> CoTPP] <sup>+</sup> [HCO <sub>3</sub> ] <sup>-</sup> · 2Pip	1.246
IV [Pip <sub>2</sub> CoTPP] <sup>+</sup> [NO <sub>3</sub> ] <sup>-</sup> · 2Pip	1.247
V Pip <sub>2</sub> CoTPP · CHCl <sub>3</sub> · 2Pip	1.266

<sup>a</sup> Abbreviated notations used: TPP<sup>2-</sup> for the dianion of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine, Pip for piperidine.

at 1°/min, consisted of the base width of 1.7° at  $2\theta = 0^\circ$  and an increment,<sup>8</sup>  $\Delta(2\theta) = (0.692 \tan \theta)^\circ$ , to allow for spectral dispersion; background counts, each of 40-sec duration, were taken at the limits of the scan. The intensities of three standard reflections, monitored every 50 reflections, displayed no trend with time. All independent data ( $\sim 9840$ ) having  $(\sin \theta)/\lambda < 0.743 \text{ \AA}^{-1}$  ( $2\theta = 63.7^\circ$ ) were thus measured.

The intensities of the independent data were reduced directly to a set of relative squared amplitudes,  $|F_o|^2$ , by the application of the standard Lorentz and polarization factor (Lp). Standard deviations were calculated from  $\sigma^2(F_o) = (Ct + k^2B)/4|F_o|^2(Lp)^2$ , where  $Ct$  is the accumulated deacount of the scan,  $k$  is the ratio of scanning time to background counting time, and  $B$  is the total background deacounts. All data for which  $|F_o| < 0.67\sigma(F_o)$  were taken as observed. This rejection level was chosen to ensure the retention of all reflections objectively observed as recognizable peaks on a strip chart record of the scan. Thus, 8415 unique reflections were retained for the determination and refinement of the structure. With the cited dimensions of the crystal and a linear absorption coefficient not greater than  $0.62 \text{ mm}^{-1}$  (that for formulation II in Table I), the maximum error in any measured intensity resulting from the neglect of absorption corrections was seen to be  $< 3\%$ .

A three-dimensional Patterson synthesis of the  $|F_o|^2$  data having  $(\sin \theta)/\lambda < 0.515 \text{ \AA}^{-1}$  clearly displayed the orientations of the porphyrinato core and of the attached phenyl groups. Rational positions for the nitrogen and carbon atoms in the porphyrinato core were obtained from the necessarily centrosymmetric Fourier synthesis<sup>9</sup> phased by the contribution from the cobalt atom at the origin. In further stages of successive approximation by Fourier synthesis, it became evident that the cobalt atom carries two piperidine ligands—thus eliminating the initially plausible formulations I and II—and, furthermore, that the porphyrin entity deviates little, if at all, from  $C_{2v}$  symmetry in the crystal. Approximate positions for two piperidine molecules of crystallization and for a four-atom grouping tentatively identified as a chloroform molecule also were forthcoming. This noncentrosymmetric structural model, which conforms to formulation V in Table I, was then subjected to isotropic block-diagonal least-squares refinement<sup>10</sup> using all of the amplitude data. The resulting transformation of the four-atom grouping into a virtually planar quasi-trigonal entity having neither the geometry nor the large scattering power of a chloroform molecule eliminated formulation V from further consideration.

At this point, the results of the auxiliary physical measurements mentioned above became available. The absence of any absorption band attributable to nitrosyl in the infrared spectrum of the crystals was in full agreement with the structural data and, furthermore, it suggested that the diamagnetism of the crystals must be ascribed to the presence of the d<sup>8</sup> cobalt(III) atom in the porphyrin to give the Pip<sub>2</sub>CoTPP<sup>+</sup> ion.<sup>11</sup> This meant that the quasi-trigonal four-atom entity must then be the required counterion. The two chemically rational candidates for this role were the nitrate ion, derived by

(8) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966, p 79.

(9) Use was made of A. Zalkin's Fourier program, FORDAP. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections for anomalous dispersion in the form factor of the cobalt atom from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(10) The block-diagonal least-squares program, REFINE, written by J. J. Park, Cornell University, was used. The function minimized was  $\sum_w (F_o - |F_c|)^2$ .

(11) An even more cogent basis for this conclusion was subsequently provided by the determination of structure for the uncharged Pip<sub>2</sub>CoTPP species.<sup>4</sup> The axial Co(II)-N bond distances in this molecule are  $\sim 0.37 \text{ \AA}$  longer than the corresponding Co(III)-N linkages in the Pip<sub>2</sub>CoTPP<sup>+</sup> ion (see Discussion).

**Table II.** Atomic Coordinates in the Unit Cell<sup>a</sup>

Atom type <sup>b</sup>	Coordinates		
	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z
Co	0	0	0
N <sub>1</sub>	1206 (2)	-1598 (2)	85 (3)
N <sub>2</sub>	1260 (2)	222 (2)	-922 (2)
C <sub>m1</sub>	-63 (3)	-2210 (3)	1286 (3)
C <sub>m2</sub>	3059 (3)	-1632 (3)	-896 (3)
C <sub>a1</sub>	2436 (3)	-2125 (3)	-309 (3)
C <sub>a2</sub>	1014 (3)	-2396 (3)	640 (3)
C <sub>a3</sub>	1117 (3)	1175 (3)	-1427 (3)
C <sub>a4</sub>	2480 (3)	-550 (3)	-1217 (3)
C <sub>b1</sub>	3009 (3)	-3265 (3)	-25 (4)
C <sub>b2</sub>	2123 (3)	-3438 (3)	542 (4)
C <sub>b3</sub>	2238 (3)	965 (3)	-2101 (4)
C <sub>b4</sub>	3080 (3)	-95 (3)	-1965 (4)
C <sub>11</sub>	-82 (3)	-3140 (3)	1908 (3)
C <sub>12</sub>	-183 (5)	-4802 (4)	3152 (6)
C <sub>13</sub>	-738 (4)	-3789 (4)	1375 (5)
C <sub>14</sub>	-784 (5)	-4622 (4)	2014 (6)
C <sub>15</sub>	542 (4)	-3344 (3)	3041 (4)
C <sub>16</sub>	491 (5)	-4183 (4)	3660 (5)
C <sub>17</sub>	4416 (3)	-2275 (3)	-1154 (3)
C <sub>18</sub>	6959 (3)	-3468 (4)	-1544 (5)
C <sub>19</sub>	5162 (3)	-1786 (3)	-484 (4)
C <sub>20</sub>	6441 (4)	-2388 (4)	-678 (5)
C <sub>21</sub>	4949 (3)	-3359 (3)	-2038 (4)
C <sub>22</sub>	6224 (4)	-3947 (4)	-2231 (4)
N <sub>3</sub>	-388 (2)	-721 (2)	-1834 (3)
C <sub>p1</sub>	-1149 (4)	-1390 (4)	-1825 (4)
C <sub>p2</sub>	-1008 (5)	-535 (4)	-4139 (4)
C <sub>p3</sub>	-1782 (5)	-1210 (4)	-4127 (5)
C <sub>p4</sub>	-1231 (5)	-2047 (4)	-3211 (4)
C <sub>p5</sub>	-928 (4)	104 (4)	-2725 (4)
C <sub>s1</sub>	4602 (13)	3605 (9)	7372 (12)
C <sub>s2</sub>	5506 (13)	2397 (11)	7223 (14)
C <sub>s3</sub>	4904 (15)	1650 (11)	6338 (23)
C <sub>s4</sub>	4639 (12)	1956 (13)	5106 (13)
C <sub>s5</sub>	4351 (16)	3817 (13)	5975 (17)
C <sub>s6</sub>	3694 (13)	3134 (15)	5354 (13)
O <sub>1</sub>	3235 (13)	6064 (10)	5148 (9)
O <sub>2</sub>	1996 (9)	7834 (10)	6066 (10)
O <sub>3</sub>	1903 (7)	6659 (11)	6783 (9)
N <sub>4</sub>	2277 (10)	6907 (11)	6022 (10)

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure. <sup>b</sup> Atoms are identified in agreement with Figures 1-4.

oxidation of the initially coordinated nitrosyl group, and the bicarbonate ion, derived by the reaction of slowly absorbed water and carbon dioxide (from the surroundings) with the strongly basic medium during the period of 3 or more weeks required for the appearance of the crystals.

The least-squares refinement was then continued with the four-atom grouping taken to be the nitrate ion and, simultaneously, with the assignment of anisotropic thermal parameters to the atoms in the complex cation. It was then noted that (1) the two piperidine solvate molecules were positioned in a nearly centrosymmetric relation to one another; (2) the estimated standard deviations in the coordinates of the atoms in the Pip<sub>2</sub>CoTPP<sup>+</sup> ion were unexpectedly large; (3) the departures from  $\bar{1}$  symmetry in this complex, both in respect to chemically analogous bond lengths and thermal parameters, followed a structurally rather implausible pattern; and (4) the apparent thermal parameters of the atoms in the nitrate ion were extraordinarily large. A difference Fourier synthesis, computed with the complex phases of this noncentrosymmetric model and with all of the observed data included, then revealed four residual peaks with densities of  $\sim 2 \text{ e/\AA}^3$  which were positioned in approximate centrosymmetric relation to the four atoms of the nitrate group. In view of these considerations, further least-squares refinement was based upon the centrosymmetric space group  $P\bar{1}$  with the nitrate ion distributed equally between two equivalent positions relative to the cobalt atom at the origin. Two cycles of refinement led to markedly smaller estimated standard deviations for the coordinates and decreased spread, to  $< 0.01 \text{ \AA}$ , in the values of chemically analogous bond lengths in the complex cation.

Fully anisotropic least-squares refinement of structure was then

**Table III.** Thermal Parameters<sup>a</sup>

Atom type <sup>b</sup>	Anisotropic parameters, ° Å <sup>2</sup>					
	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Co	1.79 (2)	1.71 (2)	2.50 (2)	-0.58 (1)	-0.05 (1)	0.75 (2)
N <sub>1</sub>	2.0 (1)	2.0 (1)	2.8 (1)	-0.6 (1)	0.0 (1)	0.9 (1)
N <sub>2</sub>	2.0 (1)	1.9 (1)	2.8 (1)	-0.6 (1)	0.1 (1)	0.8 (1)
C <sub>m1</sub>	2.6 (1)	2.1 (1)	2.9 (1)	-0.9 (1)	-0.1 (1)	1.0 (1)
C <sub>m2</sub>	2.0 (1)	2.2 (1)	3.1 (1)	-0.6 (1)	-0.0 (1)	0.7 (1)
C <sub>n1</sub>	2.0 (1)	2.2 (1)	3.3 (1)	-0.6 (1)	0.1 (1)	0.9 (1)
C <sub>a2</sub>	2.2 (1)	2.0 (1)	3.2 (1)	-0.6 (1)	-0.1 (1)	1.1 (1)
C <sub>a3</sub>	2.3 (1)	2.1 (1)	2.9 (1)	-0.8 (1)	0.0 (1)	0.9 (1)
C <sub>a4</sub>	2.0 (1)	2.2 (1)	2.9 (1)	-0.7 (1)	0.1 (1)	0.6 (1)
C <sub>b1</sub>	2.6 (1)	2.4 (1)	4.1 (2)	-0.4 (1)	0.1 (1)	1.4 (1)
C <sub>b2</sub>	2.7 (1)	2.2 (1)	4.3 (2)	-0.4 (1)	0.0 (1)	1.4 (1)
C <sub>b3</sub>	2.7 (1)	2.8 (1)	3.5 (1)	-1.0 (1)	0.4 (1)	1.1 (1)
C <sub>b4</sub>	2.6 (1)	2.7 (1)	3.8 (2)	-0.9 (1)	0.5 (1)	1.0 (1)
C <sub>11</sub>	2.7 (1)	2.2 (1)	3.4 (1)	-0.7 (1)	0.3 (1)	1.2 (1)
C <sub>12</sub>	6.1 (3)	3.1 (2)	6.7 (3)	-0.4 (2)	2.8 (2)	2.4 (2)
C <sub>13</sub>	3.9 (2)	3.3 (1)	5.9 (2)	-1.8 (1)	0.0 (2)	1.5 (2)
C <sub>14</sub>	5.2 (2)	3.5 (2)	7.7 (3)	-2.2 (2)	1.2 (2)	1.8 (2)
C <sub>15</sub>	4.2 (2)	3.1 (1)	3.5 (2)	-0.6 (1)	0.3 (1)	1.4 (1)
C <sub>16</sub>	6.1 (2)	3.7 (2)	4.3 (2)	-0.2 (2)	1.6 (2)	2.0 (2)
C <sub>17</sub>	2.0 (1)	2.4 (1)	3.4 (1)	-0.6 (1)	0.1 (1)	0.8 (1)
C <sub>18</sub>	2.3 (1)	4.5 (2)	5.4 (2)	-0.6 (1)	0.2 (1)	1.4 (1)
C <sub>19</sub>	2.6 (1)	3.4 (1)	4.5 (2)	-1.0 (1)	-0.1 (1)	0.5 (1)
C <sub>20</sub>	2.6 (1)	4.8 (2)	5.8 (2)	-1.4 (1)	-0.4 (1)	0.9 (2)
C <sub>21</sub>	2.6 (1)	3.0 (1)	4.0 (2)	-0.6 (1)	0.1 (1)	0.4 (1)
C <sub>22</sub>	2.7 (1)	3.6 (2)	4.4 (2)	-0.1 (1)	0.5 (1)	0.4 (1)
N <sub>3</sub>	2.6 (1)	2.3 (1)	2.9 (1)	-1.1 (1)	-0.3 (1)	0.9 (1)
C <sub>p1</sub>	5.0 (2)	4.5 (2)	3.2 (1)	-3.4 (2)	-0.8 (1)	1.1 (1)
C <sub>p2</sub>	7.2 (3)	5.2 (2)	3.4 (2)	-3.9 (2)	-2.0 (2)	1.9 (2)
C <sub>p3</sub>	5.5 (2)	5.0 (2)	4.0 (2)	-3.0 (2)	-1.6 (2)	1.3 (2)
C <sub>p4</sub>	6.4 (2)	4.5 (2)	3.5 (2)	-3.5 (2)	-1.3 (2)	1.1 (1)
C <sub>p5</sub>	5.9 (2)	3.5 (2)	3.3 (2)	-2.5 (2)	-1.8 (1)	1.7 (1)
C <sub>s1</sub>	18.6 (11)	8.1 (6)	11.4 (7)	-2.2 (6)	-5.8 (7)	-2.2 (5)
C <sub>s2</sub>	15.4 (10)	12.9 (8)	14.8 (9)	-6.5 (8)	-7.7 (8)	6.7 (7)
C <sub>s3</sub>	18.7 (12)	9.8 (7)	42.1 (25)	-9.5 (8)	-16.2 (15)	12.6 (11)
C <sub>s4</sub>	13.0 (8)	18.8 (11)	13.0 (8)	-4.4 (8)	0.5 (7)	-8.9 (8)
C <sub>s5</sub>	27.7 (15)	14.7 (9)	27.0 (16)	-16.6 (11)	-20.3 (14)	15.4 (10)
C <sub>s6</sub>	16.4 (11)	23.8 (15)	13.5 (8)	-13.3 (11)	-9.4 (8)	8.6 (9)
O <sub>1</sub>	15.0 (9)	8.8 (6)	5.1 (4)	-6.4 (7)	-1.5 (5)	-0.5 (4)
O <sub>2</sub>	7.2 (5)	8.3 (6)	8.0 (5)	-1.2 (4)	-3.1 (4)	-0.7 (5)
O <sub>3</sub>	4.9 (4)	12.2 (8)	5.8 (4)	-3.2 (4)	-1.4 (4)	-1.4 (5)
N <sub>4</sub>	5.0 (5)	6.8 (6)	4.3 (4)	-1.1 (4)	-2.1 (3)	-1.5 (5)

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure. <sup>b</sup> Atoms are identified in agreement with Figures 1–4. <sup>c</sup> The *B*<sub>*ij*</sub> are related to the dimensionless β<sub>*ij*</sub> employed during refinement as *B*<sub>*ij*</sub> = 4β<sub>*ij*</sub>/a\*<sub>*i*</sub>a\*<sub>*j*</sub>.

carried to convergence using all of the 8415 *F*<sub>o</sub> data with empirical weights, *w* = 1/σ<sup>2</sup>, calculated from

$$\sigma = \sum_0^3 a_n |F_o|^n$$

the *a*<sub>*n*</sub> being coefficients from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n |F_o|^n$$

With 367 parameters and a data/parameter ratio of 8415/367 = 23, values of the conventional *R*<sub>1</sub> of 0.102 and the weighted *R*<sub>2</sub> of 0.118 were obtained; the goodness of fit parameter was 0.922. A final difference Fourier synthesis had no peak above 0.80 e/Å<sup>3</sup>. Several peaks with heights in the range from 0.40 to 0.65 e/Å<sup>3</sup> were apparently associated with the somewhat disordered “half-anions” and piperidine solvate molecules, while others were positioned to be convincingly interpreted as C–H bond densities within the Pip<sub>2</sub>-CoTPP cation. Hydrogen contributions were not included in the refinement of structure owing to the excessive cost of all of the least-squares computations.<sup>12</sup>

The atomic coordinates and the associated thermal parameters in the asymmetric unit of structure are listed in Tables II and III, respectively; bond parameters<sup>13</sup> are listed in Tables IV–VII. The

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

Type <sup>b</sup>	Length (Å)	Type <sup>c</sup>	Length (Å)	Type <sup>b</sup>	Length (Å)
Co–N <sub>1</sub>	1.983 (3)	C <sub>m1</sub> –C <sub>11</sub>	1.494 (5)	C <sub>b1</sub> –C <sub>b2</sub>	1.365 (5)
Co–N <sub>2</sub>	1.974 (3)	C <sub>m2</sub> –C <sub>a1</sub>	1.395 (5)	C <sub>b3</sub> –C <sub>b4</sub>	1.355 (5)
Co–N <sub>3</sub>	2.060 (3)	C <sub>m2</sub> –C <sub>a4</sub>	1.386 (5)	N <sub>3</sub> –C <sub>p5</sub>	1.492 (5)
N <sub>1</sub> –C <sub>a1</sub>	1.380 (4)	C <sub>m2</sub> –C <sub>17</sub>	1.493 (5)	N <sub>3</sub> –C <sub>p1</sub>	1.501 (5)
N <sub>1</sub> –C <sub>a2</sub>	1.385 (4)	C <sub>a1</sub> –C <sub>b1</sub>	1.433 (5)	C <sub>p1</sub> –C <sub>p4</sub>	1.527 (6)
N <sub>2</sub> –C <sub>a3</sub>	1.386 (4)	C <sub>a2</sub> –C <sub>b2</sub>	1.432 (5)	C <sub>p2</sub> –C <sub>p3</sub>	1.522 (7)
N <sub>2</sub> –C <sub>a4</sub>	1.385 (4)	C <sub>a3</sub> –C <sub>b3</sub>	1.437 (5)	C <sub>p2</sub> –C <sub>p5</sub>	1.542 (6)
C <sub>m1</sub> –C <sub>a2</sub>	1.386 (5)	C <sub>a4</sub> –C <sub>b4</sub>	1.439 (5)	C <sub>p3</sub> –C <sub>p4</sub>	1.524 (7)
C <sub>m1</sub> –C <sub>a3</sub>	1.388 (5)				

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure. <sup>b</sup> Atoms are identified in agreement with Figures 1 and 2.

numbering scheme employed for the atoms is displayed in Figures 1–4. Primed and unprimed symbols, e.g., C<sub>*i*</sub> and C<sub>*i*'</sub>, denote a pair of atoms related by the center of inversion wherein the cobalt atom is positioned.

**Elemental Analyses.** Analyses performed by a commercial

(12) See paragraph at end of paper regarding supplementary material.  
(13) Estimated standard deviations in bond lengths and angles were calculated following 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.

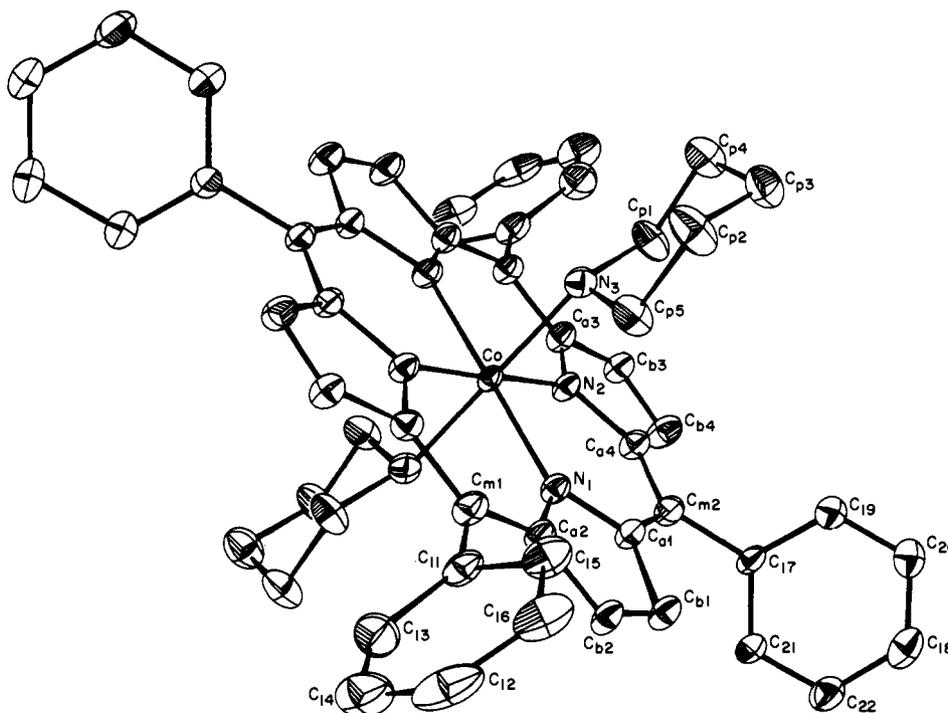


Figure 1. Computer-drawn model in perspective of the centrosymmetric  $\text{Pip}_2\text{CoTPP}^+$  cation as it exists in the triclinic crystal. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table III. Also shown is the numbering scheme used for all atoms in the ion.

Table V. Bond Angles in the Coordination Group, Porphinato Skeleton and Piperidine Ligands<sup>a</sup>

Angle <sup>b</sup>	Value (deg)	Angle <sup>b</sup>	Value (deg)
$\text{N}_2\text{CoN}_1$	90.0 (1)	$\text{N}_2\text{C}_{a4}\text{C}_{m2}$	126.2 (3)
$\text{N}_3\text{CoN}_2$	86.9 (1)	$\text{N}_2\text{C}_{a4}\text{C}_{b4}$	110.4 (3)
$\text{N}_3\text{CoN}_1$	87.7 (1)	$\text{C}_{m2}\text{C}_{a4}\text{C}_{b4}$	123.4 (3)
$\text{C}_{a1}\text{N}_1\text{C}_{a2}$	104.9 (3)	$\text{C}_{b2}\text{C}_{b1}\text{C}_{a1}$	106.8 (3)
$\text{C}_{a3}\text{N}_2\text{C}_{a4}$	104.9 (3)	$\text{C}_{b1}\text{C}_{b2}\text{C}_{a2}$	107.1 (3)
$\text{C}_{a2}\text{C}_{m1}\text{C}_{a3}'$	123.0 (3)	$\text{C}_{b4}\text{C}_{b3}\text{C}_{a3}$	107.0 (3)
$\text{C}_{a2}\text{C}_{m1}\text{C}_{11}$	118.9 (3)	$\text{C}_{b3}\text{C}_{b4}\text{C}_{a4}$	107.1 (3)
$\text{C}_{a3}'\text{C}_{m1}\text{C}_{11}$	118.1 (3)	$\text{C}_{p5}\text{N}_3\text{C}_{p1}$	108.6 (3)
$\text{C}_{a4}\text{C}_{m2}\text{C}_{a1}$	122.9 (3)	$\text{N}_3\text{C}_{p1}\text{C}_{p4}$	111.8 (3)
$\text{C}_{a4}\text{C}_{m2}\text{C}_{17}$	118.1 (3)	$\text{C}_{p3}\text{C}_{p2}\text{C}_{p5}$	110.4 (3)
$\text{C}_{a1}\text{C}_{m2}\text{C}_{17}$	118.9 (3)	$\text{C}_{p2}\text{C}_{p3}\text{C}_{p4}$	108.4 (4)
$\text{N}_1\text{C}_{a1}\text{C}_{m2}$	125.6 (3)	$\text{C}_{p3}\text{C}_{p4}\text{C}_{p1}$	111.1 (3)
$\text{N}_1\text{C}_{a1}\text{C}_{b1}$	110.7 (3)	$\text{N}_3\text{C}_{p5}\text{C}_{p2}$	112.2 (3)
$\text{C}_{m2}\text{C}_{a1}\text{C}_{b1}$	123.7 (3)	$\text{CoN}_1\text{C}_{a1}$	127.6 (2)
$\text{N}_1\text{C}_{a2}\text{C}_{m1}$	126.1 (3)	$\text{CoN}_1\text{C}_{a2}$	127.3 (2)
$\text{N}_1\text{C}_{a2}\text{C}_{b2}$	110.4 (3)	$\text{CoN}_2\text{C}_{a3}$	127.7 (2)
$\text{C}_{m1}\text{C}_{a2}\text{C}_{b2}$	123.4 (3)	$\text{CoN}_2\text{C}_{a4}$	127.4 (2)
$\text{N}_2\text{C}_{a3}\text{C}_{m1}'$	125.8 (3)	$\text{CoN}_3\text{C}_{p1}$	115.2 (2)
$\text{N}_2\text{C}_{a3}\text{C}_{b3}$	110.5 (3)	$\text{CoN}_3\text{C}_{p5}$	115.5 (2)
$\text{C}_{m1}'\text{C}_{a3}\text{C}_{b3}$	123.7 (3)		

<sup>a</sup> The number in parentheses following each datum is the estimated standard deviation in the last significant figure. <sup>b</sup> Atoms are identified in agreement with Figures 1 and 2.

microanalysis firm gave results with unsatisfactorily low values for the carbon content. Additional elemental analyses (C, H, N) were kindly performed by Dr. Alan Adler, New England Institute, and were used in an attempt to assess the content of the unit cell. *Anal.* Calcd for  $\text{C}_{63}\text{H}_{73}\text{N}_9\text{O}_3\text{Co}$  (formulation III): C, 72.74; H, 6.86; N, 10.44. Calcd for  $\text{C}_{81}\text{H}_{72}\text{N}_9\text{O}_3\text{Co}$  (formulation IV): C, 71.56; H, 6.76; N, 11.73. Found: C,  $74.29 \pm 0.52$ ; H,  $7.12 \pm 1.33$  (four determinations); N,  $9.38 \pm 0.3$  (two determinations). These data are suggestive of residual contamination of the crystalline salt from the tar-like matrix in which the crystals were embedded. We note that the disagreements with the analytical results are consistently smaller for the formulation III, with  $\text{HCO}_3^-$  as the counterion, than for the alternative choice IV (see Discussion).

Table VI. Bond Lengths in the Phenyl Groups<sup>a,b</sup>

Type I <sup>c</sup>	Length (Å)	Type II <sup>d</sup>	Length (Å)	Type III <sup>e</sup>	Length (Å)
$\text{C}_{11}\text{--C}_{13}$	1.397 (6)	$\text{C}_{13}\text{--C}_{14}$	1.404 (6)	$\text{C}_{12}\text{--C}_{14}$	1.378 (9)
$\text{C}_{11}\text{--C}_{15}$	1.389 (6)	$\text{C}_{15}\text{--C}_{16}$	1.399 (6)	$\text{C}_{12}\text{--C}_{16}$	1.379 (9)
$\text{C}_{17}\text{--C}_{19}$	1.389 (6)	$\text{C}_{19}\text{--C}_{20}$	1.404 (6)	$\text{C}_{15}\text{--C}_{20}$	1.377 (7)
$\text{C}_{17}\text{--C}_{21}$	1.393 (5)	$\text{C}_{21}\text{--C}_{22}$	1.398 (6)	$\text{C}_{18}\text{--C}_{22}$	1.380 (7)
$\text{Av}^b$	1.392 (3)	$\text{Av}^b$	1.401 (3)	$\text{Av}^b$	1.379 (2)

<sup>a</sup> The figure in parentheses following the length of a specified bond is the estimated standard deviation. <sup>b</sup> The figure in parentheses following the averaged length for a bond type is the mean deviation from the average. <sup>c</sup> Bond set lying nearest to the molecular center. <sup>d</sup> Bond set lying approximately parallel to the porphyrinato core. <sup>e</sup> Bond set lying farthest from the porphyrinato core.

Table VII. Bond Lengths and Angles of the Piperidine of Solvation and the Anion<sup>a,b</sup>

Type	(A) Bond Lengths		
	Length (Å)	Type	Length (Å)
$\text{O}_1\text{--N}_4$	1.39 (2)	$\text{C}_{82}\text{--C}_{83}$	1.57 (2)
$\text{O}_2\text{--N}_4$	1.09 (2)	$\text{C}_{84}\text{--C}_{85}$	1.41 (3)
$\text{O}_3\text{--N}_4$	1.09 (2)	$\text{C}_{84}\text{--C}_{86}$	1.44 (2)
$\text{C}_{81}\text{--C}_{82}$	1.46 (2)	$\text{C}_{85}\text{--C}_{86}$	1.46 (2)
$\text{C}_{81}\text{--C}_{85}$	1.53 (2)		
Angle	(B) Bond Angles		
	Value (deg)	Angle	Value (deg)
$\text{O}_1\text{N}_4\text{O}_2$	120.5 (15)	$\text{C}_{84}\text{C}_{83}\text{C}_{82}$	111.3 (12)
$\text{O}_1\text{N}_4\text{O}_3$	120.2 (14)	$\text{C}_{83}\text{C}_{84}\text{C}_{86}$	107.1 (11)
$\text{O}_2\text{N}_4\text{O}_3$	118.5 (14)	$\text{C}_{84}\text{C}_{86}\text{C}_{85}$	102.2 (12)
$\text{C}_{82}\text{C}_{81}\text{C}_{85}$	106.7 (11)	$\text{C}_{86}\text{C}_{85}\text{C}_{81}$	107.4 (11)
$\text{C}_{81}\text{C}_{82}\text{C}_{83}$	104.5 (10)		

<sup>a</sup> The figure in parentheses following each datum is the estimated standard deviation. <sup>b</sup> Atoms are identified in agreement with Figures 3 and 4.

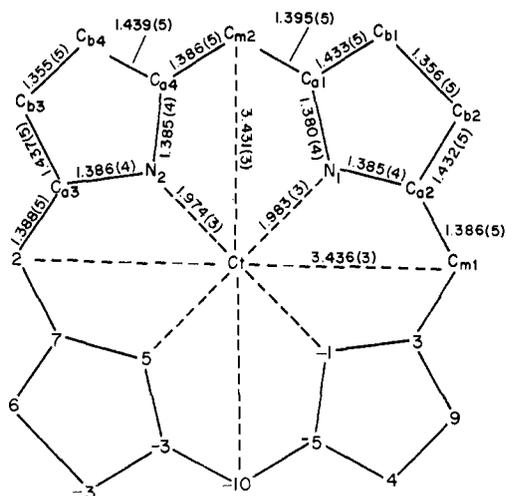


Figure 2. Diagram of the porphinato core displaying, on the upper half, the structurally independent bond lengths and the numbering scheme employed for the atoms. On the lower half of the centrosymmetric diagram, the special symbol identifying each atom is replaced by the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the porphinato core.

### Discussion

Figure 1 is a computer-drawn model of the centrosymmetric ( $\bar{1}$ )  $\text{Pip}_2\text{CoTPP}^+$  ion as it exists in the triclinic crystal. Each atom is represented by an ellipsoid<sup>14</sup> with the relative size and orientation required by the thermal parameters given in Table III.

The upper half of the diagram of the porphinato core in Figure 2 gives the values (with estimated standard deviations) of all structurally independent C-C and C-N bond distances in the core. Also displayed are the values of some structurally important radii of the core, of which  $\text{Ct} \cdots \text{N} \equiv \text{Co-N}$  in this case. In the lower half of the centrosymmetric diagram, the special symbol identifying each atom is replaced by the perpendicular displacement (in units of 0.01 Å) of this atom from the mean plane of the porphinato core. The centrosymmetrically related atoms in the upper half of the diagram have displacements of the same magnitude but with opposite sign. Departures from planarity of the porphinato core in this crystal are small relative to those in a number of other porphyrins. As is usual, local flatness is preserved at all trigonal carbon atoms of the inner great ring of the porphine skeleton and, of course, in the pyrrole rings.

Evidence that bond lengths in the porphinato core depart insignificantly from  $D_{4h}$  geometry is provided by the data listed in Table IV and displayed in Figure 2. Using  $C_a$  and  $C_b$  to denote the respective  $\alpha$  and  $\beta$  carbon atoms in a pyrrole ring,  $C_m$  for methine carbon, and  $C_p$  for a phenyl carbon atom that is bonded to the core, averaged bond lengths for the chemically analogous types of bonds are  $\text{Co-N} (= \text{Ct} \cdots \text{N}) = 1.978$  (5, 3),  $\text{N-C}_a = 1.384$  (2, 4),  $\text{C}_a\text{-C}_b = 1.435$  (3, 5),  $\text{C}_b\text{-C}_b = 1.356$  (1, 5),  $\text{C}_a\text{-C}_m = 1.389$  (4, 5), and  $\text{C}_m\text{-C}_p = 1.494$  (1, 5) Å, wherein the first figure in parentheses following each averaged value is the mean deviation and the second is the estimated standard deviation of an individually determined length of the type.<sup>15</sup> Similarly

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

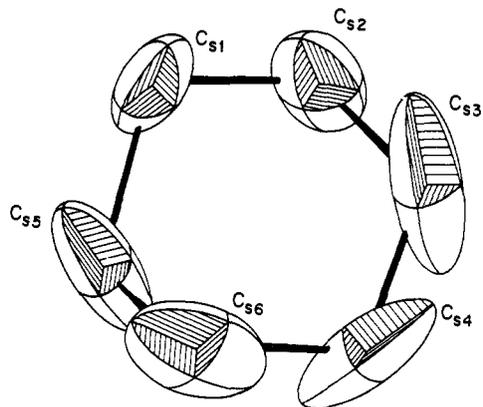


Figure 3. Computer-drawn model in perspective of the six-atom ring in a piperidine molecule of solvation. All six atoms were taken to be carbon during structure refinement;  $C_{s5}$  was subsequently identified as the nitrogen atom (see text).

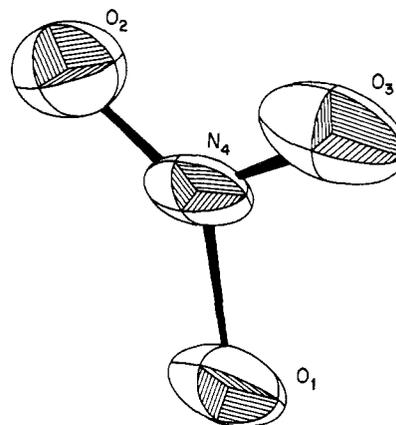


Figure 4. Computer-drawn model in perspective of the anion, taken to be  $\text{NO}_3^-$ ; see text for evidence that this ion may be  $\text{HCO}_3^-$ .

trivial departures from dimensional equivalence are observed for bond angles of a given chemical type:  $\text{NCoN} = 90.0$  (0, 1),  $\text{CoNC}_a = 127.5$  (2, 2),  $\text{C}_a\text{NC}_a = 104.9$  (0, 3),  $\text{C}_a\text{C}_m\text{C}_a = 123.0$  (1, 3),  $\text{NC}_a\text{C}_b = 110.5$  (1, 3),  $\text{NC}_a\text{C}_m = 125.9$  (2, 3),  $\text{C}_a\text{C}_b\text{C}_b = 107.0$  (1, 3), and  $\text{C}_a\text{C}_m\text{C}_p = 118.5^\circ$  (4, 3).

The dihedral angles between the mean plane of the porphinato core and the planes of the two structural classes of phenyl groups in  $\text{Pip}_2\text{CoTPP}^+$  are 69.7 and 64.9°; angles smaller than  $\sim 60^\circ$  are generally precluded by steric interactions between the pyrrole hydrogen and phenyl hydrogen atoms. The averaged length of the bond connecting the phenyl carbon atom to the methine carbon atom, 1.494 (1, 5) Å, is consistent with  $\sigma$  bonding between two trigonally hybridized carbon atoms. The averaged value of the internal angles in the phenyl rings is 120.0 (4, 4)°. The sum of the angles subtended at a carbon atom  $C_p$  is 360.0 (0, 4)°, corresponding to planar trigonal carbon atoms. The experimentally determined C-C bond distances in the two structurally independent phenyl rings (Table VI) follow a systematic pattern of foreshortening from the standard 1.397 Å separation owing to the thermal motions of these peripheral groups.

The piperidine ligand is in the chair form, with a CNC angle of 108.6 (3)°; the CCC angle opposite the

(15) This pattern of reporting averaged values for both angles and bond lengths is followed throughout the discussion.

nitrogen atom is  $108.4(4)^\circ$ . The two NCC angles average to  $112.0^\circ(2, 3)$ ; the remaining two CCC angles average to  $110.8^\circ(4, 3)$ . The agreement between structurally independent, chemically analogous bond lengths previously noted is maintained in the piperidine ligand with  $(\text{N}-\text{C})_{\text{av}} = 1.496(5, 5)$  and  $(\text{C}-\text{C})_{\text{av}} = 1.529(7, 7)$  Å.

The cobalt and the four porphinato nitrogen atoms of the octahedral ( $\bar{1}$ ) coordination group constitute a necessarily planar, very nearly square, equatorial entity with  $(\text{Co}-\text{N})_{\text{av}} = 1.978(5, 3)$  Å, and  $(\angle \text{NCoN})_{\text{av}} = 90.0^\circ(0, 1)$ . The collinear  $\text{Co}-\text{N}_3$  bonds to the piperidine ligands (Figure 1) are tipped  $3.85^\circ$  from the normal to the equatorial porphinato plane roughly within a vertical plane that bisects the  $\text{N}_1\text{CoN}_2$  angle. Because this plane serves as an approximate mirror for all of the complex excepting the peripheral phenyl groups, the cation otherwise observes the approximate symmetry of  $C_{2h}$ ; the quasi-twofold axis lies in the equatorial girdle and bisects the opposite angles,  $\text{N}_1\text{CoN}_2'$  and  $\text{N}_1'\text{CoN}_2$  (Figure 2).

Indeed, the isoelectronic  $\text{Pip}_2\text{CoTPP}^+$  and  $\text{Pip}_2\text{FeTPP}$  species are essentially isostructural as they occur in their distinctive crystalline environments; apart from the orientations of the phenyl groups, each species is allowed to approximate closely to the maximum symmetry ( $C_{2h}$ ) theoretically attainable in the absence of external constraints. The few significant differences in stereochemical parameters are those which are the direct consequence of the differing nuclear charges carried by the metal atoms. Thus for the equatorial complexing bonds,  $\text{Co(III)}-\text{N} = 1.978(5, 3)$  and  $\text{Fe(II)}-\text{N} = 2.004(4, 3)$  Å, as compared with  $\sim 1.96$  and  $1.98$  Å for the respective lengths of dative bonds to monodentate ligands, and with a  $\text{Ct}\cdots\text{N}$  radius of  $\sim 2.01$  Å for minimizing radial strain in the porphinato core.<sup>16</sup> The substantially larger stretching of the axial bonds,  $\text{Co(III)}-\text{N} = 2.060(3)$  and  $\text{Fe(II)}-\text{N} = 2.127(3)$  Å, is a necessary consequence of steric interactions between piperidine hydrogen and—most seriously but not exclusively—porphinato nitrogen atoms. Inasmuch as the detailed analysis of these interactions in the  $\text{Pip}_2\text{CoTPP}^+$  ion is quite analogous to that given for the  $\text{Pip}_2\text{FeTPP}$  molecule<sup>3</sup> (see Figure 3 therein), it suffices to point out that the cobalt(III) species can tolerate intramolecular  $\text{H}\cdots\text{N}$  and  $\text{H}\cdots\text{C}$  contacts (ranging upward from  $\sim 2.53$  Å) which are  $0.05$ – $0.10$  Å shorter than those observed in the iron(II) species.

We remark also that the foregoing steric interactions lose all importance in the neutral  $\text{Pip}_2\text{CoTPP}$  molecule,<sup>4</sup> even though this cobalt(II) species crystallizes in the same structural type as does  $\text{Pip}_2\text{FeTPP}$ . The equatorial  $\text{Co}-\text{N}$  distance of  $1.987(2)$  Å differs little from that in the  $\text{Pip}_2\text{CoTPP}^+$  ion, but the gross stretching of the axial  $\text{Co}-\text{N}$  distance to  $2.436(2)$  Å is required by the presence of the odd electron in the  $3d_z^2$  orbital of the  $d^7$  cobalt(II) atom.<sup>4</sup>

In marked contrast with the precisely defined stereochemistry of the complex cation, the bond parameters listed in Table VII for the anion and the piperidine solvate molecules are, at best, of a semiquantitative

nature. Half-occupancy of the positions assigned to the anions is conducive to a loose disordered packing with the solvate molecules; such packing gives rise to the extraordinarily large and extremely anisotropic values of the apparent thermal parameters for both species which are listed in Table III and shown graphically in Figures 3 and 4. A piperidine solvate molecule (Figure 3 and Table VII) is in the chair form, but difference Fourier syntheses are suggestive of, or at least consistent with, some orientational disorder. We note that structure refinement was carried out with a ring of six carbon atoms because the unique nitrogen atom could not be identified.

The identification of the anion (Figure 4 and Table VII) remains uncertain, although structure refinement was carried out assuming the central atom to be nitrogen. A bond length of  $1.09(2)$  Å, as listed for both  $\text{O}_2-\text{N}_4$  and  $\text{O}_3-\text{N}_4$ , is nearly  $0.15$  Å below rational expectation for either a nitrate or a carbonate ion, whereas a bond length of  $1.39(2)$  Å, as listed for  $\text{O}_1-\text{N}_4$ , is larger by only three or four standard deviations than expectation for the  $\text{C}-\text{OH}$  bond in the bicarbonate ion. Both these data and the chemical analyses fit somewhat better with the bicarbonate ion. A nitrate ion, on the other hand, might plausibly originate from the nitrosyl ligand in the  $\text{ONCoTPP}$  molecule (see Experimental Section). The intermediate oxidation of coordinated nitrosyl to a coordinated nitrite ion has been reported;<sup>17</sup> the further oxidation and displacement of this ligand (in either order) have not.

Only three types of intermolecular contacts are short enough to be suggestive of hydrogen bonding. The observed separation,  $\text{O}_1\cdots\text{C}_{53} = 2.95$  Å, which corresponds in length to a fairly strong  $\text{O}\cdots\text{HN}$  hydrogen bond, allows us to identify the unique nitrogen atom in a piperidine solvate molecule with the pseudo-carbon atom  $\text{C}_{53}$  of Figure 3. Separations of  $\text{N}_3\cdots\text{O}_2 = 3.27$  ( $\text{N}_3\text{H}\cdots\text{O}_2 = 2.37$ ) Å and  $\text{N}_3\cdots\text{O}_3 = 3.38$  ( $\text{N}_3\text{H}\cdots\text{O} = 2.50$ ) Å are perhaps more indicative of stabilizing electrostatic interactions than of a definite pattern of hydrogen bonding. Of the 33 other intermolecular contacts which lie somewhat below  $4.0$  Å, roughly half are between carbon atoms of partially overlapping aromatic groupings; none of these approach closely to the  $3.35$ – $3.40$  Å characteristic of the parallel stacking of planar aromatic species.

**Acknowledgment.** We thank Dr. Alan Adler for providing us with the elemental analyses reported above and the Computing Center of the University of Notre Dame for an allocation of computing time.

**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 ( $105 \times 148$  mm,  $20\times$  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 \$6.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-8289.

(17) (a) S. G. Clarkson and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 670 (1972); (b) J. A. Kaduk and W. R. Scheidt, manuscript in preparation.

(16) J. L. Hoard, *Science*, **174**, 1295 (1971), and references cited therein.