If $\zeta_1 = \zeta_2$, these expressions reduce to those reported previously.[34]

A Fortran IV computer program has been used to calculate the G_k, B_k, and C_k integrals for specified r_0 and radial functions (Slater or double-ζ type).

Registry No. Mn(acac)$_3$, 14284-89-0.

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, 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1864.

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Stereochemistry of Low-Spin Cobalt Porphyrins. V. Molecular Stereochemistry of Nitro-α,β,γ,δ-tetraphenylporphinato(3,5-lutidine)cobalt(III)

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Nitro-α,β,γ,δ-tetraphenylporphinato(3,5-lutidine)cobalt(III) (1) is obtained by the oxidation of nitrosyl-α,β,γ,δ-tetraphenylporphinatocobalt in the presence of 3,5-lutidine. Crystals of 1 crystallize in the orthorhombic system, space group *Fdd*2. The unit cell has a = 22.01 (1) Å, b = 34.29 (2) Å, and c = 10.884 (6) Å and contains eight molecules. The molecule has a crystallographically imposed twofold axis of symmetry. The calculated and experimental densities are 1.33 and 1.30 g/cm^3 at 20 ± 1°. Diffracted intensities were recorded with graphite-monochromated Mo Kα radiation on a computer-controlled diffractometer with θ–2θ scanning. All independent reflections for $(\sin\theta)/\lambda \leqslant 0.742$ Å^{-1} were measured; 3239 reflections were retained as observed. These data were employed for the determination of structure using the heavy-atom technique and least-squares refinement of the 272 structural parameters. The final conventional and weighted discrepancy factors are 0.045 and 0.059, respectively. The octahedral coordination group has an average equatorial $\mathrm{Co{-}N_p}$ distance of 1.954 Å; the axial bond to lutidine nitrogen is 2.036 (4) Å and to the nitro nitrogen is 1.948 (4) Å. The effect of the porphyrin conformation on the $\mathrm{Co{-}N_p}$ distances is discussed.

The earlier papers in this series have emphasized the importance and the origin of our interest in the stereochemistry of low-spin cobalt porphyrins.[1-4] In particular, our interest in nitrosylcobalt porphyrins has been detailed in our report on the molecular stereochemistry of nitrosyl-α,β,γ,δ-tetraphenylporphinatocobalt, ONCoTPP.[1] Our attempts to prepare crystals of a six-coordinate derivative, ONCoTPP(B), in which B is one of several amines, were frustrated by the facile decomposition of the desired nitrosyl complexes to other products. In the course of investigating the nature of these other products, we prepared single crystals of nitro-α,β,γ,δ-tetraphenylporphinato(3,5-lutidine)cobalt(III) *via* the conversion of coordinated nitric oxide to coordinated nitrite ion. We now report the quantitative stereochemistry of O_2N(3,5-lut)CoTPP. While this structure determination was in progress, a preliminary study of similar reactions of oxygen and cobalt nitrosyl complexes was reported.[5]

As we have emphasized elsewhere,[1,6] the stereochemical parameters of the octahedral cobalt(III) porphyrins serve as useful standards of reference for the low-spin cobalt(II), iron(II), and iron(III) porphyrins. Furthermore, crystals of O_2N(3,5-lut)CoTPP would appear to provide an exceptionally convenient diamagnetic host for orientated single-crystal esr studies of paramagnetic nitrosyl metalloporphyrins. Finally, the structural parameters provide an (unanticipated) test and confirmation of Hoard's[7] recent treatment of the effects of porphinato skeletal ruffling on the metal–porphine nitrogen bond distances.

Experimental Section

Large single crystals of O_2N(3,5-lut)CoTPP were obtained by the slow evaporation (in air) of 1:1 chloroform–3,5-lutidine solutions of ONCoTPP.[1] Preliminary photographic examination established an orthorhombic unit cell with observed systematic absences of $h + k$, $k + l = 2n + 1$ for hkl, $k + l = 4n + 1$ for $0kl$, and $l + h = 4n + 1$ for $h0l$ which suggest the space group *Fdd*2.[8] Lattice constants, a = 22.01 (1) Å, b = 34.29 (2) Å, and c = 10.884 (6) Å (λ 0.71069 Å), came from a least-squares refinement of the setting angles of 25 reflections, each collected at $\pm 2\theta$. These constants led to a calculated density at 20 ± 1° of 1.33 g/cm^3 for eight molecules in the unit cell. The experimental density, measured by flotation, was 1.30 g/cm^3. Thus the molecule has a crystallographically required twofold axis of symmetry.

Intensity data were measured on a Syntex $P\bar{1}$ diffractometer with graphite-monochromated Mo Kα radiation; the sample crystal had dimensions of 0.35 × 0.35 × 0.60 mm. All independent data for which $(\sin\theta)/\lambda \leqslant 0.742$ Å^{-1} ($2\theta = 63.7°$) were measured by θ–2θ scanning. Variable scan rate techniques were employed;[3] the base width of the scan was 1.0° at $2\theta = 0.0°$ and background counts were taken at the extremes of the scan for a time equal to the time required for the scan itself. Four standard reflections were used for periodic checking (every 50 reflections) of the alignment and possible deterioration of the crystal; only small random variations in the intensities were noted. Data were processed as described previously[3] and all data having $F_o > 2\sigma_{F_o}$ were taken as observed. A total of 3239 independent reflections, ~90% of the theoretical number possible, were retained and used for the determination and refinement of the structure. With the cited dimensions of the crystal and a linear absorption coefficient of 0.48 mm^{-1} for Mo Kα radiation, the maximum error in a structure amplitude occasioned by the neglect of absorption corrections was seen to be ⩽2.5%.

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

(2) W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973).

(3) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 84 (1974).

(4) W. R. Scheidt, *J. Amer. Chem. Soc.*, **96**, 90 (1974).

(5) S. G. Clarkson and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 670 (1972); *Inorg. Chem.*, **12**, 1528 (1973).

(6) J. L. Hoard, *Science*, **174**, 1295 (1971).

(7) J. L. Hoard, *Ann. N. Y. Acad. Sci.*, **206**, 18 (1973).

(8) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, p 129.

The structure was solved by the heavy-atom method; the z coordinate of the cobalt atom was fixed at 0 to define the origin. The structure was refined by block-diagonal least-squares techniques.[9] A difference Fourier map showed electron densities appropriately located for most hydrogen atoms. Hydrogen atoms were then placed in the theoretically calculated positions (C-H = 1.09 Å) and assigned isotropic temperature factors one unit higher than that of the associated carbon atom. The refinement was then carried to convergence using anisotropic temperature factors for all heavy atoms. The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$ was 0.050; that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ was 0.069. Further refinement with $(\bar{h}\bar{k}\bar{l})$ assumed (which defines the mirror image of the enantiomorph previously assumed) led to $R_1 = 0.045$ and $R_2 = 0.059$.[10] The second enantiomorph is clearly the correct choice and its coordinates are reported herein.

The estimated standard deviation of an observation of unit weight is 0.93. Empirical weights, $w = 1/\sigma^2$, were calculated as previously described.[2] A final difference Fourier synthesis was judged to be free of any significant features with no peaks greater than 0.21 e Å^{-3}.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II. Bond parameters are listed in Tables III-V.[11] The numbering scheme employed for the atoms is displayed in Figures 1-3. Primed and unprimed symbols, *e.g.*, C_i and C_i', denote a pair of atoms related by the twofold axis.

Discussion

Figure 1 is a computer-drawn model of the porphinato core of $O_2N(3,5\text{-lut})CoTPP$ as it exists in the crystal. Figure 2 displays the computer-drawn model of the coordination group of the complex. Each atom is represented by an ellipsoid[12] with the relative size and orientation required by the thermal parameters given in Table II. The crystallographically required twofold axis of symmetry passes through atoms C_3, N_3, N_4, and Co.

The lower half of the diagram of the porphinato core in Figure 3 gives the values (with estimated standard deviations) of all structurally independent C-C and C-N bond distances in the core. Also displayed are the values of some structurally important radii of the core, of which Ct· · ·N = Co-N in this case. In the upper half of the diagram, the special symbol identifying each atom is replaced by the perpendicular displacement (in units of 0.01 Å) of this atom from the mean plane of the porphinato core. The twofold related atoms in the lower half of the diagram have displacements of the same magnitude. As is usual, local flatness (to within 0.02 Å) is maintained in the pyrrole groups. However, local flatness is not maintained at all trigonal carbon atoms of the great inner ring of the porphyrin skeleton; the average value of the sum of angles subtended at the C_a carbon atoms (Figure 3) is 359.6° or 0.4° less than required for the condition of planarity.

The ruffling of the core closely corresponds to that required by the point group D_{2d} with the complexing Co-N bonds on the twofold axes and the methine carbon atoms (C_m) in the dihedral mirror planes of D_{2d}. The displacements of the methine carbon atoms from the mean plane (Figure 3) are 0.56 and −0.64 Å; the corresponding displacement for tetragonal H_2TPP[13] is ±0.38 Å, for CuTPP[14] ±0.42 Å, and for

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type	10^4x	10^4y	10^4z
Co	0^b	0^b	0^b
N_1	776 (1)	272 (1)	49 (3)
N_2	−428 (1)	501 (1)	−25 (3)
N_4	0^b	0^b	1872 (3)
N_3	0^b	0^b	−1790 (3)
O	−383 (3)	−142 (3)	−2358 (4)
C_{a1}	1334 (1)	116 (1)	332 (3)
C_{b1}	1797 (1)	412 (1)	211 (3)
C_{b2}	1522 (1)	738 (1)	−223 (3)
C_{a2}	883 (1)	653 (1)	−298 (3)
C_{a3}	−181 (1)	854 (1)	−337 (3)
C_{b3}	−629 (1)	1155 (1)	−202 (4)
C_{b4}	−1143 (1)	983 (1)	232 (4)
C_{a4}	−1023 (1)	570 (1)	294 (3)
C_{m1}	432 (1)	924 (1)	−596 (3)
C_{m2}	−1458 (1)	281 (1)	511 (3)
C_1	74 (1)	330 (1)	2489 (3)
C_2	67 (2)	349 (1)	3772 (3)
C_3	0^b	0^b	4416 (5)
C_m	127 (2)	741 (2)	4423 (5)
C_{11}	618 (1)	1294 (1)	−1228 (3)
C_{12}	935 (2)	1596 (1)	−650 (5)
C_{13}	1119 (2)	1920 (1)	−1350 (6)
C_{14}	993 (2)	1939 (1)	−2584 (7)
C_{15}	686 (2)	1645 (2)	−3145 (5)
C_{16}	491 (2)	1321 (1)	−2472 (4)
C_{21}	−2105 (1)	387 (1)	791 (3)
C_{22}	−2443 (2)	613 (2)	−20 (6)
C_{23}	−3060 (2)	686 (2)	224 (9)
C_{24}	−3328 (2)	547 (2)	1268 (7)
C_{25}	−2998 (2)	324 (2)	2064 (5)
C_{26}	−2382 (2)	242 (1)	1851 (4)

[a] The figure in parentheses following each number is the estimated standard deviation in the last significant figure. [b] Parameter fixed by symmetry.

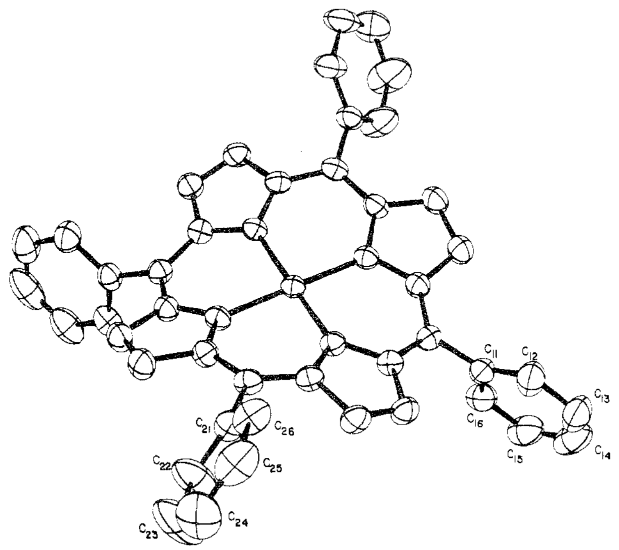

Figure 1. Computer-drawn model in perspective of the porphinato core of the $O_2N(3,5\text{-lut})CoTPP$ molecule as it exists in the crystal. Each atom is represented by an ellipsoid having the orientation and relative size required by thermal parameters listed in Table II. Also shown is the numbering scheme employed for atoms of the phenyl groups. The crystallographic twofold axis passes through the central cobalt atom and is perpendicular to the mean plane of the core.

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

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

(11) Estimated standard deviations in bond lengths and angles were calculated following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

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

(13) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 86, 1938 (1964); H_2TPP is *meso*-tetraphenylporphyrin.

(14) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 86, 2342 (1964).

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å^2
Co	2.14 (1)	2.76 (1)	2.36 (1)	0.12 (1)	0	0	2.41
N_1	2.3 (1)	2.9 (1)	2.7 (1)	0.1 (1)	0.0 (1)	0.2 (1)	2.64
N_2	2.3 (1)	2.9 (1)	2.9 (1)	0.2 (1)	0.1 (1)	0.0 (1)	2.69
N_4	2.6 (1)	3.9 (1)	2.5 (1)	−0.3 (1)	0	0	2.93
N_3	3.2 (1)	3.4 (1)	2.4 (1)	0.2 (1)	0	0	2.97
O	13.2 (4)	29.6 (7)	2.9 (1)	−14.3 (5)	−2.2 (2)	−2.5 (3)	7.83
C_{a1}	2.3 (1)	3.4 (1)	2.9 (1)	−0.2 (1)	−0.2 (1)	0.1 (1)	2.83
C_{b1}	2.5 (1)	3.8 (1)	3.9 (1)	−0.3 (1)	−0.2 (1)	0.2 (1)	3.33
C_{b2}	2.6 (1)	3.3 (1)	4.3 (1)	−0.3 (1)	0.0 (1)	0.3 (1)	3.33
C_{a2}	2.9 (1)	3.0 (1)	2.9 (1)	−0.1 (1)	0.2 (1)	0.0 (1)	2.94
C_{a3}	2.7 (1)	2.9 (1)	3.3 (1)	0.2 (1)	0.0 (1)	−0.0 (1)	2.94
C_{b3}	3.5 (1)	3.0 (1)	4.5 (2)	0.6 (1)	0.0 (1)	0.1 (1)	3.57
C_{b4}	3.0 (1)	3.4 (1)	5.0 (2)	0.6 (1)	0.4 (1)	−0.5 (1)	3.60
C_{a4}	2.6 (1)	3.2 (1)	3.2 (1)	0.4 (1)	0.2 (1)	−0.3 (1)	2.95
C_{m1}	2.8 (1)	2.9 (1)	3.1 (1)	−0.1 (1)	0.1 (1)	0.0 (1)	2.93
C_{m2}	2.3 (1)	3.5 (1)	3.0 (1)	0.3 (1)	0.2 (1)	−0.3 (1)	2.88
C_1	3.1 (1)	3.7 (1)	3.0 (1)	−0.1 (1)	0.1 (1)	−0.4 (1)	3.24
C_2	3.5 (1)	5.4 (2)	3.1 (1)	−0.6 (1)	−0.0 (1)	−0.9 (1)	3.80
C_3	4.0 (2)	7.2 (3)	2.6 (2)	−0.8 (2)	0	0	4.19
C_m	6.2 (2)	7.3 (3)	4.8 (2)	−1.4 (2)	0.4 (2)	−2.8 (2)	5.43
C_{11}	2.8 (1)	3.0 (1)	4.1 (1)	0.3 (1)	0.3 (1)	0.4 (1)	3.23
C_{12}	4.3 (2)	3.6 (1)	6.2 (2)	−0.4 (1)	−0.2 (2)	0.2 (1)	4.52
C_{13}	4.1 (2)	3.6 (2)	10.5 (4)	−0.6 (1)	0.4 (2)	0.9 (2)	5.25
C_{14}	4.3 (2)	5.6 (2)	10.4 (4)	0.8 (2)	1.8 (2)	4.0 (3)	5.22
C_{15}	5.2 (2)	6.2 (2)	6.1 (2)	1.2 (2)	1.2 (2)	2.9 (2)	5.28
C_{16}	4.1 (1)	4.5 (1)	4.2 (1)	1.1 (1)	0.6 (1)	1.0 (1)	4.07
C_{21}	2.6 (1)	3.8 (1)	4.2 (1)	0.2 (1)	0.8 (1)	−0.6 (1)	3.37
C_{22}	3.0 (1)	7.6 (3)	7.9 (3)	0.8 (1)	0.8 (2)	2.9 (3)	5.28
C_{23}	3.2 (1)	9.5 (3)	12.9 (6)	2.0 (2)	1.3 (3)	4.3 (4)	6.66
C_{24}	3.1 (1)	7.4 (3)	11.4 (5)	0.9 (2)	2.4 (2)	−0.5 (3)	5.89
C_{25}	4.3 (2)	6.9 (2)	5.9 (2)	−0.8 (2)	2.4 (2)	−2.0 (2)	4.96
C_{26}	4.0 (1)	5.2 (2)	3.8 (1)	−0.5 (1)	1.0 (1)	−1.1 (1)	4.11

[a] Numbers in parentheses are the estimated standard deviations. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and Lutidine Ring[a,b]

Type	Length, Å	Type	Length, Å	Type	Length, Å
Co-N_1	1.949 (2)	C_{b1}-C_{b2}	1.356 (5)	C_{m1}-C_{11}	1.499 (5)
Co-N_2	1.958 (2)	N_2-C_{a3}	1.373 (4)	C_{m2}-C_{a4}	1.394 (5)
Co-N_4	2.036 (4)	N_2-C_{a4}	1.376 (4)	C_{m2}-C_{a1}'	1.408 (5)
Co-N_3	1.948 (4)	C_{a3}-C_{b3}	1.436 (4)	C_{m2}-C_{21}	1.500 (4)
N_3-O	1.155 (5)	C_{b4}-C_{a4}	1.449 (5)	N_4-C_1	1.330 (4)
N_1-C_{a1}	1.372 (4)	C_{b3}-C_{b4}	1.360 (5)	C_1-C_2	1.400 (6)
N_1-C_{a2}	1.375 (4)	C_{m1}-C_{a2}	1.404 (4)	C_2-C_3	1.400 (6)
C_{a1}-C_{b1}	1.444 (4)	C_{m1}-C_{a3}	1.395 (4)	C_2-C_m	1.515 (7)
C_{a2}-C_{b2}	1.438 (4)				

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] Primed and unprimed atoms denote a pair of atoms related by the twofold axis.

NiOEP[15] ±0.51 Å. Thus, departures from planarity of the porphinato core in this crystal are larger than those observed in a number of other highly ruffled porphyrins.

Bond lengths in the porphinato skeleton depart immaterially from fourfold geometry as can be seen from the data listed in Table III and displayed in Figure 3. Using C_a and C_b to denote the respective α- and β-carbon atoms in a pyrrole ring, C_m for methine carbon, and C_p for a phenyl carbon atom that is bonded to the core, averaged bond lengths for the chemically analogous types of bonds are Co-N = 1.954 (4, 2), N-C_a = 1.374 (2, 4), C_a-C_b = 1.442 (5, 4), C_b-C_b = 1.358 (2, 5), C_a-C_m = 1.400 (6, 5), and C_m-C_p = 1.500 (0, 5) Å, wherein the first figure in parentheses following each averaged value is the mean deviation and the second is the estimated standard deviation of an individually determined length of the type.[16] Similar dimensional equivalence is observed for bond angles of a given chemical type; the average values of the angles are given in Table VI. Also listed in Table VI

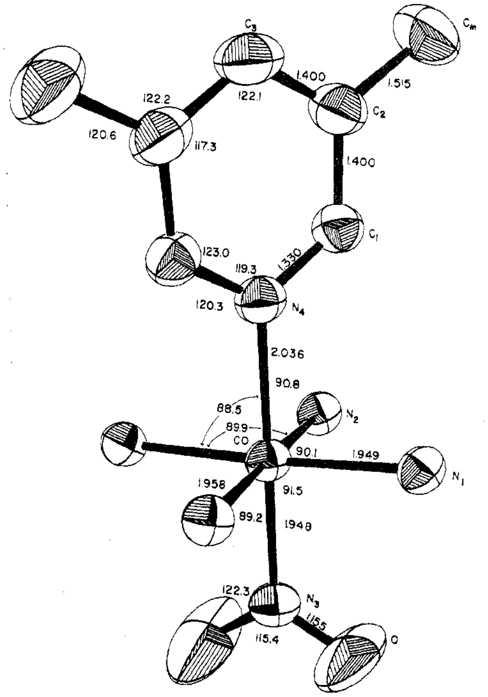

Figure 2. Computer-drawn model of the coordination group atoms and the axial ligands of $O_2N(3,5\text{-lut})CoTPP$. The crystallographically required twofold axis of the molecule passes through C_3, N_4, Co, and N_3.

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(15) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, 28, 2162 (1972); NiOEP is octaethylporphinatonickel(II).

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

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and Lutidine Ring[a,b]

Type	Value, deg	Type	Value, deg	Type	Value, deg
N_4CoN_1	88.5 (1)	$N_1C_{a1}C_{b1}$	109.8 (3)	$C_{a2}C_{m1}C_{11}$	118.3 (3)
N_4CoN_2	90.8 (1)	$N_1C_{a2}C_{b2}$	110.2 (3)	$C_{a3}C_{m1}C_{11}$	120.2 (3)
N_4CoN_3	180.0	$N_2C_{a3}C_{b3}$	109.8 (3)	$C_{a4}C_{m2}C_{21}$	121.0 (3)
N_3CoN_1	91.5 (1)	$N_2C_{a4}C_{b4}$	109.1 (3)	$C_{a1}'C_{m2}C_{21}$	116.7 (3)
N_3CoN_2	89.2 (1)	$C_{a1}C_{b1}C_{b2}$	107.0 (3)	$C_{m1}C_{11}C_{12}$	123.7 (4)
N_1CoN_2	90.1 (1)	$C_{b1}C_{b2}C_{a2}$	106.7 (3)	$C_{m1}C_{11}C_{16}$	116.6 (3)
N_2CoN_1'	89.9 (1)	$C_{a3}C_{b3}C_{b4}$	107.1 (3)	$C_{m2}C_{21}C_{22}$	120.8 (4)
CoN_3O	122.3 (3)	$C_{b3}C_{b4}C_{a4}$	106.9 (3)	$C_{m2}C_{21}C_{26}$	119.8 (4)
ON_3O'	115.4 (6)	$C_{a1}N_1C_{a2}$	106.0 (2)	$C_{16}C_{11}C_{12}$	119.6 (4)
CoN_4C_1	120.3 (2)	$C_{a3}N_2C_{a4}$	106.8 (2)	$C_{11}C_{12}C_{13}$	118.9 (5)
$C_1N_4C_1'$	119.3 (4)	$N_1C_{a2}C_{m1}$	124.9 (3)	$C_{12}C_{13}C_{14}$	120.6 (5)
$N_4C_1C_2$	123.0 (4)	$N_2C_{a3}C_{m1}$	125.8 (3)	$C_{13}C_{14}C_{15}$	120.4 (4)
$C_1C_2C_m$	120.6 (4)	$N_2C_{a4}C_{m2}$	125.3 (3)	$C_{14}C_{15}C_{16}$	120.4 (6)
$C_1C_2C_3$	117.3 (4)	$N_1C_{a1}C_{m2}$	125.7 (3)	$C_{15}C_{16}C_{11}$	120.1 (4)
$C_mC_2C_3$	122.2 (4)	$C_{a2}C_{m1}C_{a3}$	121.5 (3)	$C_{26}C_{21}C_{22}$	119.3 (4)
$C_2C_3C_2'$	120.1 (5)	$C_{a4}C_{m2}C_{a1}$	121.8 (3)	$C_{21}C_{22}C_{23}$	119.8 (6)
CoN_1C_{a1}	127.1 (2)	$C_{m1}C_{a2}C_{b2}$	124.8 (3)	$C_{22}C_{23}C_{24}$	120.5 (6)
CoN_1C_{a2}	126.6 (2)	$C_{m1}C_{a3}C_{b3}$	124.0 (3)	$C_{23}C_{24}C_{25}$	119.7 (4)
CoN_2C_{a3}	126.0 (2)	$C_{m2}C_{a4}C_{b4}$	125.3 (3)	$C_{24}C_{25}C_{26}$	121.5 (5)
CoN_2C_{a4}	127.2 (2)	$C_{m2}'C_{a1}C_{b1}$	123.7 (3)	$C_{25}C_{26}C_{21}$	119.1 (5)

[a] The number in parentheses following each datum is the estimated standard deviation in units of 0.1°. [b] Primed and unprimed atoms denote a pair of atoms related by the twofold axis.

Table V. Bond Lengths in the Phenyl Groups[a,b]

Type I[c]	Length, Å	Type II[d]	Length, Å	Type III[e]	Length, Å
$C_{11}-C_{12}$	1.398 (6)	$C_{12}-C_{13}$	1.414 (7)	$C_{13}-C_{14}$	1.364 (11)
$C_{11}-C_{16}$	1.389 (6)	$C_{15}-C_{16}$	1.395 (6)	$C_{14}-C_{15}$	1.372 (10)
$C_{21}-C_{22}$	1.384 (7)	$C_{22}-C_{23}$	1.413 (6)	$C_{23}-C_{24}$	1.362 (11)
$C_{21}-C_{26}$	1.397 (6)	$C_{25}-C_{26}$	1.401 (6)	$C_{24}-C_{25}$	1.361 (10)
Av[b]	1.392 (6)	Av[b]	1.406 (8)	Av[b]	1.365 (4)

[a] The figure in parentheses following the length of a specific bond is the estimated standard deviation in units of 0.001 Å. [b] The figure in parentheses following the averaged length for a bond type is the mean deviation from the average in units of 0.001 Å. [c] Bond set lying nearest to the molecular center. [d] Bond set lying at an intermediate distance from the center. [e] Terminal set of bonds.

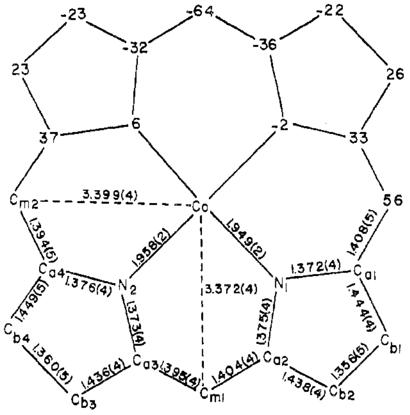

Figure 3. Diagram of the porphinato core displaying, on the lower half, the structurally independent bond lengths and the numbering scheme employed for the atoms. On the upper half of the diagram, the symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core.

are the averaged values of bond lengths and bond angles for three other cobalt porphyrins.

The dihedral angles between the mean plane of the porphinato core and the planes of two structurally nonequivalent phenyl groups in $O_2N(3,5\text{-lut})CoTPP$ are 78.2 and 60.2°. The averaged value of the internal angles in the phenyl rings is 120.0 (8, 5)°. The sum of the angles subtended at a carbond atom C_p is 359.9 (0, 4)°. The individually determined C-C bond distances in the two structurally independent phenyl rings are listed in Table V.

The geometry of the coordinated nitro group is similar to that of other nitrocobalt(III) complexes. The C-N(nitro) distance of 1.948 (4) Å (1.954 Å corrected for thermal motion[17]) is a normal Co^{III}-N bond distance and is within the range of reported distances.[18] The apparent N-O bond distance is 1.155 (5) Å; after correction for thermal motion the distance is 1.35 Å.[17] The orientation of the nitro group with respect to the porphinato core can be specified by the N_1CoN_3O dihedral angle of 1.6°. This orientation can be clearly seen in Figures 2 and 4. The orientation and high thermal parameters of the oxygen atom are entirely consistent with some positional disorder of this atom.

The Co-N bond to the axial 3,5-lutidine ligand is 2.036 (4) Å, substantially longer than the normal ~1.96-Å length of a dative nitrogen bond to Co(III). The stretching of this axial bond is, at least in part, attributable to steric interactions between the lutidine hydrogen atoms and atoms of the porphinato core. The orientation of the axial ligand with respect to the porphinato core (Figure 4) defined by the dihedral angle between the plane of the axial ligand and the N_4CoC_{m1} plane is 8.6°. A value of 0° corresponds to the most favorable orientation of the axial ligand in minimizing the steric interactions, especially between the lutidine hydrogen atoms and the porphinato nitrogen atoms; a value of 45° corresponds to the most unfavorable orientation of the axial ligand. The relatively favorable orientation of the lutidine notwithstanding, the lutidine $H_{C1}\cdots N_2$ contact is a tight 2.55 Å and the remaining close contacts are $H_{C1}\cdots C_{a3}$ = 2.76 Å and $H_{C1}\cdots N_1$ = 2.78 Å; the normal packing separation is ~2.90 Å.

The averaged length of the two independent complexing bonds to porphinato nitrogen atoms is $Co-N_p$ = 1.954 (4, 2) Å. This value is characteristic of low-spin cobalt(III) complexes in which the central cobalt atom is bonded to nitrogen atoms of six monodentante ligands.[19] This distance is significantly shorter (>0.02 Å) than the $Co-N_p$ distances (Table VI) observed for other low-spin cobalt(III) and -(II)

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(17) Correction for riding motion assumes that the second atom rides on the first.

(18) N. C. Payne, *Inorg. Chem.*, 11, 1376 (1972); P. W. R. Corfield, J. C. Dabrowiak, and E. S. Gore, *ibid.*, 12, 1734 (1973); I. Oonishi, H. Fujimaki, F. Muto, and Y. Komiyama, *Bull. Chem. Soc. Jap.*, 43, 733 (1970).

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Table VI. Comparison of Average Bond Parameters of Cobalt Porphyrins[a]

Type	$O_2N(3,5\text{-lut})$[b]	$(pip)_2Co^+$[c]	$(pip)_2Co$[d]	MImCo[e]
		A. Bond Lengths, Å		
$Co-N_p$	1.954 (4, 2)	1.978 (5, 3)	1.987 (0, 2)	1.977 (5, 3)
N_p-C_a	1.374 (2, 4)	1.384 (2, 4)	1.380 (2, 2)	1.387 (5, 5)
C_a-C_m	1.400 (5, 4)	1.389 (4, 5)	1.392 (2, 2)	1.385 (3, 6)
C_a-C_b	1.442 (5, 4)	1.435 (3, 5)	1.444 (3, 3)	1.441 (6, 6)
C_b-C_b	1.358 (2, 5)	1.356 (1, 5)	1.344 (3, 3)	1.350 (10, 6)
C_m-C_p	1.500 (0, 5)	1.494 (1, 5)	1.498 (3, 3)	1.506 (6, 6)
		B. Bond Angles, Deg		
N_pCoN_p	90.0 (1, 1)	90.0 (0, 1)	90.0 (0, 1)	
CoN_pC_a	126.7 (4, 2)	127.5 (2, 2)	127.4 (1, 1)	127.6 (4, 3)
$C_aN_pC_a$	106.4 (4, 2)	104.9 (0, 3)	104.8 (0, 1)	104.6 (1, 3)
$N_pC_aC_b$	109.7 (4, 3)	110.5 (1, 3)	110.5 (1, 2)	110.7 (2, 4)
$N_pC_aC_m$	125.4 (3, 3)	125.9 (2, 3)	125.8 (1, 2)	125.4 (2, 4)
$C_mC_aC_b$	124.5 (6, 3)	123.6 (2, 3)	123.6 (1, 2)	123.8 (3, 4)
$C_aC_mC_a$	121.6 (2, 3)	123.0 (1, 3)	123.4 (1, 2)	123.5 (2, 4)
$C_aC_bC_b$	106.9 (1, 3)	107.0 (1, 3)	107.0 (1, 2)	107.0 (3, 4)
$C_aC_mC_p$	119.0 (15, 3)	118.5 (4, 3)	118.4 (2, 2)	118.2 (7, 4)

[a] The axial ligands and charge of the tetraphenylporphinatocobalt derivative are given in the heading of each column. The mean value, the average deviation from the mean, and the esd in the least significant digit are given for each entry. [b] Nitro-α,β,γ,δ-tetraphenylporphinato(3,5-lutidine)cobalt(III); this work. [c] Bis(piperidine)-α,β,γ,δ-tetraphenylporphinatocobalt(III); reference 2. [d] Bis(piperidine)-α,β,γ,δ-tetraphenylporphinatocobalt(II); reference 3. [e] (1-Methylimidazole)-α,β,γ,δ-tetraphenylporphinatocobalt(II); reference 4.

porphyrins. The shortening of the $Co-N_p$ bonds in this complex compared to the other cobalt porphyrins is attributable to the difference in the conformation of the porphinato cores. The porphinato core in $O_2N(3,5\text{-lut})CoTPP$ is strongly ruffled; the porphinato cores of the other two six-coordinate cobalt porphyrin derivatives listed in Table VI are nearly planar.

Hoard[7] has recently discussed the effect of a symmetrical D_{2d} ruffling of the porphinato core on the bond parameters therein, including also the $M-N_p$ bond distance. The structural subunit of principal importance is the planar entity consisting of a pyrrole ring and its attached pair of C_a-C_m bridging bonds. A D_{2d} ruffling of the core then corresponds to a rotation of each structural subunit through an angle ϕ around the twofold axis along the Co-N bond. The combined rotations require that the C_m carbon atoms be displaced alternately above and below the mean plane of the core in agreement with S_4 symmetry. The bond parameters are subject to the exact relationship[7]

$$(M-N_p) + (N_p-C_a)\cos C_aN_pC_a/2 - (C_a-C_m)\sin\alpha = [(N_p-C_a)\sin C_aN_pC_a/2 + (C_a-C_m)\cos\alpha]\cos\phi \qquad (1)$$

wherein $\alpha = 90 + C_aN_pC_a/2 - N_pC_aC_m$; $(M-N_p)$, (N_p-C_a), and (C_a-C_m) represent bond lengths and $C_aN_pC_a$ and $N_pC_aC_m$ are bond angles. This relation can be used to suggest the bond parameter changes (relative to the planar conformation) needed to accommodate the observed ruffling of the porphinato core. It should be noted that this relation implicitly requires adjustment of the $C_aC_mC_a$ angle to retain ring closure.

The rotation of the pyrrole rings from the mean plane in $O_2N(3,5\text{-lut})CoTPP$ is calculated to be 18.2°. Using this value of ϕ and the average bond parameters of the $(pip)_2CoTPP^+$ and $(pip)_2CoTPP$ cores (Table VI) in eq 1 give a calculated $Co-N_p$ bond distance of 1.860 Å. Since this calculated $Co-N_p$ distance is almost 0.1 Å shorter than the observed distance, modifications in bond parameters of the porphinato core are to be expected for this ruffled core. The stretching of the C_a-C_m bond, the shortening of the N_p-C_a bond, and the opening of the $C_aN_pC_a$ angle (Table VI) all contribute to an increased $Co-N_p$ complexing bond; substitution of these bond parameters (along with $\phi = 18.2°$) into eq 1 leads to a calculated $Co-N_p$ bond length of 1.918 Å. Substitution of the observed $Co-N_p$ distance, along with the other observed bond parameters of $O_2N(3,5\text{-lut})CoTPP$, into eq 1 gives a calculated ϕ of 15.4°. The difference between the calculated and observed value of ϕ corresponds to a folding of ~6° of each trigonal bond system centered at the bridgehead carbon atom (C_a); the sum of the angles subtended at a C_a carbon atom is 0.4° short of fulfilling the condition for planarity.

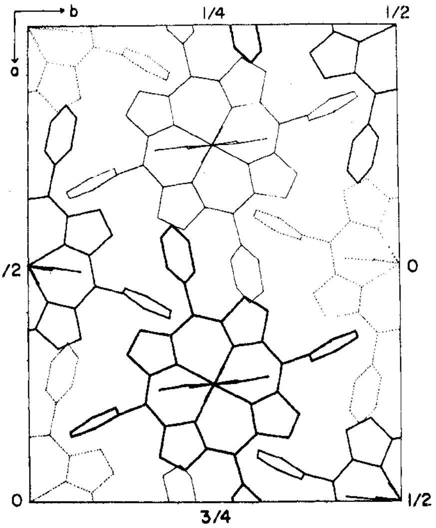

Figure 4. Projection of $O_2N(3,5\text{-lut})CoTPP$ on the *ab* plane. Half of the *b* axis (0–½) is depicted; consequently, half the unit cell is displayed. Fractional *z* coordinates of the metal atoms are shown.

Inasmuch as the ruffling of the porphinato core in $O_2N(3,5\text{-lut})CoTPP$ is sufficient to allow substantially shorter $Co-N_p$ complexing distances than the distances observed, it is a rational assumption that the ruffling of the core primarily results from packing constraints in the crystal and is not induced by the cobalt ion. The packing relationships in the unit cell of $O_2N(3,5\text{-lut})CoTPP$ are displayed in Figure 4. The observation that six of the ten C···C contacts less than 3.75 Å and the two less than 3.5 Å are between phenyl carbon atoms and C_b carbon atoms is entirely consistent with the ruffling of the core arising from packing constraints.

We are currently studying whether the iron and manganese nitrosyl porphyrins undergo similar reactions with oxygen.

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Registry No. $O_2N(3,5\text{-lut})CoTPP$, 51364-55-7.

Supplementary Material Available. A listing of the observed and calculated structure factor amplitudes (×10) 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 of this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1875.

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada

Eight-Coordination and Hydrogen Bonding in a Complex of Scandium: Crystal Structure of the Acid Dimer of Tetrakis(tropolonato)scandium(III)

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The acid dimer of tetrakis(tropolonato)scandium(III) $(HScT_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 11.624$ (3) Å, $b = 11.986$ (3) Å, $c = 10.004$ (3) Å, $\alpha = 95.33$ (1)°, $\beta = 116.27$ (1)°, $\gamma = 102.32$ (1)°, and $Z = 2$. Of the 4212 reflections measured by counter methods (Mo Kα radiation λ_{α_1} 0.70926 Å), 2732 $\geqslant 2.3\sigma$ were used for structure determination. Full-matrix least-squares refinement gave a final R factor of 5.9%. The molecules exist as centrosymmetrically related hydrogen-bonded dimers (O···O separation of 2.484 (4) Å). Each scandium atom is eight-coordinate; oxygen atoms are at the vertices of a polyhedron which is best described as an irregular bicapped trigonal prism distorted toward a dodecahedron (Sc–O lengths range from 2.161 (3) to 2.310 (3) Å). The four tropolonato ligands are of three types. Two are symmetrically coordinated and show regularly decreasing C–C bond lengths with increasing distance from the oxygen atoms. The other two rings are asymmetrically coordinated and are different from each other; the differences in ring type can be attributed to the degree of hydrogen bond involvement. The hydrogen atom is asymmetrically placed (despite the short O···O contact) and this is further reflected by the different bond length alternation in these two rings.

Introduction

The many chelated species that occur in high coordination have been thoroughly reviewed,[1,2] and the delicate balance between configurational types in eight-coordination can be conveniently studied in complexes having multidentate ligands. The tropolonato ligand, $C_7H_5O_2^-$ (abbreviated to T^-), forms stable complexes with many different metals; its compact shape, skeletal rigidity, and small interoxygen atom separation make it a very suitable ligand for attempting to force a high coordination number.

The lightest covalently bonded eight-coordinate atom known to us is scandium in the form of the tetrakis(tropolonato)scandium(III) anion[3] shown originally as $M^+ScT_4^-$ where $M^+ = H^+$ or Na^+. The initial intention in studying $HScT_4$ was to determine the arrangement of the eight-coordinated oxygens about scandium and to correlate this arrangement with the existing theories of high coordination geometry due originally to Hoard and coworkers[4] and recently extended to the M(biden)$_4$ system by Kepert and Blight.[5]

Experimental Section

The species $HScT_4$ was prepared according to the method reported by Muetterties and Wright.[1] Scandium chloride (0.01 mol) was dissolved in water and added to a solution of tropolone (0.04 mol) in ethanol; crystallization was carried out by adding acetonitrile to the reaction mixture and allowing the solvent to evaporate slowly over a number of days. Small yellow crystals were obtained, and one of approximate dimensions 0.13 × 0.22 × 0.40 mm was mounted for the purpose of data collection.

Weissenberg photographs of the reciprocal lattice layers *hk*0 and *hk*1 and precession photographs of the *h*0*l* and 0*kl* zones were taken using copper radiation (λ 1.5418 Å), and as a result of these, triclinic Laue symmetry was assigned.

Accurate dimensions were determined from counter measurement of 29 of the strongest reflections having $2\theta > 25°$, using a Picker FACS-1 computer-controlled four-circle diffractometer and Mo Kα_1 radiation (λ 0.70926 Å). The takeoff angle was 1.0°, and the crystal was mounted with the c axis (corresponding to the needle axis) approximately parallel to the ϕ axis.

Crystal Data. $HScT_4$, formula weight 530.42, crystallizes in the triclinic space group $P\bar{1}$: $a = 11.624$ (3) Å, $b = 11.986$ (3) Å, $c = 10.004$ (3) Å, $\alpha = 95.33$ (1)°, $\beta = 116.27$ (1)°, $\lambda = 102.32$ (1)°, $V = 1207.2$ Å^3, $d_m = 1.46$ (2) g cm^{-3} (flotation), $Z = 2$, $d_x = 1.46$ g cm^{-3}, μ(Mo Kα) = 3.69 cm^{-1}, $T = 21°$ (±1°).

Reflections for the unique set of data for $\sin\theta < 0.4226$ were collected using a scintillation detector with pulse height analysis. Measurement was made using niobium-filtered molybdenum radiation (λ(Mo Kα) 0.70926 cm^{-1}) and a takeoff angle of 3.0° with a symmetrical θ–2θ scan of 1.6° base width increased to allow for α_1–α_2 dispersion. Background counts of 10 sec were measured at both scan limits. After each 70 reflections, 2 standard reflections were measured; their variation was ±3.0% over the entire data collection. The intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to introduce a maximum error of ±3.0% in I. A total of 4212 reflections were measured, of which 2732 were considered observed (*i.e.*, greater than 2.3σ, where $\sigma_I(\text{net}) = [\text{TC} + (t_s t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ where TC is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the total background-count time, k is a constant set to 0.03, and I is the net count.)

Structure Determination and Refinement. Examination of the

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