Stereochemistry of Low-Spin Cobalt Porphyrins. I. Structure and Bonding in a Nitrosylcobalt Porphyrin and Their Bearing on One Rational Model for the Oxygenated Protoheme[1]

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Abstract: Nitrosyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(II), ONCoTPP, crystallizes preferentially from solutions in which the six-coordinate ONCoN$_b$TPP [N$_b$ = piperidine) is presumably the most plentiful complexed species. With a square-pyramidal coordination group, but a strongly kinked Co–N–O linkage, the ONCoTPP molecule observes statistically required C_{4h} symmetry in an eightfold-disordered variant of a well-known structural type based on the tetragonal space group, $I4/m$. Cell data are: $a = 13.434$, $c = 9.754$ Å; $Z = 2$; $\rho_{\text{calcd}} = 1.32$, $\rho_{\text{exptl}} = 1.31$ g/cm^3 at 20°. Intensity data for 1241 independent reflections having $(\sin\theta)/\lambda < 0.73$ Å^{-1}, recorded with Zr-filtered Mo Kα radiation on a computer-controlled four-circle diffractometer, were employed for refinement of the statistically averaged structure. Bond parameters in the porphinato core agree well with those observed in the low-spin iron porphyrins. The displacement of the cobalt atom from the porphinato core (Ct···Co) and the displacement of the nitrosyl nitrogen atom (N$_2$) from the fourfold axis are obscured in the statistical model, although their reality is supported by a variety of indirect evidence. Using a Fourier superposition technique, Ct···Co is estimated as 0.094 (52) Å which, with Ct···N$_2$ = 1.927 (10) Å, gives Co–N$_2$ = 1.833 (52) Å. Displacement off-axis of the N$_2$ atom by $\gtrsim$0.10 Å corresponds to a CoN$_2$O angle $\lesssim$128.5° and O–N$_2$ $\gtrsim$ 1.10 Å as compared with 135.2° and 1.03 Å in the averaged model. The stereochemistry of the axial Co–N–O linkage in the ONCoTPP molecule closely resembles that in the six-coordinate $\mathrm{ONCo(NH_3)_5{}^{2+}}$ and $\mathrm{ONCo(Cl)(en)_2{}^{+}}$ [en = ethylenediamine] species. Formulation of the unique complexing bond in the three complexes as Co(II)–NO with a limited overlay of back-π-bonding to the π^* orbital of the doubly bonded ($\sigma + \pi$) ligand affords a rational correlation with the pronounced structural trans effects and other pertinent data. In the stereochemically analogous model for the oxygenated protoheme, by contrast, the dative formulation Fe(III)–$\mathrm{O_2{}^-}$, associated with strongly developed back-π-bonding, is indicated in first approximation.

Earlier work that is especially relevant to our quantitative stereochemical studies of low-spin cobalt porphyrins may be cited as follows: Walker's electron spin resonance studies[3a] of numerous low-spin cobalt(II) porphyrins in toluene glasses at 77°K and her equilibrium studies[3b,c] of the complexing in toluene solution of respectively one[3b] and two[3c] molecules of a nitrogen base by a low-spin cobalt(II) porphyrin, the preparation and characterization by Hoffman and coworkers[4] of cobaltohemoglobin—the product of replacement in hemoglobin of the protohemes by molecules of the analogous cobalt(II) protoporphyrin, Perutz's[5] stereochemical mechanism for the reversible oxygenation of hemoglobin, and our own investigations dating onward from 1965 of iron porphyrin stereochemistry.[6]

The bearing of the earlier work on our program is readily indicated if we first specify the cobalt porphyrins for which we have obtained definitive stereochemical data. X-Ray analyses of crystalline structure for five cobalt porphyrins derived from the free base, $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (written H$_2$TPP), have been completed. The stereochemical parameters of the diamagnetic nitrosylcobalt(II) derivative, ONCoTPP, are reported herein; those of the charged bis(piperidine)-cobalt(III) derivative,[7a] [Pip$_2$CoTPP]$^+$, of the paramagnetic ($S = {}^1/_2$) bis(piperidine)cobalt(II) derivative,[7b] Pip$_2$CoTPP, of the paramagnetic ($S = {}^1/_2$) 1-methylimidazolecobalt(II) derivative,[7c] 1-MeImCoTPP, and of the nitro-3,5-lutidinecobalt(III) derivative,[7d] O$_2$NCo(3,5-Lut)TPP, are forthcoming in papers II to V of this series. As emphasized earlier,[6] the stereochemical parameters of the octahedral cobalt(III) porphyrins[7a,d] serve as useful standards of reference for the otherwise more interesting low-spin cobalt(II), iron(II), and iron(III) porphyrins.

Walker reports[3a] three distinctive patterns of esr spectra from the metalloporphyrins formed by the d^7 cobalt(II) atom accordingly as the axial ligand system involves the complexing of just one molecule of a nitrogen base, two molecules of the base, or one molecule each of a nitrogen base and of reversibly bound oxygen. She reports also that the complexing in toluene solution of one molecule of a nitrogen base is attended by a mod-

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[2] (a) Cornell University; (b) University of Notre Dame.

[3] (a) F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970); (b) *ibid.*, **95**, 1150 (1973); (c) *ibid.*, **95**, 1154 (1973); (d) see also D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, **95**, 1796 (1973).

[4] (a) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci.*, **67**, 637 (1970); (b) B. M. Hoffman, C. A. Spilburg, and D. H. Petering, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 343 (1971); (c) G. C. Hsu, C. A. Spilburg, C. Bull, and B. M. Hoffman, *Proc. Nat. Acad. Sci.*, **69**, 2122 (1972).

[5] (a) M. F. Perutz, *Nature (London)*, **228**, 726 (1970); (b) M. F. Perutz and L. F. Ten Eyck, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 295 (1972).

[6] See J. L. Hoard, *Science* **174**, 1295 (1971), for a critical review in which the results of three studies published during 1972 are included.

[7] (a) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973); (b) W. R. Scheidt, *ibid.*, in press; (c) W. R. Scheidt, *ibid.*, in press; (d) J. A. Kaduk and W. R. Scheidt, manuscript in preparation.

est decrease in enthalpy (7–11 kcal/mol at 25°) which varies with the chemical and steric character of the base[3b] and that the complexing of a second molecule of the base, when sterically allowed, involves little further reduction in enthalpy ($\sim$2 kcal/mol).[3c] The correlation of these thermodynamic data with structure is displayed in our studies of the six-coordinate Pip$_2$CoTPP[7b] and five-coordinate 1-MeImCoTPP[7c] species.

The further stimulus to our interest in the cobalt porphyrins was the demonstration by Hoffman, *et al.*,[4] that the reversible uptake of oxygen by cobaltohemoglobin, as with hemoglobin, is modulated by cooperative interactions of the four subunits in the molecule. Noting that the proximal histidine residue of the globin framework is bonded to the metal atom, it appears that the low-spin cobalt atom serves as a qualitatively appropriate substitute for the iron atom both in the high-spin five-coordinate hemes of deoxyhemoglobin and in the low-spin oxygenated hemes of oxyhemoglobin. This behavior is correlated with the distribution of the electron density associated with the odd electron in the axial bond system of the cobalt atom; in the five-coordinate species, this electron density is largely confined to the 3d$_{z^2}$ orbital of the cobalt atom, whereas in the oxygenated species, it is considered to be largely concentrated in the 2pπ^* antibonding orbital of the dioxygen ligand.[4c]

In Perutz's[5] stereochemical mechanism for the oxygenation of hemoglobin, cooperative interaction of the subunits is triggered by the shrinkage of $\sim$0.90 Å in the distance ($N_\epsilon \cdots P_m$) separating the axially complexed histidine nitrogen atom (N_ϵ) from the mean plane (P_m) of the porphine skeleton that accompanies transition of the iron atom from high-spin five-coordination to low-spin six-coordination. This axial connection ($N_\epsilon \cdots P_m$) between the heme and the globin framework in deoxyhemoglobin is stretched by $\sim$0.30 Å beyond the value which applies in an externally unconstrained molecule of a high-spin imidazoleiron(II) porphyrin.[8,9] The question whether a similar stereochemical trigger for cooperative interaction is applicable to the oxygenation of cobaltohemoglobin is considered elsewhere.[9]

Concurrently with unsuccessful attempts to prepare single crystals for X-ray analysis of some of the oxygenated cobalt porphyrins identified by Walker, we undertook the preparation of the analogous six-coordinate porphyrin in which a molecule of nitric oxide replaces dioxygen as the second axial ligand; the coordination group in such a nitrosyl complex is isoelectronic with that in the oxygenated protoheme. The unanticipated crystallization of the five-coordinate ONCoTPP species lent some credence to the possibility that excision of the nitrogen base might be associated with a preference for a Co–N–O linkage of the linear type exemplified by the Fe–N–O linkage in the nitroprusside ion.[10]

Experimental Section

Preparation of ONCoTPP. All reactions were carried out under argon using modified Schlenk tubes. Four-coordinate CoTPP was prepared as previously described[11] and purified by chromatography on alumina using chloroform as the eluent. A solution of 250 mg of CoTPP in 60 ml of dichloromethane was carefully degassed, and 1.5 ml of piperidine (freshly distilled from BaO) was added to it. Nitric oxide (J. T. Baker Specialty Gases), purified by passing through KOH and Dry Ice traps, was bubbled into the solution for 20 min. Excess nitric oxide was removed by bubbling a stream of argon through the solution. The solution was transferred to a beaker and heated to boiling, and methanol was added until crystals appeared. The solution was cooled and the product isolated by filtration and recrystallized from dichloromethane–methanol to give lustrous purple crystals of ONCoTPP. *Anal.* Calcd for $CoC_{44}H_{28}N_5O$: C, 75.33; H, 4.02; N, 9.98. Found: C, 74.86; H, 4.01; N, 10.05.

The absence of piperidine from the crystalline product was rather surprising because there was no apparent reaction between the nitric oxide and the porphyrin when piperidine was excluded from the reaction mixture.

Sundry Physical Data. From measurement of the magnetic susceptibility by the nmr method of Evans,[12] the complex was found to be diamagnetic. The infrared spectrum of the crystals was recorded on a Perkin-Elmer 337 spectrometer using a KBr pellet; the absorption at 1689 cm^{-1} was assigned as ν(NO). The principal features of the mass spectrum, as obtained on an AEI MS-902 spectrometer, were peaks at m/e 671 (CoTPP$^+$) and 30 (NO$^+$); the parent ion (m/e 701) was not observed. A sensitive test for piezoelectricity in the crystals, using a Geibe–Schiebe detector, was negative.

Crystallographic and X-Ray Data. Crystals of ONCoTPP suitable for X-ray study were grown by allowing methanol to diffuse slowly into a chloroform solution of the porphyrin. Photographically recorded diffraction patterns from a crystal of tetragonal bipyramidal habit displayed the (Laue) point group symmetry of $4/m$-C_{4h}. Systematic extinctions were limited to those demanded by a body-centered lattice, thus leaving only $I4$, $I\bar{4}$, and $I4/m$ as possible space groups.[13] Precise lattice constants were obtained by least-squares refinement[14] of the diffraction geometry based on the angular settings of 32 reflections which were distributed equally between positive and negative 2θ. All measurements were made on a computer-controlled four-circle diffractometer at the ambient laboratory temperatue of 20 ± 1°. The lattice constants, a = 13.434 (1) and c = 9.754 (1) Å (Mo Kα_1; λ 0.70926 Å), were thus obtained. These constants led to a calculated density of 1.32 g/cm^3 for a cell content of two molecules of ONCoTPP; an experimental density of 1.31 g/cm^3 was determined by flotation in aqueous zinc chloride solution.

X-Ray intensity data were collected using Zr-filtered Mo Kα radiation with a takeoff angle of $\sim$3° on a computer-controlled four-circle diffractometer. The crystal specimen was a tetragonal bipyramid with edge lengths of 0.41, 0.41, and 0.19 mm. All independent reflections for which $(\sin \theta)/\lambda < 0.7254$ Å^{-1} were scanned by the θ–2θ technique at the rate of 1.0°/min. All scans included a variable increment in angle to allow for spectral dispersion; background counts of 40-sec duration were taken at the extremes of the scan. Three standard reflections monitored every 100 reflections throughout the data collection showed no fall-off as a function of X-ray exposure by the crystal. With a linear absorption coefficient of but 0.55 mm^{-1} no absorption corrections were deemed necessary. The intensity data were reduced to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factors. Data were retained as objectively observed for $|F_o| > 2\sigma_F$, σ_F being the standard deviation computed from $\sigma^2_F = (ct + k^2B)/4|F_o|^2(Lp)^2$, with ct the total count from the scan, k the ratio of scanning time to the total background counting time, and B the total background count. Data (1241) were retained as observed, some 88% of the total number of reflections accessible in the range of $(\sin \theta)/\lambda$ scanned.

Determination and Refinement of Structure. Consideration of the data made it evident that, whichever of the three possible space groups was applicable, the cobalt atoms were positioned in a precisely body-centered array. The point group symmetry (real or statistically effective) required of the ONCoTPP molecule was seen

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[8] L. J. Radonovich, J. P. Collman, C. Reed, and J. L. Hoard, manuscript in preparation.

[9] J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci.*, in press.

[10] (a) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963); (b) P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, **87**, 3340 (1965).

[11] (a) D. W. Thomas and A. E. Martell, *ibid.*, **81**, 511 (1959); (b) A. D. Adler, R. K. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

[12] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[13] "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, The Kynoch Press, Birmingham, England, 1965, p 177.

[14] Use was made of the PICK II computer program, a minor revision of W. C. Hamilton's MODE I program.

to be C_4 in $I4$, S_4 in $I\bar{4}$, or C_{4h} in I_4/m. Only in $I4$ (and then only if the Co–N–O bond system were linear) would it be possible to place the molecules in a fully ordered crystalline array. But a structure based upon $I4$ would require the molecular dipoles to be all in parallel alignment along the c axis and thus, in disagreement with observation, to give rise to rather pronounced piezoelectricity.

Earlier structure determinations for tetragonal crystals of the chloroiron(III),[15a] aquozinc(II),[15b] and aquomagnesium(II)[15c] derivatives of tetraphenylporphine had shown that these metalloporphyrins crystallize in a disordered variant of the structural type, based upon $I4/m$, for which crystals of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatodichlorotin(IV),[16] Cl_2SnTPP, afford the ordered prototype. The disordered variant is characterized by the statistically equal probability for parallel and antiparallel orientation of the unique molecular axis relative to the c axis of the crystal. It was found, however, that no less than eight equally probable orientations of the ONCoTPP molecule contribute to the crystalline disorder and to the structure of the statistically averaged molecule of C_{4h} symmetry. This result, the direct consequence of the markedly nonlinear geometry of the Co–N–O bond system, is illustrated in Figure 1 for the eight distinctive orientations of the coordination group. The nitrosyl oxygen atom appears as eight equivalent fractions, each carrying only one-eighth of the integrated charge density of the oxygen atom. Consequently, the presence of the oxygen atom was not detected in the initial Fourier synthesis of the structure amplitudes with phases determined by the contribution from the cobalt atoms. This synthesis did give positions for all carbon and nitrogen atoms in the asymmetric unit of structure (one-eighth of the statistically averaged molecule), the nitrosyl nitrogen atom as half-atoms on the fourfold axis at $00z$ and $00\bar{z}$. Full-matrix least-squares refinement[17] of this trial structure, followed by Fourier difference synthesis, then yielded the xyz coordinates of the fractional atom of oxygen in the asymmetric unit as a peak $\sim$1.0 Å from the half-atom of nitrosyl nitrogen to which it was bonded. The peak density was 0.65 e/Å^3 as compared with 5.3 and 2.3 e/Å^3 for the porphine nitrogen atom and the nitrosyl nitrogen half-atom, respectively.

At this point it had become clear that the displacement of the cobalt atom from the plane of the porphine nitrogen atoms, a physically real property of the individual ONCoTPP molecule, was very probably too small to be evaluated in the disordered crystalline arrangement by the procedure which was successfully employed to estimate the out-of-plane displacements of the metal atoms in the earlier studies[15] of this class of disordered structures, namely by the least-squares refinement of the variable z coordinate for half-atoms of the metal positioned at $00z$ and $00\bar{z}$. Given the rather wide range, $(\sin\theta)/\lambda \lesssim 0.725$ Å^{-1}, within which precisely measured intensity data were recorded, accurate positions for all carbon and nitrogen atoms in the statistically averaged molecule were then obtained by the objective evaluation, as described earlier,[18] of the positions of the electron density peaks in the Fourier synthesis of all F_o data; small corrections to the F_o data for the anomalous scattering of the cobalt atoms and to the observed positions of the peaks for finite termination of the Fourier series were included.[18] A new difference synthesis then gave improved coordinates for the fractional atom of oxygen. Fixed atomic positions from the syntheses were used in full-matrix least-squares refinement to give anisotropic thermal parameters (isotropic for oxygen) and, in conjunction with further difference syntheses, to detect the minor peaks in electron density associated with all of the C–H bonds. The empirical weighting scheme described earlier[18] was employed.

Apparent thermal parameters for the cobalt atom at 000 of $B_{11} = B_{22} = 2.86$ and $B_{33} = 4.21$ Å^2 were thus obtained. Inasmuch as the simultaneous evaluation of B_{33} and the z parameter for cobalt in the half-atom model[15] by least-squares refinement was precluded by the high correlation of these parameters, the value of z was independently estimated by the following objective procedure. The sum (superposition) of four Gaussian curves approximating to the distributions of electron density along the c axis of the half-atoms of cobalt at $\pm z$ and the half-atoms of nitrosyl nitrogen at $\pm z'$ was fitted by least-squares to the experimentally derived electron density along this axis. The position of the center, the half-width, and the height of each class of peak were allowed to vary. This fitting of the strongly overlapped peaks of the half-atoms of cobalt led to a physically rational displacement from the symmetry plane of ± 0.094 Å, accompanied, however, by the very large estimated standard deviation of 0.052 Å. The position thus obtained for the fully resolved nitrogen half-atom differed insignificantly from that already determined. The only change in the quantitative description of the structure which resulted from the introduction of cobalt half-atoms at $z = \pm 0.0096$ in final cylces of least-squares refinement was the reduction of B_{33} for cobalt to 3.50 Å^2, as compared with 4.21 Å^2 for $z = 0$. This refinement gave the same values for both reliability indices as that with the cobalt atom at the origin: 0.060 for the conventional R and 0.079 for the weighted R. Final difference syntheses suggested that the displacement out-of-plane of the cobalt atom resulted in a very slightly better fitting of the experimentally derived electron densities. The parameters of the structure, including both the averaged and the most probable values of z and B_{33} for the cobalt atom, are listed in Table I.[19] The bond parameters calculated from the data of Table I are given in Table II.

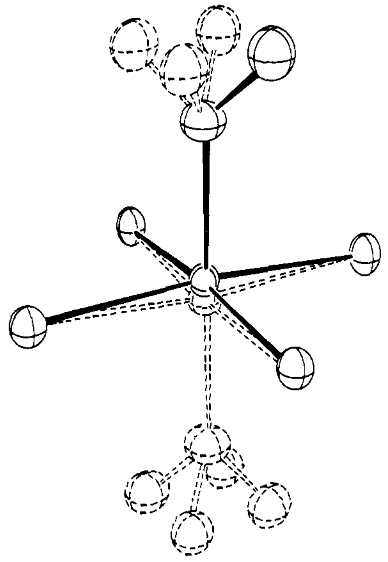

Figure 1. Computer-drawn diagram of the statistically disordered coordination group of the ONCoTPP molecule in the tetragonal crystal. The solid lines delineate the bonding pattern for one orientation of the molecule.

The restriction of the coordinates of the carbon and heavier atoms to the values (Table I) derived primarily by Fourier methods (refinement I) was relaxed in additional least-squares refinements (II, III, and IV). Hydrogen contributions were ignored in refinement II, but were included in III with fixed values of the parameters; they were also included *pro forma* in IV which was characterized by the exclusion from the refinement of the low-angle data from within the chromium Kα limiting sphere. These additional refinements, especially IV, were carried out because the earlier study[16] of crystalline Cl_2SnTPP had demonstrated that, given precise intensity data of extraordinary range in $(\sin\theta)/\lambda$, a refinement of type IV was certainly preferable to II and III and was perhaps preferable to the predominantly Fourier methods of I, for the realistic positioning of all atoms save hydrogen. No such detailed conclusions were suggested by the several refinements of the disordered ONCoTPP structure.

Discussion of Results

Stereochemistry of the ONCoTPP Molecule. The perspective diagram of the ONCoTPP molecule shown in Figure 2 is drawn with one of the eight equivalent

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(15) (a) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); (b) M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967); (c) R. Timkovich and A. Tulinsky, *ibid.*, **91**, 4430 (1969).

(16) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *ibid.*, **94**, 6689 (1972).

(17) The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$. The computations followed W. R. Busing, K. O. Martin, and H. A. Levy, "OR-FLS, a Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections, real and imaginary, for the anomalous scattering of the cobalt atom from D. T. Cromer, *ibid.*, **18**, 17 (1965).

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

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

Table I. Coordinates and Thermal Parameters of the Atoms in the Crystal[a]

Atom type	Atomic coordinates			Anisotropic thermal parameters,[b] Å^2				
	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B^c
Co	0	0	0	2.86 (6)	2.86 (6)	4.21 (4)	0	3.26
Co^d	0	0	96 (53)	2.87 (6)	2.87 (6)	3.50 (4)	0	3.07
N_2	0	0	1976 (10)	5.5 (5)	5.5 (5)	4.6 (4)	0	5.2
N_1	363 (2)	1425 (2)	0	3.2 (1)	3.2 (1)	5.2 (1)	0.0 (1)	3.7
C_1	−268 (2)	2234 (2)	0	3.9 (1)	3.1 (1)	5.2 (2)	0.3 (1)	4.0
C_2	280 (3)	3146 (2)	0	4.4 (1)	3.3 (1)	7.1 (2)	−0.1 (1)	4.7
C_3	1262 (3)	2896 (2)	0	4.0 (1)	3.4 (1)	7.1 (2)	−0.4 (1)	4.6
C_4	1302 (2)	1831 (2)	0	3.4 (1)	3.5 (1)	5.3 (1)	−0.3 (1)	4.0
C_5	−1307 (2)	2195 (2)	0	3.3 (1)	3.8 (1)	4.9 (1)	−0.3 (1)	3.9
C_6	−1868 (2)	3161 (2)	0	3.1 (1)	3.8 (1)	5.8 (2)	−0.2 (1)	4.1
C_7	−2941 (3)	4935 (3)	0	3.2 (1)	4.4 (1)	10.0 (3)	−0.4 (1)	5.2
$C_8{}^e$	−2124 (3)	3603 (2)	1224 (3)	5.2 (1)	7.6 (2)	5.7 (1)	−2.2 (1)	5.8
$C_9{}^f$	−2670 (3)	4498 (2)	1223 (4)	5.1 (1)	7.7 (2)	8.2 (2)	−1.7 (1)	6.5
O	−310 (10)	430 (10)	2710 (20)					5.7 (3)

[a] Figures in parentheses are the estimated standard deviations. [b] Note that $B_{13} = B_{23} = 0$ except for atoms C_8 and C_9. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$. [d] Position from curve fitting analysis; see text. [e] $B_{13} = -0.1$ (1), $B_{23} = -0.5$ (1) Å^2. [f] $B_{13} = -1.2(1)$, $B_{23} = -1.0(2)$ Å^2.

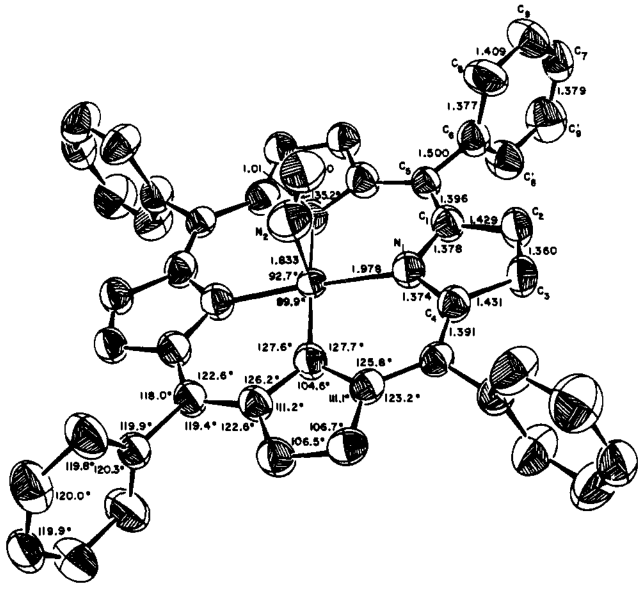

Figure 2. Computer-drawn diagram in perspective of the ONCoTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table I. The bond parameters are from Table II.

Table II. Stereochemical Parameters of the ONCoTPP Molecule[a]

Distances, Å		Angles, deg	
Ct···Co[b]	0.094 (52)	N_1CoN_2	92.7 (2)
Ct···N_2[b]	1.927 (10)	N_1CoN_1'	89.9 (1)
Co–N_2	1.833 (53)	CoN_2O	135.2 (8)
O–N_2	1.01 (2)	CoN_1C_1	127.7 (2)
Ct···N_1[b]	1.976 (3)	CoN_1C_4	127.6 (2)
Co–N_1	1.978 (4)	$N_1C_1C_5$	125.8 (3)
N_1–C_1	1.378 (4)	$N_1C_4C_5'$	126.2 (3)
N_1–C_4	1.374 (4)	$C_1C_5C_4'$	122.6 (3)
C_1–C_2	1.429 (4)	$C_1N_1C_4$	104.6 (2)
C_4–C_3	1.431 (4)	$N_1C_1C_2$	111.1 (3)
C_2–C_3	1.360 (5)	$N_1C_4C_3$	111.2 (3)
C_1–C_5	1.396 (5)	$C_1C_2C_3$	106.7 (3)
C_4–C_5'	1.391 (4)	$C_4C_3C_2$	106.5 (3)
C_5–C_6	1.500 (4)	$C_1C_5C_6$	118.0 (3)
C_6–C_8	1.377 (3)	$C_5C_6C_8$	119.9 (2)
C_8–C_9	1.409 (4)	$C_8C_6C_8'$	120.3 (3)
C_9–C_7	1.379 (5)	$C_6C_8C_9$	119.8 (3)
Ct···C_5[b]	3.427 (3)	$C_8C_9C_7$	120.0 (3)
N_1···N_2	2.760 (7)	$C_9C_7C_9'$	119.9 (4)

[a] Figures in parentheses are the estimated standard deviations. [b] Ct denotes the center of the statistically averaged molecule of C_{4h} symmetry.

orientations (Figure 1) of the Co–N–O bond system and with the most probable displacement (0.094 Å) of the cobalt atom from the center (Ct) of the statistically averaged molecule; apart from the axial bond system, the experimentally derived description of the molecule necessarily conforms to full C_{4h} symmetry. Using C_a and C_b to denote the respective α- and β-carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for the phenyl carbon atom which is bonded to the porphinato core, bonds of the N_1–C_a, C_a–C_b, and C_a–C_m chemical classes are divided each by C_{4h} into two structurally nonequivalent subclasses. The largest of the dimensional variations between two subclasses is observed for the C_1–C_5 and C_4–C_5' bonds of the C_a–C_m chemical class; these bonds (Figure 2) differ in length only by an apparent 0.005 Å or just one estimated standard deviation (esd). This result was not expected inasmuch as, in the ordered prototypal structure of Cl_2SnTPP,[16] the refinement of structure by any of the several procedures employed led invariably to wholly trivial departures from D_{4h} geometry.

By contrast with the Cl_2SnTPP study, wherein the C_b–C_b distance was the only bond length in the porphinato core which was in the least sensitive to the refinement procedure,[16] the position assigned to the nitrogen atom (N_1) in the core of ONCoTPP by refinements II–IV (as an averaged result) differs by an apparent 0.011 Å from that obtained from the internally more consistent refinement I. The effect of this difference on the apparent Co–N_1 and N_1–C_a bond lengths is made evident by comparing the values listed in the second and third columns of Table III. The bond lengths given in the fourth column of Table III, each of which is the mean of the corresponding values listed in columns 2 and 3, are seen to be objectively compatible with both of the alternative sets. We note further that the N–C and C–C bond lengths in column four differ insignificantly from those listed in the last column for the bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) cation, $[Im_2FeTPP]^+$, a species which, along with the chloride ion, crystallizes with no required symmetry from methanol solution to give an ordered monoclinic solvate.[20] The more precise structural data reported for triclinic crystals of bis(piperidine)-α,β,γ,δ-tetraphenylporphinatoiron(II), Pip_2FeTPP, provide just one averaged bond length in the core which might differ significantly from that in ONCoTPP; namely, C_a–C_b = 1.444 (3, 5) Å wherein the figures in parentheses are respectively the mean deviation from the average and the esd of an individual determination.[21]

Table III. Averaged Lengths (Å) of Selected Chemical Classes of Bonds[a]

Class of bond	Length in ONCoTPP from			Length in Im_2FeTPP^+
	Ref I	Ref II–IV[b]	All refs[c]	
N_1–C_a	1.376 [2]	1.385 [6]	1.381	1.378 [8]
C_a–C_m	1.394 [3]	1.387 [3]	1.391	1.392 [9]
C_a–C_b	1.430 [1]	1.435 [2]	1.433	1.437 [8]
C_b–C_b	1.360	1.342 [2]	1.351	1.350 [7]
C_m–C_p	1.500	1.498 [2]	1.499	1.498 [5]
M–N_1[d]	1.978	1.969 [2]	1.974	1.989 [5]
M–N_2[d]	1.833	1.835 [2]	1.834	1.972 [17][e]
O–N_2	1.01	1.04 [2]	1.03	

[a] The bracketed figure following a bond length is the mean deviation from the average. [b] Average from the three refinements. [c] Mean of the corresponding values in columns 2 and 3. [d] M ≡ Co in columns 2-4, but Fe in column 5. [e] The stretching of one axial bond by 0.03–0.04 Å correlates with a misorientation of the corresponding imidazole ligand.[20]

Turning now to the stereochemical pattern exhibited by the axial bond system in ONCoTPP, we first emphasize that the markedly nonlinear geometry of the Co–N_2–O linkage is not attributable to the packing of the molecules in the crystal. Given the linear Co–N_2–O geometry which is concomitant with the complexing of NO^+ as a Lewis base by Co(I), the oxygen atom on the fourfold axis would have as its nearest and next nearest neighbors the four H_7 and four H_9 hydrogen atoms carried by the respective C_7 and C_9 carbon atoms of the four neighboring molecules. But with any remotely plausible value of the Ct···O distance, 2.90–3.20 Å, both O···H_7 and O···H_9 always would be at least 0.40 A larger than the normal van der Waals separation of 2.60 Å.

We then remark that the kinking of the Co–N_2–O configuration specified by the data in Tables I and II requires two fairly short O···H_9 separations of 2.51 and 2.58 Å but no O···H_7 distance below 2.86 Å. These data correspond, however, to a CoN_2O angle of ~135° which is substantially larger than the theoretically anticipated value of 120° for the complexing of NO^- as a Lewis base by Co(III), and to an apparent O–N_2 bond length of 1.03 (2) Å which is implausibly shorter than the bond length of 1.10 Å in molecular nitrogen. It is then readily seen that the O···H_9 contacts would be further eased if the CoN_2O angle were allowed to decrease; indeed, the purely intermolecular packing would be fully compatible with a CoN_2O angle of 120° and an O–N_2 distance of at least 1.15 Å achieved by suitable readjustment in the position of the oxygen atom. But although the position assigned to the eightfold disordered oxygen atom carries a rather large esd (0.015–0.020 Å), the determination of this position from the fully resolved peak in the Fourier synthesis is free of theoretical ambiguity and is little altered by subsequent least-squares refinement (*vide supra*).

The real eightfold disorder in the position of the nitrogen atom, by contrast, is reduced to a twofold disorder in the statistically averaged structure. Indirect evidence that the nitrogen atom is not precisely centered on the fourfold axis is given by data listed in Table I; the apparent thermal parameter of this atom for vibration normal to the fourfold axis, $B_{11} = B_{22} = 5.5$ Å^2, is nearly as large as the isotropic thermal parameter of the oxygen atom, 5.7 Å^2, and, moreover, the isotropic thermal parameter of the N_2 atom, 5.2 Å^2, is otherwise exceeded only by those of peripheral carbon atoms in the phenyl substituents. Consequently, we look for tight O···N_1 contacts within the individual molecule which might force the N_2 atom off axis and thus give rise, in the statistically averaged molecule, to distorted values for the CoN_2O angle and the O–N_2 bond distance.

Steric interactions of the intramolecular O···N_1 type are minimized by orienting the plane of the axial bond system so that it makes an angle of 45° with an axial plane determined by N_2, Ct, and N_1 (Figure 2). With this ideal dihedral angle and the observed Ct···N_2 distance of 1.93 Å from the statistically avaraged molecule, but with a CoN_2O angle of 120° and an O–N_2 distance of 1.10 to 1.15 Å, the pair of equal O···N_1 contacts would be 2.88–2.90 Å, as compared with the sum, 3.10 Å, of the van der Waals radii for oxygen and aromatic nitrogen. The observed value of the dihedral angle is 39.7° and the two unequal O···N_1 distances are 3.04 and 3.09 Å. The modifications in the CoN_2O angle and O–N_2 distance achievable by displacing the nitrogen atom off axis in the plane of the axial bond system are readily calculated: displacements, taken normal to the axis, of 0.075, 0.100, and 0.200 Å lead to CoN_2O angles of 130.2, 128.5, and 122.1° and to O–N_2 distances of 1.08, 1.10, and 1.18 Å, respectively. These calculated parameters assume enhanced interest as we consider the stereochemical data reported for related complexes by other investigators.

Conventional refinement by Snyder and Weaver[22] of the ordered structure taken by a crystalline salt containing the *trans*-$ClCo(NO)(en)_2^+$ cation (en = ethylenediamine) affords bond parameters for the coordination group that (ignoring the chloride ligand) serve in many respects as a nearly quantitative description of the coordination group in the ONCoTPP molecule. Thus the cobalt atom is displaced ~0.095 Å from the equatorial plane toward the nitrosyl ligand, the respective axial and (averaged) equatorial Co–N bond lengths are 1.820 (11) and 1.964 Å, and the O–N bond length is 1.043 (17) Å. Especially notable is the displacement of the nitrosyl nitrogen atom off axis by ~0.075 Å which allows the CoNO bond angle to retain the relatively low value of 124.4 (11)° (instead of 129–130°). Correction of the conventionally refined O–N distance of 1.04 A for the foreshortening produced by thermal motion, assuming that the oxygen atom "rides" on the nitrogen of the Co–N bond,[23] raises this bond length to 1.10 Å.[22]

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[20] D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972).

[21] L. J. Radonovich, A. Bloom, and J. L. Hoard, *ibid.*, **94**, 2073 (1972).

[22] D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).

[23] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

The rigid-group model employed by Ibers, *et al.*,[24] to refine the axial bond parameters in the $\mathrm{ONCo(NH_3)_5^{2+}}$ cation, as this disordered species occurs with statistically required *mm*2 symmetry in the crystalline dichloride, enabled them to demonstrate that a model for the Co–N–O bond system with the nitrogen atom displaced by ~0.33 Å from the twofold axis, a CoNO angle of 119.0 (9)°, and an O–N distance of 1.154 (7) Å was just as compatible with the X-ray data as was the statistically averaged model with the nitrogen atom on the twofold axis, a CoNO angle of 143.0 (6)°, and an O–N distance of only 0.920 (7) Å. Further applications of Ibers' rigid-group model[24a] to the resolution of similar structural disorders in the axial Ir–N–O linkages of two square-pyramidal iridium complexes[25] led again to the conclusion that a displacement off axis of the nitrogen atom was in each case the critical feature which was obscured in the statistically averaged model.

All of the foregoing considerations are indicative of, or at least consistent with, a small displacement off axis of the nitrosyl nitrogen atom in the ONCoTPP molecule. Inasmuch as a displacement $\gtrsim 0.10$ Å corresponds to $\mathrm{CoN_2O} \lesssim 128.5°$, the conclusion that this angle corresponds to a trigonally hybridized sp^2 pattern of σ binding for the nitrogen atom is thereby strengthened.

Although we have $\mathrm{Ct \cdots N_2}$ = 1.927 (10) Å, the additive components of this quantity, $\mathrm{Ct \cdots Co}$ = 0.094 (52) Å and $\mathrm{Co–N_2}$ = 1.833 (53) Å, are only roughly estimated. A rational lower limit for the $\mathrm{Co–N_2}$ bond length would seem to be the 1.746 (7) Å observed in the square pyramidal coordination group of the $\mathrm{ONCo[S_2CN(CH_3)_2]_2}$ molecule,[26] wherein the cobalt atom lies 0.52 Å from the plane of the sulfur atoms. Marked structural trans effects are to be seen in the axial bond systems of the $\mathrm{ClCo(NO)(en)_2^+}$ and $\mathrm{ONCo(NH_3)_5^{2+}}$ species. With chloride as the *trans* ligand,[22] Co–NO = 1.820 (11) and Co–Cl = 2.575 (3) Å, whereas in the $\mathrm{ONCo(NH_3)_5^{2+}}$ ion,[24] Co–NO = 1.871 (6), $\mathrm{Co–NH_3}$ (cis) = 1.981 (4), and $\mathrm{Co–NH_3}$ (trans) = 2.220 (4) Å. Consideration of these data suggests that $\mathrm{Co–N_2}$ = 1.83 Å is a probable upper limit for this parameter in the *five-coordinate* ONCoTPP molecule.

It is a rational assumption that the pattern of a long bond trans to the short Co–NO bond carries over to six-coordinate nitrosylcobalt porphyrins ($\mathrm{ONCoN_bPorph}$) in which the second axial ligand ($\mathrm{N_b}$) may be either an aliphatic or an aromatic nitrogen base. This pattern is suggestive of significant dissociation, even in moderately concentrated solution, of the nitrogen base from the parent species. The choice between the six-coordinate porphyrin and the simpler five-coordinate species as the product of crystallization is then determined by the relative merits of the respective crystalline phases. Lacking any information on the unknown (through presumably ordered) crystalline phase containing the piperidinenitrosylcobalt derivative of tetraphenylporphine, the energetically sound, entropically favorable, thermodynamic nature of the observed ONCoTPP phase may still be emphasized.

Bonding Considerations. The idealized symmetry of the ONCoTPP, $\mathrm{ONCo(NH_3)_5^{2+}}$, and $\mathrm{ClCo(NO)(en)_2^+}$ complexes is just C_s, a single mirror plane containing the axial Co–N–O bond system. With the conventional choice of molecular axes whereby the four equatorial ligands are positioned, nearly or exactly, on the x and y axes, the plane of the Co–N–O system bisects the angle between the xz and yz coordinate planes. In their illuminating discussion of the criteria which determine whether a linear or a strongly kinked M–N–O configuration is appropriate to a nitrosyl complex of specified composition, Pierpont and Eisenberg[27] assume that a kinked M–N–O bond system lies always in a coordinate (xz) plane. Consequently their Figure 1, which displays the correlation of the orbitals in a complex of C_{4v} symmetry (linear M–N–O) with those in a complex of C_s symmetry (kinked M–N–O) requires some obvious relabeling to make it applicable to the three cobalt complexes of immediate interest.

As pointed out by other investigators,[22,24,27] a CoNO bond angle of 120–130° bespeaks trigonal sp^2 hybridization of the nitrogen atom and leads to a simple theoretical description of the nitrosyl ligand, *formally* as $\mathrm{NO^-}$, in the geometry observed for the axial bond system. Ignoring the four K-shell electrons, this formulation calls for trigonal sp^2 hybridization of both atoms, a planar system of σ orbitals in which ten of the 12 valence-shell electrons are accommodated, and the filling of the bonding $2p\pi$ molecular orbital to give a closed-shell configuration. The formal pattern of σ bonding is completed by utilizing one of the two lone pairs of electrons on the nitrogen atom for the complexing of the $\mathrm{NO^-}$ ligand to the cobalt(III) atom. Some contribution from back-π-bonding, with charge transfer from the cobalt atom (equally from the $3d_{xz}$ and $3d_{yz}$ orbitals) into the antibonding $2p\pi^*$ molecular orbital of the nitrosyl ligand, may also be admitted.

The foregoing representation of the complexing Co–NO linkage as a dative bond of the familiar type in which an *independently stable* closed-shell ligand (*e.g.*, $\mathrm{NO_2^-}$, $\mathrm{NCS^-}$, or $\mathrm{NH_3}$) is complexed to a cobalt(III) atom is clearly quite artificial; it displays no evident correlation with either the strongly developed structural trans effect or the observation that Co–NO bond lengths are 0.08–0.14 Å shorter than the 1.95–1.96 Å which is usual for the standard Co–N dative bond.[28] If, by contrast, we consider that the d^7 cobalt(II) atom and the nitric oxide molecule each contribute one electron to the formation of an almost nonpolar σ linkage, we see that disproportionate usage to this end of, in particular, the $3d_{z^2}$ orbital of the cobalt(II) atom should require a short Co–NO bond and the simultaneous weakening of the dative bond in the trans position.

Strongly developed back-π-bonding might conceivably account for a gross shortening of the Co–NO bond, but not without concomitant expectations of an N–O distance appreciably longer, and a stretching frequency,

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[24] (a) J. A. Ibers, *Acta Crystallogr., Sect. B*, **27**, 250 (1971); (b) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

[25] (a) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971); (b) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, 10, 1043 (1971).

[26] J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 718 (1972).

[27] C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971). These authors cite numerous references to earlier papers which deal with stereochemistry and bonding in individual nitrosyl complexes.

[28] Thus in the nitro-3,5-lutidinecobalt(III) derivative of tetraphenylporphine,[7d] $\mathrm{O_2NCo(3,5\text{-}Lut)TPP}$, the $\mathrm{Co–NO_2}$ distance is 1.95 Å. The trans Co–N bond to lutidine is 2.04 Å, somewhat stretched by reason of steric interaction between porphinato nitrogen and lutidine hydrogen atoms; *cf.* A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 3620 (1972).

ν(NO), significantly smaller, than the values associated with strong ($\sigma + \pi$) double bonding. Following substantial upward correction for thermal motion, the N–O distance of 1.10 (2) Å in the *ordered* structure of the $ClCo(NO)(en)_2^+$ ion[22] is ostensibly just equal to the bond length in the triply bonded ($\sigma + 2\pi$) nitrogen molecule and, consequently, is suggestive of especially strong double bonding not appreciably weakened by back-π-bonding.

Values for ν(NO) of 1610, 1611, and 1689 cm^{-1} in the respective $ONCo(NH_3)_5^{2+}$, $ClCo(NO)(en)_2^+$, and ONCoTPP complexes are, on the other hand, indirectly suggestive of appreciable back-π-bonding. The higher value of ν(NO) in the ONCoTPP molecule is rationally attributable to competition from the porphinato core for charge density from the d_{xz} and d_{yz} orbitals of the cobalt atom. A further small increase in ν(NO) may be anticipated for a six-coordinate $ONCoN_bPorph$ molecule in which the nitrogen base (N_b) is a π acceptor.

The sensitivity of the stretching frequency, ν(NO), to back-π-bonding is exhibited in the molecular orbital treatments[29,30] accorded a family of six pentacyanonitrosyl complexes wherein the metal atom is iron, manganese, chromium, or vanadium in an appropriate oxidation state, and the linearity of the M–N–O bond system allows the species to retain C_{4v} symmetry. In simplified paraphrase of just one aspect of these studies,[29,30] the formal treatment of the linear M–N–O bond system involves the transfer of an electron from the NO molecule to the metal atom, σ complexing of the closed-shell (N_2-like) NO^+ ion as a Lewis base, and the partial recovery of charge by the ligand as *paired* electron density in its antibonding $p_x\pi^*$ and $p_y\pi^*$ orbitals by back-π-bonding from the d_{xz} and d_{yz} orbitals of the metal atom. For the range in ν(NO), 1935–1515 cm^{-1}, covered in the six complexes, Fenske and DeKock[30] show that linearity of the squared frequency with the fractional occupation of the pair of nitrosyl π^* orbitals (as determined by a Mulliken population count) is rather well observed. A short extrapolation of this linear relation to half occupancy of the π^* orbitals, corresponding to a *formal* bond order of two achieved with six bonding and two antibonding electrons, gives ~1400 cm^{-1} for ν(NO).

Such an "overstuffed" double bond would surely be expected to have a lower force constant, and to be longer, than a double bond which is achieved with just four bondng electrons. It is instructive, nonetheless, to note that, on the foregoing scale, the frequency of 1689 cm^{-1} from the ONCoTPP molecule corresponds to a *formal* bond order of 2.20. Furthermore, the ν(NO) of 1935 cm^{-1} from the $ONFe(CN)_5^{2-}$ ion (with linear Fe–N–O) corresponds to a bond order of ~2.45 and a measured N–O bond length[10a] of 1.13 (2) Å.

Rather modest contributions from back-π-bonding in the nitrosylcobalt(II) complexes are suggested by the foregoing analysis. Nor do we expect that such π bonding, even if it be strongly developed, should give rise to the pronounced structural trans effects which are observed in the species of interest. Indeed, the very short Fe–NO bond length of 1.63 (2) Å in the $ONFe(CN)_5^{2-}$ ion[10,29,30] is not accompanied by any hint of a structural trans effect; the trans Fe–C bond length, 1.90 (2) Å, is ostensibly (but not objectively) shorter than the averaged value, 1.92 Å, of the five Fe–C distances, even though the iron atom is displaced ~0.20 Å from the plane of the equatorial ligands away from the trans cyanide carbon atom.[10a] All of the cited evidence appears to support the conclusion that it is the dominant σ component of the complexing Co(II)–NO linkage which is responsible for both the observed structural trans effect and the shortening, relative to the standard dative value, of the Co–NO bond distance. Estimates of the disproportionations in the usage not only of the cobalt $3d_{z^2}$ orbital but also of the higher lying 4s and $4p_z$ orbitals, for bonding to the two axial ligands in the six-coordinate nitrosylcobalt(II) species, must await a theoretical treatment quite as detailed as those accorded the pentacyanonitrosyl complexes.[29,30]

Remarks on Related Six-Coordinate Species. Whereas a diamagnetic, six-coordinate, dioxygeniron(II) porphyrin, O_2FeN_bPorph, such as the oxygenated protoheme, is isoelectronic with the analogous nitrosylcobalt(II) porphyrin, $ONCoN_bPorph$, one additional valence shell electron must be accommodated in the paramagnetic species, O_2CoN_bPorph, obtained by oxygenation of the five-coordinate cobalt(II) porphyrin, $N_bCoPorph$. The pattern proposed by other investigators for the axial bonding in an O_2CoN_bPorph molecule[4] and in related model systems[31] involves the complexing of a trigonally hybridized oxygen atom of a superoxide (O_2^-) ion by a cobalt(III) atom to give a strongly kinked Co–O–O linkage similar in configuration to that of the Co–N–O linkage in the nitrosylcobalt(II) complexes. Support for this bonding pattern and the concomitant geometry is provided by the structural data reported for crystalline $O_2CoN_bBzacen$,[32] wherein N_b is pyridine and Bzacen is *N*,*N*′-ethylenebis(benzoylacetoniminide). A CoOO angle of 126 (2)° and bond lengths of O–O = 1.26 (4), Co–O = 1.86, and Co–N_b = 2.02 Å are in agreement with the bonding pattern,[33] and are also consistent with the more precise data from structure determinations for binuclear complexes wherein pairs of octahedrally coordinated cobalt(III) atoms are bridged through superoxide ions.[34] No structural trans effect is evident in any of the cited complexes.[32,34] Furthermore, the dative Co(III)–O_2^- bond lengths in all these species are confined to the range from 1.86 to 1.89 Å, in agreement with the 1.88 Å observed for unstrained bonds to carboxylate oxygen in the octahedral coordination group of the ethylenediaminetetraacetatocobalt(III) anion.[35] Inasmuch as in both of the binuclear complexes[34] five of the octahedrally coordinated atoms are nitrogen, a Co–O bond length of ~1.88 Å would appear

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[29] P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

[30] R. F. Fenske and R. L. DeKock, *ibid.*, **11**, 437 (1972).

[31] (a) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970); (b) B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, **92**, 61 (1970).

[32] G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).

[33] Correction of the O–O distance for the foreshortening arising from thermal motion should lead to a value nearer the 1.30 Å anticipated for the superoxide ion wherein the odd electron is housed in the $2p\pi^*$ antibonding orbital.[34] The length of the bond to the pyridine ligand, 2.02 Å, compares favorably with the 2.04 Å observed for the analogous distance in the $O_2NCo(3,5\text{-Lut})TPP$ molecule.[28] We note further that the planes of the pyridine and the Co–O–O bond system are mutally orthogonal and are oriented diagonally to the *xz* and *yz* coordinate planes.

[34] (a) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966); (b) G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 291 (1969).

[35] H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 954 (1959).

to be appropriate in the six-coordinate O_2CoN_bPorph species.[36] Given also Co–N_b = 1.95 Å, the value anticipated for an imidazole ligand,[20] and Co–N_p = 1.98 Å for the four equatorial bonds, we obtain an elegantly compact, quasi-C_{4v}, octahedral coordination group which, we judge, serves as the most likely model for the coordination group in the cobalt protoporphyrin IX of oxygenated cobaltohemoglobin.[4]

A similar geometry of octahedral coordination and strongly kinked M–O–O axial bonding is evidently a rational expectation for the oxygenated protoheme. By contrast with the analogous dioxygencobalt species, the dioxygen ligand in the protoheme is free to accept charge as *paired* electron density in its π^* orbital from the d_{xz} and d_{yz} orbitals of the low-spin d^6 iron atom. Relative to the isoelectronic nitrosylcobalt species, moreover, both the smaller nuclear charge of the iron atom and the greater electron affinity of the dioxygen ligand are conducive to the enhancement of back-π-bonding in the oxygenated protoheme. The associated transfer of charge must then encourage forward charge transfer in the donor–acceptor σ contribution to the complexing linkage, a cooperative "push–pull" mechanism for stabilization of the complex. Probably the effective oxidation state of the iron atom is rather nearer three than two, thus suggesting the formalism, Fe(III)–O_2^-, for brief characterization of the complexing linkage.[37] Although this bonding pattern is not unique in its apparent capacity to provide a rational description of a strongly kinked Fe–O–O geometry,[38] it does emerge as a logical extension of considerations which are apparently applicable to the analogous nitrosylcobalt and dioxygencobalt species as well as to appropriate model systems. The stereochemical parameters anticipated for this model of the oxygenated protoheme differ very little from those specified for the corresponding cobalt porphyrin.

In putting forward these models for the oxygenated porphyrins, we do not overlook the several complexes[40–42] wherein essentially symmetrical coordination of both atoms of a dioxygen ligand to a cobalt,[40] a rhodium,[41] or an iridium[41,42] atom has been established. A complex of this type is sterically characterized by an irregular octahedral packing geometry of the *six* coordinated atoms which allows close approach of the ligand to the metal atom; values of M–O_{Ax}, the distance from the metal atom to the midpoint of the O–O axis,[38] range downward from 1.96 Å in an iridium complex[42a] which displays reversible oxygenation to 1.75 Å in a cobalt complex[40] which does not. Detailed consideration of the data suggests that reversible oxygenation of a cobalt complex in the biologically pertinent range of oxygen partial pressures sets an upper limit of ~1.85 Å for Co–O_{Ax}.[38]

Symmetrical coordination of the dioxygen ligand in the protoheme or its cobalt analog demands, by contrast, the awkward packing geometry of seven coordination,[43] the shortness of the O–O bond (1.30–1.50 Å) notwithstanding. For M–O_{Ax} = 2.20 Å and the metal atom centered among the porphinato nitrogen atoms, packing relations in the seven-coordination group are closely comparable with those in the already compact octahedral model with just one coordinated oxygen atom. But concomitant with M–O_{Ax} < 2.00 Å is gross steric strain which—however distributed—appears to be more than sufficient to destabilize symmetrical coordination of the dioxygen ligand.[38,43–45]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× 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 $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8281.

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[36] A Co–O distance of 1.88 Å applies also to the dative Co(III)–O_2^{2-} bonds in the $[(H_3N)_5CoO_2Co(NH_3)_5]^{4+}$ ion wherein the O–O separation in the bridging peroxy group is 1.47 (1) Å; W. P. Schaefer, *Inorg. Chem.*, 7, 725 (1968).

[37] That other physical data are suggestive of this effective oxidation state for the iron atom has been emphasized by (a) J. J. Weiss, *Nature (London)*, 202, 83 (1964); (b) J. B. Wittenberg, B. A. Wittenberg, J. Peisach, and W. E. Blumberg, *Proc. Nat. Acad. Sci. U. S.*, **67**, 1846 (1970); (c) A. S. Koster, *J. Chem. Phys.*, **56**, 3161 (1972). The character and significance of these data are discussed elsewhere.[38]

[38] J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci. U. S.*, to be submitted for publication. Thus Pauling's formulation[39] of the Fe–O–O linkage, when partially recast in molecular orbital terminology, explicitly displays the general character demanded by other investigators.[37]

[39] (a) L. Pauling, *Nature (London)*, 203, 182 (1964); (b) "Haemoglobin," F. J. W. Roughton and J. C. Kendrew, Ed., Butterworths, London, 1949, p 57.

[40] N. W. Terry, III, E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, **94**, 653 (1972).

[41] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 6301 (1969).

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[44] Inconclusive experimental observations which have been interpreted in support of one or the other of the very different models for the oxygenated protoheme or its cobalt analog are considered elsewhere.[38]

[45] NOTE ADDED IN PROOF. An authoritative determination of the probable stereochemistry of the Fe–O_2 linkage in the oxygenated protoheme is forthcoming from a determination of crystalline structure by J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley (private communication from J. P. Collman) for the dioxygen-1-methylimidazoleiron(II) porphyrin prepared and characterized by J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973). Preliminary structural data for the strongly bent Fe–O–O linkage appear to be in better agreement with the model described above than with Pauling's formulation.[38,39]