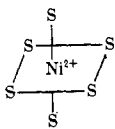
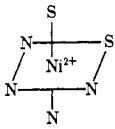
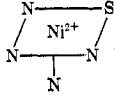
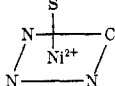


**Table IV.** Rate Constants for the Breaking of  $\text{CH}_3\text{CN}\cdots\text{Ni}$  Bonds in Various Species at the Temperatures Indicated ( $^\circ\text{C}$ )

Reacting species <sup>a</sup>	Notional geometry <sup>b</sup>	$10^{-3}k$ , $\text{sec}^{-1}$
$[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$		$0.34^c, d$ ( $25^\circ$ )
$[\text{Ni}(\text{tren})(\text{CH}_3\text{CN})_2]^{2+}$		$165^d, e$ ( $25^\circ$ ) $\geq 2000^d, f$ ( $-40^\circ$ )
$[\text{Ni}(\text{Me}_6\text{tren})(\text{CH}_3\text{CN})]^{2+}$		$<0.1^d$ ( $80^\circ$ )
$[\text{NiLCl}(\text{CH}_3\text{CN})]^+$		$700^g$ ( $20^\circ$ )

<sup>a</sup> tren =  $(\text{H}_2\text{NCH}_2\text{CH}_2)_3\text{N}$ ; Me<sub>6</sub>tren =  $(\text{Me}_2\text{NCH}_2\text{CH}_2)_3\text{N}$ ; L =  $(\text{Et}_2\text{NCH}_2\text{CH}_2)_2\text{NH}$ . <sup>b</sup> The actual geometries may be distorted forms of the structures indicated; S = solvent  $\text{CH}_3\text{CN}$ . <sup>c</sup> Corrected for a statistical factor of 6. <sup>d</sup> R. J. West and S. F. Lincoln, *Inorg. Chem.*, **12**, 494 (1973). <sup>e</sup> S trans to tertiary N of tren. <sup>f</sup> S cis to tertiary N of tren. <sup>g</sup> This work.

than in  $[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$ . In this as in other systems<sup>28</sup> a strongly held ligand weakens the bonds to the remaining solvent molecules. It should be borne in mind

(28) W. J. McKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, **93**, 4379 (1971).

that the above discussion is based on the assumption of the dissociative exchange mechanism of Eigen.<sup>27</sup> There is some evidence that this does not always apply in nonaqueous solvents<sup>29</sup> and one cannot rule out the possibility of a second-order solvent- or ligand-assisted exchange in some cases.

Turning now to the value of  $k_{32}$  we may note that it approaches the value expected for a diffusion-controlled reaction. In line with this, preliminary investigations using the laser technique show that the activation energy is of the same order of magnitude as the quantity  $B$  defined by the expression for the temperature variation of solvent viscosity,  $\eta \propto \exp(B/RT)$ .

### Conclusions

The thermodynamic results strongly support the mechanism denoted by (2) involving the participation of the species  $\text{NiLCl}^+\cdots\text{Cl}^-$  in which the solvent  $\text{CH}_3\text{CN}$  is weakly bound in the fifth coordination position. The mechanism also allows a satisfactory interpretation of the kinetic data and it appears that under the experimental conditions employed the interconversion of  $\text{NiLCl}^+\cdots\text{Cl}^-$  and five-coordinate  $\text{NiLCl}_2$  is not rate determining in the readjustment of the successive equilibria following perturbation.

**Acknowledgments.** We thank the Queen's University of Belfast for the award of a postdoctoral fellowship to H. H. One of us (H. H.) acknowledges helpful discussions with Professors R. G. Pearson and M. L. Bender. We are grateful to the Science Research Council for a grant in support of this research.

(29) E. F. Caldin and M. W. Grant, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1648 (1973).

## Stereochemistry of Cobalt Porphyrins. I. The Structure and Characterization of 2,3,7,8,12,13,17,18-Octaethylporphinato-bis(3-methylpyridine)cobalt(II)

Robert G. Little and James A. Ibers\*

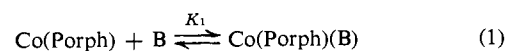
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received December 28, 1973

**Abstract:** The six-coordinate Co(II) porphyrin,  $\text{Co}(\text{3-pic})_2(\text{OEP})$  (3-pic = 3-picoline = 3-methylpyridine), has been prepared and characterized by a complete X-ray structural determination. The structure has been refined anisotropically to a final conventional  $R$  value (on  $F$ ) of 0.036 based on 3628 values of  $F_o^2$  above background. The complex crystallizes in the triclinic space group  $C_1^1-P\bar{1}$  with  $a = 10.187$  (3) Å,  $b = 11.258$  (4) Å,  $c = 9.753$  (3) Å,  $\alpha = 93.10$  (2)°,  $\beta = 92.32$  (2)°,  $\gamma = 113.28$  (2)°, and  $Z = 1$ . Hence the molecule has a crystallographically imposed center of symmetry. The axial Co-N(3-pic) bond length of 2.386 (2) Å is long compared with the average equatorial Co-N bond length of 1.992 (1) Å. The lengthening of the axial bond is attributed to the occupancy of the  $d_{z^2}$  orbital by a single unpaired electron.

**S**olution studies of Co(II) porphyrins<sup>1-5</sup> have shown that these complexes add one or two molecules of

- (1) F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).
- (2) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 1790 (1973).
- (3) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1150 (1973).
- (4) F. A. Walker, *J. Amer. Chem. Soc.*, **95**, 1154 (1973).
- (5) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U. S.*, **67**, 637 (1970).

various nitrogenous bases to form five- and six-coordinate complexes.



The equilibria and thermodynamics of these reactions have been studied in some detail by esr<sup>3</sup> and visible

spectroscopy.<sup>2,4</sup> Thus Walker<sup>3</sup> has shown that the formation constant,  $K_1$ , of the five-coordinate piperidine complex is  $10^{3.4} M^{-1}$  while  $K_2$  is  $10^{0.4} M^{-1}$ . By comparison  $K_1$  and  $K_2$  for 3,4-lutidine are  $\sim 10^3$  and  $\sim 10^{-1} M^{-1}$ . These data indicate that the five-coordinate complexes are much more stable than the six-coordinate complexes.

Both Walker<sup>3</sup> and Stynes, *et al.*,<sup>2</sup> have shown that the formation constants may be correlated with the  $pK_a$ 's of the bases ( $BH^+$ ), with the bulkiness of the bases, and to some extent with the relative  $\pi$ -bonding capabilities of these bases. Thus for a given  $pK_a$ ,  $K_1$  increases in the order amines < pyridines < imidazoles. This has been taken to be indicative of increasing metal-ligand  $\pi$ -bonding.

Studies of ferrous porphyrins<sup>6-10</sup> have similarly indicated the importance of metal-ligand  $\pi$ -bonding. By contrast, only  $\sigma$ -donor strength seems to be important in Ni, Zn, and Mg porphyrin complexes.<sup>11-13</sup>

We therefore believe it is of interest to report the characterization and structure of a six-coordinate Co(II) porphyrin, Co(3-pic)<sub>2</sub>(OEP),<sup>14</sup> in which the axial ligands have strong  $\pi$ -bonding capabilities. This structure is of especial interest for comparison with the recently reported structure of Co(pip)<sub>2</sub>(TPP).<sup>16</sup>

In the following paper<sup>17</sup> we report the structure of the six-coordinate Co(III) porphyrin, Co(Im)<sub>2</sub>(TPP)<sup>+</sup>. The structure of this d<sup>6</sup> complex demonstrates that the long axial bond lengths in the Co(II) porphyrins result from occupancy of the  $d_{z^2}$  orbital by a single unpaired electron. That structure also provides an estimate of the Co-N(histidine) bond length in oxycoboglobin. In the third and final paper<sup>18</sup> we report the structure and characterization of the five-coordinate complex, Co(1-Me-Im)(OEP). This complex serves as a model for the porphyrin prosthetic group in deoxycoboglobin and strongly suggests that the out-of-plane displacement of the central metal atom in coboglobin is significantly less than in hemoglobin. This has important implications<sup>19</sup> with regard to the trigger mechanism proposed by Perutz<sup>20</sup> to explain the cooperative effects observed in hemoglobin.

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(9) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **93**, 2153 (1971).

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(14) The following abbreviations are used throughout: 1-Me-Im, 1-methylimidazole; Im, imidazole; py, pyridine; 3-pic, 3-methylpyridine; 3,4-lut, 3,4-dimethylpyridine; pip, piperidine; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion;<sup>15</sup> PP-IX, 2,7,12,18-tetramethyl-3,8-divinylporphyrin-13,17-dipropionic acid dianion; PP-IX-DME, dimethyl ester of PP-IX; TPP, *meso*-tetraphenylporphyrin dianion; TPYP, *meso*-tetra(4-pyridyl)porphyrin dianion; F<sub>6</sub>-acac, hexafluoroacetylacetonate anion; DMG, dimethylglyoximate dianion.

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(18) R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, **96**, 4452 (1974).

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## Preparation of Compound and Collection of Diffraction Data

Although the formation constants<sup>2,3,21</sup> indicate that five-coordinate complexes are much more stable than the six-coordinate complexes, crystallization of Co(OEP) with pyridine bases leads to six-coordinate complexes. The 3-methylpyridine complex was chosen for study because of the favorable morphology of the crystals and because the substitution of the pyridine ring provided no unfavorable steric interactions.

Crystals of Co(3-pic)<sub>2</sub>(OEP) were grown from a solution of Co(OEP) in pure 3-methylpyridine by slow cooling of a hot saturated solution.<sup>22</sup> The 3-methylpyridine had been distilled *in vacuo* from CaH<sub>2</sub>. On standing in air the crystals so formed lose a molecule of base. Therefore, freshly prepared crystals were sealed in thin-walled, glass capillaries for crystallographic examination.

Preliminary precession photographs taken with Mo K $\alpha$  radiation showed only the required center of symmetry and hence the space group is either  $P1$  or  $P\bar{1}$ . The crystal selected for data collection was a parallelepiped with major bounding faces of the forms  $\{100\}$ ,  $\{001\}$ , and  $\{110\}$  and minor faces  $\{010\}$ . The distances between the faces of these forms are 0.26, 0.69, 0.51, and 0.64 mm. The crystal was mounted with the  $[120]$  direction approximately along the spindle axis.

The lattice parameters, obtained as previously described<sup>23</sup> by hand centering of 15 reflections in the range  $30 < 2\theta < 38^\circ$  on a FACS-I diffractometer using Mo K $\alpha$  radiation ( $\lambda$  0.70930 Å), are  $a = 10.187$  (3) Å,  $b = 11.258$  (4) Å,  $c = 9.753$  (3) Å,  $\alpha = 93.10$  (2)°,  $\beta = 92.32$  (2)°, and  $\gamma = 113.28$  (2)°. The calculated density, based on one molecule per unit cell, is 1.26 g/cm<sup>3</sup> and agrees well with an observed value of 1.25 (1) g/cm<sup>3</sup>, as measured by flotation of the crystals in aqueous zinc chloride solution.

Data were collected in shells of  $2\theta$  by the  $\theta$ - $2\theta$  scan method using Mo K $\alpha$  radiation prefiltered with 3-mil Nb foil. The initial scan range in  $2\theta$  was from 0.75° below the Mo K $\alpha_1$  peak to 1.0° above the Mo K $\alpha_2$  peak. The takeoff angle was 2.1° and the receiving counter was positioned 32 cm from the crystal with an aperture 5.0 mm high and 5.0 mm wide. The pulse height analyzer was set to admit about 90% of the Mo K $\alpha$  peak. Initially background counts of 10 sec were taken at the end of each scan range. Past a  $2\theta$  of 25° this was increased to 20 sec. A scan rate of 2° and  $2\theta$  per minute was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts per second during a scan. The attenuators were of Cu foil and gave attenuator factors of about 2.3. Data were collected in the range  $3^\circ < 2\theta < 55^\circ$ . Data collection was terminated when less than 10% of the measured reflections were statistically observable. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. The deviations of these standards were all within counting statistics.

The data were processed as previously described using a value of 0.04 for  $p$ .<sup>23,24</sup> Of the 5559 reflections measured, 4838 are unique and of these 3628 have  $F_o^2 > 3\sigma(F_o^2)$  and were used in subsequent refinements. Data were collected with  $k \leq 1$ , so Friedel pairs of the type  $h0l$  and  $h1l$  were measured. Since these 721 pairs of reflections deviate by 1.7% from their average values, the centrosymmetric space group  $P\bar{1}$  seems most probable (*vide infra*). Sample calculations<sup>25</sup> for an absorption correction were made using a linear absorption coefficient of 4.55 cm<sup>-1</sup>. The transmission

(21) H. C. Stynes, Thesis, Northwestern University, Evanston, Ill., 1972.

(22) The compounds Co(L)<sub>2</sub>(OEP), L = pyridine and *tert*-butylpyridine, have also been prepared. We find that both crystallize in the triclinic space group  $P1$  or  $P\bar{1}$ . Co(*t*-Bu(py))<sub>2</sub>(OEP):  $a = 10.13$ ,  $b = 10.45$ ,  $c = 10.00$  Å;  $\alpha = 99.34$ ,  $\beta = 114.56$ ,  $\gamma = 98.99^\circ$ ;  $Z = 1$ . Co(py)<sub>2</sub>(OEP):  $a = 10.30$ ,  $b = 10.29$ ,  $c = 9.96$  Å;  $\alpha = 90.67$ ,  $\beta = 114.56$ ,  $\gamma = 98.99^\circ$ ;  $Z = 1$  (precession photographs).

(23) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(24) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(25) In addition to local programs for the CDC 6400, local modifications of the following programs were employed: Zalkin's FORDAF Fourier program, the AGNOST absorption program, Johnson's ORTEP 11 thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, Dewar's program FAME for Wilson statistics and generation of normalized structure factors. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

Table II. Atomic Parameters for CoC<sub>48</sub>N<sub>6</sub>H<sub>56</sub>

Atom	x	y	z	B (Å <sup>2</sup> ) or					
				β <sub>11</sub> <sup>a</sup>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
Co	0	0	0	772 (5)	485 (3)	674 (4)	-150 (3)	200 (3)	95 (2)
N(1)	-0.0097 (2) <sup>b</sup>	0.1238 (1)	-0.1422 (1)	69 (17)	56 (1)	69 (2)	-21 (1)	9 (1)	9 (1)
N(2)	-0.1245 (2)	0.1469 (1)	0.1204 (1)	70 (17)	56 (1)	71 (2)	-20 (1)	11 (1)	8 (1)
N(3)	0.2044 (2)	0.0246 (2)	0.1039 (2)	90 (20)	75 (2)	102 (2)	-28 (1)	11 (2)	6 (1)
C(1)	0.0529 (2)	0.0950 (2)	-0.2690 (2)	68 (20)	67 (2)	68 (2)	-28 (2)	4 (2)	12 (1)
C(2)	0.0197 (2)	0.2116 (2)	-0.3436 (2)	70 (20)	75 (2)	72 (2)	-32 (2)	-2 (2)	21 (1)
C(3)	-0.0634 (2)	0.3116 (2)	-0.2610 (2)	66 (20)	66 (2)	82 (2)	-28 (2)	-5 (2)	22 (1)
C(4)	-0.0814 (2)	0.2560 (2)	-0.1362 (2)	60 (19)	58 (2)	83 (2)	-23 (1)	0 (2)	16 (1)
C(5)	-0.1596 (2)	0.3262 (2)	-0.0254 (2)	70 (21)	48 (2)	95 (2)	-17 (1)	10 (2)	12 (1)
C(6)	-0.1796 (2)	0.2763 (2)	0.0946 (2)	60 (19)	54 (2)	85 (2)	-18 (1)	10 (2)	4 (1)
C(7)	-0.2599 (2)	0.3531 (2)	0.2102 (2)	66 (20)	58 (2)	91 (2)	-23 (2)	13 (2)	-5 (1)
C(8)	-0.2534 (2)	0.2690 (2)	0.3071 (2)	69 (20)	66 (2)	78 (2)	-24 (2)	11 (1)	-7 (1)
C(9)	-0.1684 (2)	0.1407 (2)	0.2501 (2)	71 (20)	64 (2)	70 (2)	-25 (2)	12 (2)	1 (1)
C(10)	-0.1348 (2)	0.0281 (2)	0.3193 (2)	83 (22)	77 (2)	63 (2)	-30 (2)	15 (2)	6 (1)
C(11)	0.0745 (2)	0.2161 (2)	-0.4834 (2)	105 (26)	91 (2)	80 (2)	-37 (2)	9 (2)	29 (2)
C(12)	0.2215 (3)	0.2182 (3)	-0.4784 (3)	130 (33)	174 (4)	136 (3)	-77 (3)	38 (3)	15 (3)
C(13)	-0.1259 (2)	0.4535 (2)	-0.2883 (2)	95 (24)	69 (2)	99 (2)	-27 (2)	3 (2)	30 (2)
C(14)	-0.0397 (3)	0.5259 (2)	-0.2260 (3)	164 (38)	90 (2)	184 (4)	-67 (3)	-9 (3)	26 (2)
C(15)	-0.3358 (2)	0.4978 (2)	0.2187 (2)	92 (24)	60 (2)	111 (2)	-23 (2)	26 (2)	-8 (2)
C(16)	-0.4955 (2)	0.5461 (2)	0.1974 (3)	100 (28)	90 (2)	145 (3)	-9 (2)	1 (2)	-3 (2)
C(17)	-0.3201 (2)	0.2987 (2)	0.4454 (2)	101 (25)	79 (2)	75 (2)	-30 (2)	17 (2)	-14 (2)
C(18)	-0.4577 (2)	0.2772 (2)	0.4507 (2)	121 (30)	124 (3)	104 (3)	-53 (2)	44 (2)	-13 (2)
C(19)	0.2499 (2)	0.1131 (2)	0.0640 (2)	111 (27)	81 (2)	111 (2)	-38 (2)	2 (2)	14 (2)
C(20)	0.3738 (2)	0.1252 (2)	0.1105 (2)	119 (28)	83 (2)	103 (2)	-48 (2)	23 (2)	-16 (2)
C(21)	0.4577 (3)	0.0379 (2)	0.2033 (3)	114 (30)	115 (3)	137 (3)	-56 (2)	-14 (2)	-6 (2)
C(22)	0.4113 (3)	-0.0525 (3)	0.2488 (3)	155 (38)	130 (3)	161 (4)	-70 (3)	-59 (3)	52 (3)
C(23)	0.2853 (3)	-0.0554 (2)	0.1979 (2)	122 (30)	102 (2)	127 (3)	-54 (2)	-17 (2)	35 (2)
C(24)	0.4168 (3)	0.2274 (3)	0.0590 (3)	195 (45)	131 (3)	178 (4)	-105 (3)	15 (3)	7 (3)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The anisotropic thermal parameters have all been multiplied by 10<sup>4</sup>, except those for the metal atom, which have been multiplied by 10<sup>6</sup>. <sup>b</sup> Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures.

factors calculated ranged from 0.73 to 0.90, and an absorption correction was therefore applied.

### Solution and Refinement of the Structure

Normalized structure factors ( $|E|$ 's) scaled such that  $\langle E^2 \rangle = 1.0$  were calculated from the measured structure amplitudes. Using the quantities  $|E^2 - 1|$  a sharpened, origin removed Patterson map was calculated, and the positions of the all of the non-hydrogen atoms were obtained.

The structure was refined by full-matrix least-squares techniques. The quantity minimized is  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and where the weights,  $w$ , are taken as  $4F_o^2/\sigma^2(F_o^2)$ . The agreement indices are defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$$

Values of the atomic scattering factors and the anomalous terms<sup>26</sup> were taken from the usual sources.

Four cycles of least-squares refinement of the 28 independent atoms, using isotropic temperature factors and a random half of the data, reduced  $R$  and  $R_w$  to 0.110 and 0.149. The coordinates of the H atoms at the porphyrin methine and methylene positions and those on the pyridine ring were idealized (C-H = 0.95 Å,  $B(H) = B(C) + 1.0$  Å<sup>2</sup>) and added as fixed contributions. One cycle of least-squares refinement, using anisotropic temperature factors for all the non-hydrogen atoms and a random two-thirds of the data, reduced  $R$  and  $R_w$  to 0.065 and 0.088.

The highest peaks in a difference Fourier map, calculated at this point, corresponded to the positions of the remaining 15 methyl H atoms. The positions of all the 29 H atoms were now idealized (H-C-H = 109.5°, C-H = 0.95 Å) and assigned temperature factors 1 Å<sup>2</sup> greater than the isotropic temperature factors of the carbon atoms to which they were attached. The H atom contribu-

tion was then added as a fixed contribution to two cycles of anisotropic, full-matrix, least-squares refinement. The least-squares refinement, which used all data for which  $F_o^2 \geq 3\sigma(F_o^2)$ , converged with  $R$  and  $R_w$  equal to 0.036 and 0.048.

An analysis of  $\sum w(|F_o| - |F_c|)^2$  as a function of setting angles, magnitude of  $|F_o|$ , and Miller indices showed no unusual trends. The standard deviation of an observation of unit weight is 1.71 electrons.

A structure factor calculation for the 624 reflections having  $F_o^2 < 3\sigma(F_o^2)$ , which were omitted from the refinement, showed only four reflections having  $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$ . These 624 reflections were omitted from Table I<sup>27</sup> where the values of  $10|F_o|$  and  $10|F_c|$  are given.

The final atomic parameters and their errors are listed in Table II. The calculated atomic parameters for the hydrogen atoms are given in Table III.<sup>27</sup> Table IV presents the root-mean-square amplitudes of thermal vibration.

### Description of the Structure

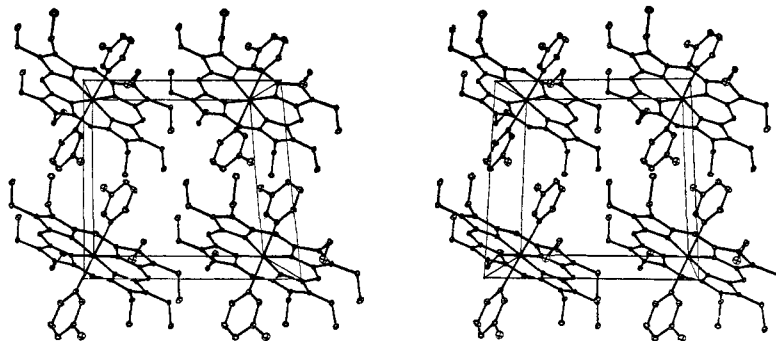
The structure consists of discrete, monomeric molecules of Co(3-pic)<sub>2</sub>(OEP). A view of the packing is shown in Figure 1. The closest intermolecular contacts are between the methyl groups of one OEP molecule and those of an adjacent porphyrin.

Each molecule has a crystallographically imposed center of symmetry. The central cobalt atom sits in a tetragonal environment, with relatively long bonds to the axial 3-picoline ligands. Table V gives the averaged and individual bond distances and angles obtained in this determination. Figure 2 indicates the numbering scheme.

The two crystallographically independent metal-nitrogen bond lengths within the porphyrin average 1.992 (1) Å, while the bond to the axial base is 2.386 (2) Å in length. The plane of the axial 3-picoline molecule

(26) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, in press; D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

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



**Figure 1.** Stereoscopic view of the packing of the molecules in the crystal. The view is approximately along the  $y$  axis, which points toward the viewer. The positive  $z$  axis runs from the right to the left. For clarity only the four molecules in the rear face of the cell have been included in the drawing.

**Table IV.** Root-Mean-Square Amplitudes of Vibration ( $\text{\AA}$ )

Atom	Min	Inter	Max	Angle $\Gamma^a$
Co	0.1525 (5)	0.1604 (6)	0.2168 (5)	15
N(1)	0.163 (2)	0.171 (2)	0.197 (2)	28
N(2)	0.165 (2)	0.170 (2)	0.201 (2)	25
N(3)	0.195 (2)	0.203 (2)	0.227 (2)	38
C(1)	0.163 (2)	0.178 (3)	0.200 (2)	57
C(2)	0.163 (2)	0.174 (3)	0.217 (2)	67
C(3)	0.164 (2)	0.169 (3)	0.217 (2)	65
C(4)	0.162 (2)	0.165 (2)	0.209 (2)	58
C(5)	0.158 (3)	0.177 (2)	0.221 (2)	44
C(6)	0.159 (3)	0.177 (2)	0.205 (2)	46
C(7)	0.165 (3)	0.179 (2)	0.214 (2)	57
C(8)	0.168 (3)	0.186 (2)	0.205 (2)	75
C(9)	0.165 (2)	0.187 (2)	0.195 (2)	24
C(10)	0.159 (2)	0.198 (2)	0.210 (2)	37
C(11)	0.162 (3)	0.216 (3)	0.246 (2)	45
C(12)	0.188 (3)	0.279 (3)	0.307 (3)	77
C(13)	0.164 (3)	0.205 (3)	0.242 (2)	45
C(14)	0.195 (3)	0.266 (3)	0.303 (3)	78
C(15)	0.172 (3)	0.201 (2)	0.244 (3)	40
C(16)	0.191 (3)	0.254 (3)	0.274 (3)	103
C(17)	0.171 (3)	0.220 (3)	0.222 (2)	100
C(18)	0.179 (3)	0.250 (3)	0.272 (3)	121
C(19)	0.201 (3)	0.221 (3)	0.236 (3)	56
C(20)	0.193 (3)	0.207 (3)	0.251 (3)	47
C(21)	0.201 (3)	0.249 (3)	0.269 (3)	87
C(22)	0.209 (3)	0.242 (3)	0.327 (3)	93
C(23)	0.202 (3)	0.221 (3)	0.272 (3)	81
C(24)	0.204 (3)	0.291 (3)	0.310 (4)	47

<sup>a</sup>  $\Gamma$  is the angle that the major axis of the vibrational ellipsoid makes with the normal to the least-squares planes through the porphyrin.

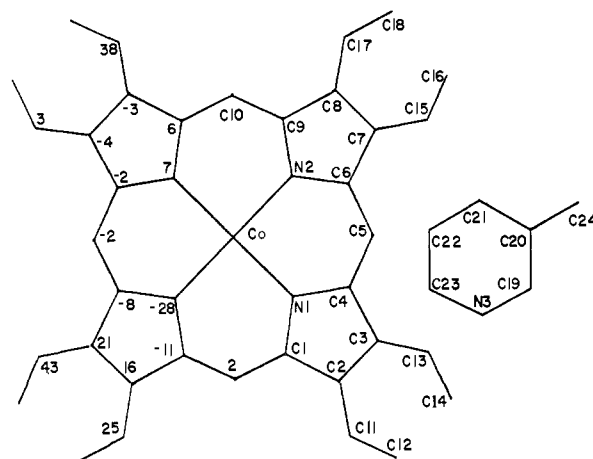
is nearly perpendicular to the plane of the porphyrin ( $93.6^\circ$ ) and is oriented approximately parallel to the Co–N(1) vector (vector to plane-normal angle =  $79.6^\circ$ ).

The porphyrin itself is essentially undistorted and is nearly planar. The deviations from the least-squares planes through the molecule are presented in Table VI. The largest deviation involves pyrrole 2 (see Figure 2) which is tilted by  $1.2^\circ$  with respect to the plane of the porphyrin.

The bond distances and angles within the axial 3-picoline molecule are self-consistent and agree well with the dimensions of the pyridine rings observed in Ni(3,5-lut)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>,<sup>28</sup> Ni(3,4-lut)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>,<sup>29</sup> Fe(py)<sub>4</sub>-(SCN)<sub>2</sub>,<sup>30</sup> Cu(F<sub>6</sub>-acac)<sub>2</sub>(py)<sub>2</sub>,<sup>31</sup> Co(acac)<sub>2</sub>(py)<sub>2</sub>,<sup>32</sup> Ni-

(28) F. Madaulle-Aubry, W. R. Busing, and G. M. Brown, *Acta Crystallogr., Sect. B*, **24**, 745 (1968).

(29) F. Madaulle-Aubry, W. R. Busing, and G. M. Brown, *Acta Crystallogr., Sect. B*, **24**, 754 (1968).



**Figure 2.** Drawing to indicate the numbering sequence used in this paper for the 28 independent, non-hydrogen atoms. The left-hand side of the diagram gives the displacement, in units of 0.001  $\text{\AA}$ , of the atoms from the weighted least-squares plane through the centrosymmetric porphyrin molecule. See Table VI.

(acac)<sub>2</sub>(py)<sub>2</sub>,<sup>33</sup> and Zn(TPyP)(py).<sup>34</sup> On the other hand they are significantly different from the dimensions of the 3-picoline molecule reported by Schuchart–Wasson, *et al.*<sup>35</sup> The bond lengths in the 3-picoline molecule, uncorrected for thermal motion, are definitely shorter than those obtained by Bak, *et al.*,<sup>36</sup> in the microwave study of pyridine.

## Discussion

A comparison of the structure of Co(3-pic)<sub>2</sub>(OEP) with that of other OEP complexes is difficult. There are only two comparably accurate structural determinations: the tetragonal<sup>37</sup> and triclinic<sup>38,39</sup> forms of

(30) I. Sotofte and S. E. Rasmussen, *Acta Chem. Scand.*, **21**, 2028 (1967).

(31) K. Pradilla-Sorzano and J. P. Fackler, *Inorg. Chem.*, **12**, 1174 (1973).

(32) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(33) R. C. Elder, *Inorg. Chem.*, **7**, 2316 (1968).

(34) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

(35) S. J. Schuchart-Wasson, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **12**, 187 (1973).

(36) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **2**, 361 (1958).

(37) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **28**, 2162 (1972).

(38) D. L. Cullen and E. F. Meyer, Jr., Abstract A1, American Crystallographic Association, Winter Meeting, Gainesville, Fla., Jan 1973.

(39) D. L. Cullen and E. F. Meyer, Jr., *J. Amer. Chem. Soc.*, **96**, 2095 (1974).

Table V. Bond Distances (Å) and Angles (deg) in Co(3-pic)<sub>2</sub>(OEP)<sup>a</sup>

Average			Average		
Co-N(1)	1.991 (1)	1.992 (1) Co-N <sub>porph</sub> <sup>b</sup>	C(1)-N(1)-C(4)	104.9 (1)	105.0 (1) C <sub>a</sub> -N-C <sub>a</sub>
Co-N(2)	1.993 (1)		C(6)-N(2)-C(9)	105.0 (1)	
Co-N(3)	2.386 (2)		N(1)-C(1)-C(2)	110.8 (2)	
N(1)-C(1)	1.378 (2)	1.374 (3) N-C <sub>a</sub>	N(1)-C(4)-C(3)	111.0 (2)	111.0 (2) N-C <sub>a</sub> -C <sub>b</sub>
N(1)-C(4)	1.374 (2)		N(2)-C(6)-C(7)	111.0 (2)	
N(2)-C(6)	1.372 (2)		N(2)-C(9)-C(8)	111.1 (2)	
N(2)-C(9)	1.372 (2)	1.449 (2) C <sub>a</sub> -C <sub>b</sub>	N(1)-C(1)-C(10)*	124.7 (2)	124.5 (3) N-C <sub>a</sub> -C <sub>m</sub>
C(1)-C(2)	1.448 (2)		N(1)-C(4)-C(5)	124.3 (2)	
C(3)-C(4)	1.448 (2)		N(2)-C(6)-C(5)	124.3 (2)	
C(6)-C(7)	1.448 (2)	1.355 (3) C <sub>b</sub> -C <sub>b</sub>	N(2)-C(9)-C(10)	124.9 (2)	124.4 (3) C <sub>m</sub> -C <sub>a</sub> -C <sub>b</sub>
C(8)-C(9)	1.451 (2)		C(10)-C(1)-C(2)	124.4 (2)	
C(2)-C(3)	1.355 (3)		C(5)-C(4)-C(3)	124.7 (2)	
C(7)-C(8)	1.355 (3)	1.381 (2) C <sub>a</sub> -C <sub>m</sub>	C(5)-C(6)-C(7)	124.7 (2)	106.5 (3) C <sub>a</sub> -C <sub>b</sub> -C <sub>b</sub>
C(1)-C(10)*	1.379 (3)		C(10)-C(9)-C(8)	124.0 (2)	
C(4)-C(5)	1.381 (2)		C(1)-C(2)-C(3)	106.6 (2)	
C(5)-C(6)	1.382 (2)	1.501 (4) C <sub>b</sub> -C1(Et)	C(4)-C(3)-C(2)	106.6 (2)	125.8 (5) C <sub>a</sub> -C <sub>m</sub> -C <sub>a</sub>
C(9)-C(10)	1.383 (2)		C(6)-C(7)-C(8)	106.6 (2)	
C(2)-C(11)	1.506 (2)		C(9)-C(8)-C(7)	106.3 (2)	
C(3)-C(13)	1.502 (3)	1.509 (5) C1(Et)-C2(Et)	C(4)-C(5)-C(6)	126.2 (2)	113.7 (5) C <sub>b</sub> -C1(Et)-C2(Et)
C(7)-C(15)	1.501 (3)		C(1)-C(10)-C(9)	125.5 (2)	
C(8)-C(17)	1.497 (2)		C(2)-C(11)-C(12)	113.1 (2)	
C(11)-C(12)	1.506 (3)	1.509 (5) C1(Et)-C2(Et)	C(3)-C(13)-C(14)	113.8 (2)	128.0 (4) C <sub>b</sub> -C <sub>b</sub> -C1(Et)
C(13)-C(14)	1.508 (3)		C(7)-C(8)-C(17)	128.1 (2)	
C(15)-C(16)	1.507 (3)		C(8)-C(7)-C(15)	127.4 (2)	
C(17)-C(18)	1.516 (3)	89.8 (5) N-Co-N	C(1)-C(2)-C(11)	125.0 (2)	125.4 (5) C <sub>a</sub> -C <sub>b</sub> -C1(Et)
N(3)-C(19)	1.335 (3)		C(4)-C(3)-C(13)	125.1 (2)	
N(3)-C(23)	1.332 (3)		C(6)-C(7)-C(15)	126.0 (2)	
C(19)-C(20)	1.379 (3)		C(9)-C(8)-C(17)	125.6 (2)	
C(20)-C(21)	1.373 (3)		N(3)-C(19)-C(20)	125.0 (2)	
C(21)-C(22)	1.379 (4)		N(3)-C(23)-C(22)	123.1 (2)	
C(22)-C(23)	1.370 (3)		C(19)-N(3)-C(23)	116.2 (2)	
C(20)-C(24)	1.498 (3)		C(19)-C(20)-C(21)	117.3 (2)	
HC(19)-N(1)	2.647 <sup>d</sup>		C(19)-C(20)-C(24)	121.3 (2)	
HC(19)-C(1)	3.167 <sup>d</sup>		C(20)-C(21)-C(22)	118.8 (2)	
HC(19)-C(4)	2.856 <sup>d</sup>		C(21)-C(20)-C(24)	121.4 (2)	
HC(23)-N(1)	2.630 <sup>d</sup>		C(21)-C(22)-C(23)	119.5 (2)	
HC(23)-C(1)	3.073 <sup>d</sup>				
HC(23)-C(5)	3.406 <sup>d</sup>				
N(1)-Co-N(2)	89.92 (6)	89.8 (5) N-Co-N			
N(1)-Co-N(2)*	90.08 (6)				
N(1)-Co-N(3)	90.29 (6)				
N(2)-Co-N(3)	89.10 (6)				

<sup>a</sup> The figure in parentheses following an average value is the larger of the standard deviations estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. <sup>b</sup> The notation C<sub>a</sub>, C<sub>b</sub>, and C<sub>m</sub> is that of Hoard.<sup>40</sup> <sup>c</sup> Atoms superscripted with an asterisk are the centrosymmetric equivalents of the nonsuperscripted atoms. <sup>d</sup> Intramolecular, nonbonded contacts calculated on the basis of idealized H atom positions.

Ni(OEP). The relevant bond distances are presented in Table VII. Although the bond lengths (and angles) in the planar form of Ni(OEP) and in Co(3-pic)<sub>2</sub>(OEP) are very similar, it does appear that there are some small differences in the C<sub>m</sub>-C<sub>a</sub> and C<sub>b</sub>-C<sub>b</sub><sup>40</sup> bond lengths, which are related to the contraction of the porphyrin macrocycle in the Ni(II) complex. Similarly, there may be significantly more double bond character to the N-C<sub>a</sub> and C<sub>b</sub>-C<sub>b</sub> bonds in these planar OEP complexes than in the ruffled form of Ni(OEP).

The bond distances in the Co(3-pic)<sub>2</sub>(OEP) molecule may also be compared (Table VII) with those observed by Scheidt<sup>16</sup> in Co(pip)<sub>2</sub>(TPP). The agreement is exceptionally good for all the bond distances (and angles), except for those about the methine, C<sub>m</sub>, carbon atoms. In agreement with previous workers,<sup>41,42</sup> we note that the C<sub>m</sub>-C<sub>a</sub> bond distances are longer and the C<sub>a</sub>-C<sub>m</sub>-C<sub>a</sub>

bond angles smaller in the meso-substituted TPP porphyrin complex than in the complexes of OEP.

The bond from the cobalt atom to the axial 3-picoline molecule (2.386 (2) Å) is significantly longer than normal Co(II)-N distances. However, similarly long axial bonds in Co(II) complexes have been observed by Glick, *et al.*, in Co([14]dieneN<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>,<sup>43</sup> (Co-O, 2.482 (5) Å) and by Scheidt in Co(pip)<sub>2</sub>(TPP)<sup>16</sup> (Co-N, 2.436 (2) Å). We estimate that unhindered Co(II)-N(sp<sup>2</sup>) bond lengths should be about 2.05 Å in length.<sup>44</sup> The lengthening of ~0.3 Å observed here can be attributed to the single unpaired electron located principally in the d<sub>z<sup>2</sup></sub> orbital. In the following paper<sup>17</sup> we demonstrate that the axial Co-N bond length decreases to 1.93 (2) Å when the d<sub>z<sup>2</sup></sub> orbital is unoccupied as in the low-spin Co(III) complex Co(Im)<sub>2</sub>(TPP)<sup>+</sup>. The dramatic lengthening of metal-ligand bond distances with the occupancy of the d<sub>z<sup>2</sup></sub> orbital has previously been demonstrated by

(40) The notation C<sub>a</sub>, C<sub>b</sub>, and C<sub>m</sub> is that of J. L. Hoard, *Science*, **174**, 1295 (1971).

(41) P. W. Codding and A. Tulinsky, *J. Amer. Chem. Soc.*, **94**, 4151 (1972).

(42) J. W. Lauher and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 5148 (1973).

(43) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 5092 (1973). [14]dieneN<sub>4</sub> is a tetradentate macrocyclic ligand.

(44) If one takes the value of 2.114 (9) Å observed in Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup><sup>45,46</sup> and subtracts 0.06 (1) Å to take into account the sp<sup>2</sup> hybridization of the imidazole N atom then one arrives at 2.05 (2) Å.

**Table VI.** Deviations (Å) ( $10^3$ ) and Equations of Weighted Least-Squares Planes<sup>a,b</sup>

Atom	Plane 1	Plane 2	Plane 3	Plane 4
Co	0	-16		234
N(1)	7 (2)	1 (2)		
N(2)	-28 (2)		0 (2)	
C(1)	6 (2)	0 (2)		
C(2)	-3 (2)	-1 (2)		
C(3)	-4 (2)	2 (2)		
C(4)	-2 (2)	-2 (2)		
C(5)	-2 (2)	0	11	
C(6)	-8 (2)	-13	0 (2)	
C(7)	21 (2)		1 (2)	
C(8)	16 (2)		-1 (2)	
C(9)	-11 (2)		1 (2)	
C(10)	2 (2)		26	
C(11)	38			
C(13)	2			8 (2)
C(15)	43			-1 (2)
C(17)	25			-6 (2)
N(3)				20 (2)
C(19)				-4 (3)
C(20)				-18 (2)
C(21)				-8 (3)
C(22)				
C(23)				
C(24)				

Coefficients of the Plane Equation $Ax + By + Cz = D$				
Plane	A	B	C	D
1	9.305	4.819	3.510	0.000
2	9.307	4.875	3.494	0.016
3	9.365	4.671	3.409	-0.069
4	3.080	-4.873	-7.075	-0.234

Angles between Normals to the Planes			
Plane A	Plane B	Angle (deg)	
1	2	0.3	
1	3	1.2	
1	4	93.6	
2	3	1.4	

<sup>a</sup> The entries for which an error is *not* indicated are for atoms which were not included in the calculation of the plane. <sup>b</sup> The plane is in triclinic coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Barnet, *et al.*,<sup>45,46</sup> who showed that the six Co-NH<sub>3</sub> bond lengths in the Co(II) and Co(III) hexaammines differ by 0.18 Å. The effect is accentuated in the TPP, OEP, and [14]dieneN<sub>4</sub> complexes because of the geometrical constraints of these macrocyclic chelates. These constraints may also be the origin of the enhanced kinetic lability of axial ligands in porphyrin complexes.<sup>47-51</sup> An alternative estimate of the effect of porphyrin on the axial bond lengths may be obtained from the structure of *trans*-Co(acac)<sub>2</sub>(py)<sub>2</sub>,<sup>32</sup> in which the axial Co-N(pyridine) distances average to 2.187 (10) Å.

The axial bond length of 2.386 (2) Å in Co(3-pic)<sub>2</sub>(OEP) is significantly shorter than the 2.436 (2) Å Co-

(45) T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

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(51) R. F. Pasternack and M. A. Cobb, *Biochem. Biophys. Res. Commun.*, **51**, 507 (1973).

**Table VII.** Comparisons of Selected Bond Lengths (Å) and Angles (deg) in the Porphyrin Core

Bond length or angle	Co(3-pic) <sub>2</sub> (OEP)	Ni(OEP) planar	Ni(OEP) ruffled	Co(pip) <sub>2</sub> (TPP)	"Average porphyrin" <sup>a</sup>
M-N	1.992 (1)	1.958 (2)	1.929 (3)	1.987 (2)	2.013
N-C <sub>a</sub>	1.374 (3)	1.376 (6)	1.386 (4)	1.380 (2)	1.384
C <sub>a</sub> -C <sub>b</sub>	1.449 (2)	1.443 (3)	1.444 (4)	1.444 (3)	1.449
C <sub>b</sub> -C <sub>b</sub>	1.355 (3)	1.346 (2)	1.362 (5)	1.344 (3)	1.358
C <sub>a</sub> -C <sub>m</sub>	1.381 (2)	1.371 (4)	1.373 (5)	1.392 (2)	1.389
C <sub>a</sub> -N-C <sub>a</sub>	105.0 (1)	103.9 (4)	105.1 (3)	104.8 (1)	
N-C <sub>a</sub> -C <sub>m</sub>	124.5 (3)	124.4 (3)	124.0 (2)	125.8 (2)	
N-C <sub>a</sub> -C <sub>b</sub>	111.0 (2)	111.6 (3)	110.6 (2)	110.5 (2)	
C <sub>a</sub> -C <sub>b</sub> -C <sub>b</sub>	106.5 (3)	106.5 (4)	106.8 (3)	107.0 (2)	
C <sub>a</sub> -C <sub>m</sub> -C <sub>a</sub>	125.8 (5)	125.1 (1)	124.1 (2)	123.4 (2)	
Ref	This work	38, 39	37	16	40

<sup>a</sup> These are the averaged bond distances given by Hoard<sup>40</sup> for the four structures Fe(PP-IX)Cl, Fe(O-CH<sub>3</sub>)(MP-IX-DME), Fe(TPP)Cl, and Pd(TPP).

N(piperidine) bond length observed in Co(pip)<sub>2</sub>(TPP).<sup>16</sup> The shorter bond to 3-picoline compared with piperidine can be attributed to the differences in the covalent radii of the sp<sup>3</sup> and sp<sup>2</sup> hybridized nitrogen atoms, to metal-ligand π-bonding, to the difference in the porphyrins, or to some combination of effects. Steric factors can be ruled out because of the significantly shorter nonbonded contacts made by the axial base in Co(3-pic)<sub>2</sub>(OEP) (2.63 Å), compared with Co(pip)<sub>2</sub>(TPP) (2.84 Å).

In Table VIII we compare metal-N bond lengths observed in a variety of complexes involving sp<sup>3</sup> or sp<sup>2</sup> hybridized nitrogen atoms. We have restricted ourselves to comparisons among structures where steric

**Table VIII.** A Comparison of Selected Metal-N(sp<sup>2</sup>) and -N(sp<sup>3</sup>) Bond Lengths

Complex	M-N	Bond length (Å)	Δ	Ref
Co(NH <sub>3</sub> ) <sub>5</sub> (N <sub>3</sub> ) <sup>2+</sup>	Co-NH <sub>3</sub>	1.968 (7)	0.025 (9)	<i>a</i>
	Co-N <sub>3</sub>	1.943 (5)		
Co(NH <sub>3</sub> ) <sub>5</sub> (NO <sub>2</sub> ) <sup>2+</sup>	Co-NH <sub>3</sub>	1.978 (7)	0.057 (22)	<i>b</i>
	Co-NO <sub>2</sub>	1.921 (21)		
Co(NH <sub>3</sub> ) <sub>5</sub> (NO <sub>2</sub> ) <sub>3</sub>	Co-NH <sub>3</sub>	1.96 (1)	0.04 (1)	<i>c</i>
	Co-NO <sub>2</sub>	1.92 (1)		
[Pd(NO <sub>2</sub> )(NH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>	Pd-NO <sub>2</sub>	1.984 (8)	0.059 (11)	<i>d</i>
[Pd(NH <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>4</sub>	Pd-NH <sub>3</sub>	2.043 (8)		
<i>trans</i> -Pt(NH <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub>	Pt-NH <sub>3</sub>	2.038 (18)	0.081 (26)	<i>e</i>
	Pt-NH <sub>2</sub>	1.957 (18)		
<i>trans</i> -Pt(1-Me-Im) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	Pt-NH <sub>3</sub>	2.07 (3)	0.06 (4)	
	Pt-Im	2.01 (2)		
Co(NH <sub>3</sub> ) <sub>5</sub> (NO) <sup>2+</sup>	Co-NH <sub>3</sub>	1.981 (6)	0.110 (8)	<i>g</i>
	Co-NO	1.871 (6)		
Fe(pip) <sub>2</sub> (TPP)	Fe-pip	2.127 (3)	0.142 (6)	<i>h</i>
Fe(Im) <sub>2</sub> (DMG) <sub>2</sub>	Fe-Im	1.985 (5)		<i>i</i>
[Co(pip) <sub>2</sub> (TPP)] <sup>+</sup>	Co-pip	2.060 (3)	0.134 (20)	<i>j</i>
[Co(Im) <sub>2</sub> (TPP)] <sup>+</sup>	Co-Im	1.926 (20)		<i>k</i>

<sup>a</sup> G. Palenik, *Acta Crystallogr.*, **17**, 360 (1964). <sup>b</sup> F. A. Cotton and W. T. Edwards, *ibid.*, **24**, 474 (1968). <sup>c</sup> M. Laing, S. Baines, and P. Sommerville, *Inorg. Chem.*, **10**, 1057 (1971). <sup>d</sup> F. P. Boer, V. B. Carter, and J. W. Turley, *ibid.*, **10**, 651 (1971). <sup>e</sup> N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 801 (1962). <sup>f</sup> J. W. Carmichael, N. Chan, A. W. Cordes, C. K. Fair, and D. A. Johnson, *Inorg. Chem.*, **11**, 1117 (1972). <sup>g</sup> C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971). <sup>h</sup> J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972). <sup>i</sup> K. Bowman, A. P. Gaughan, and Z. Dori, *ibid.*, **94**, 727 (1971). <sup>j</sup> Reference 16. <sup>k</sup> Reference 17.

effects are minimal. For this reason complexes containing chelates such as ethylenediamine, bipyridine, and phenanthroline are not included. We note, however, that Lewis, *et al.*,<sup>52</sup> have compared Ni-N distances in a large number of planar nickel chelates. They find a consistent difference of 0.05 (1) Å in the Ni-N(sp<sup>3</sup>) and Ni-N(sp<sup>2</sup>) bond lengths. Similarly, Bonnet and Jeannin<sup>53</sup> found an average difference of 0.08 (2) Å in the Cu-N bond lengths they surveyed. With the notable exception of the last three comparisons, the entries in Table VIII indicate a difference of 0.03–0.08 Å in N(sp<sup>3</sup>)– and N(sp<sup>2</sup>)–metal bond lengths. The data in Table VIII do not allow one to distinguish the contribution of metal–ligand  $\pi$ -bonding to the shortening of the M–N(sp<sup>2</sup>) bond length. However, differences of 0.06 Å in N–C bond lengths are quite normally observed<sup>54</sup> in organic compounds in cases where  $\pi$ -bonding can be discounted. On this basis we conclude that the 0.05 Å difference in the axial bond lengths in Co(3-pic)<sub>2</sub>(OEP) and Co(pip)<sub>2</sub>(TPP) arises from the hybridization of the ligand nitrogen atoms and is not indicative of  $\pi$ -bonding or of sensitivity of this bond length to the nature of the porphyrin.

The exceptions listed in Table VIII may be attributed, respectively, to the overwhelming electronic effect of the nitrosyl group in [Co(NH<sub>3</sub>)<sub>5</sub>(NO)]<sup>2+</sup> and to the steric interaction of the bulky axial piperidine molecules in Co(pip)<sub>2</sub>(TPP)<sup>+</sup> and Fe(pip)<sub>2</sub>(TPP).

The available thermodynamic data<sup>2–4</sup> do not appear to show any clear-cut differences between pyridine and

(52) R. M. Lewis, G. H. Nancollis, and P. Coppens, *Inorg. Chem.*, **11**, 1371 (1972).

(53) J. J. Bonnet and Y. Jeannin, *Acta Crystallogr., Sect. B*, **26**, 318 (1970).

(54) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 221.

piperidine. On the other hand these data clearly indicate that the stability of a five-coordinate complex is much greater than that of a six-coordinate complex. This is consistent with the structural results for Co(1-Me-Im)(OEP)<sup>18</sup> and Co(3-pic)<sub>2</sub>(OEP). The long axial Co–N bond lengths in the latter complex are indicative of destabilization of six-coordination by the single electron in the d<sub>z<sup>2</sup></sub> orbital.

Although the thermodynamic data do not allow one to distinguish differences between imidazoles and other bases, it is significant that there is no evidence for the formation of six-coordinate Co(II) complexes with imidazoles. Both the preparative work reported here and the epr work of Hoffman and Marchant<sup>55</sup> and of Stynes<sup>21</sup> have shown that there is no appreciable six-coordinate complex formation, even in pure 1-methylimidazole or in 1-methylimidazole–toluene glasses at low temperatures.

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**Supplementary Material Available.** Tables I and III 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. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4440.

(55) B. M. Hoffman and L. Marchant, personal communication.