Preparation and Structure of a Six-Coordinate Cobalt(III) Complex Containing the Quinquedentate Ligand *N,N'*-Bis(salicylidene)dipropylenetriamine

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The preparation and X-ray structure of the complex [Co(saldpt)(1-methylimidazole)] bromide monohydrate, [Co(C$_{20}$N$_3$-O$_2$H$_{23}$)(C$_4$N$_2$H$_6$)]Br·H$_2$O, where saldptH$_2$ is the quinquedentate ligand *N,N'*-bis(salicylidene)dipropylenetriamine, are reported. The complex crystallizes in the orthorhombic system, space group $P2_12_12_1$, with cell constants $a = 16.195$ (9) A, $b = 17.401$ (12) A, $c = 8.888$ (4) A, $Z = 4$, $d_m = 1.52$ (1) g cm^{-3}, and $d_c = 1.53$ g cm^{-3}. Intensity data were collected by the θ–2θ scan technique using graphite-monochromatized molybdenum radiation. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement has led to a final R value of 0.058 based on 1492 independent reflections. The octahedral coordination about the cobalt consists of the quinquedentate saldpt ligand arranged such that the nitrogen and oxygen atoms of the salicylidene rings occupy trans positions in an equatorial plane with the secondary amine nitrogen and the imidazole ligand in axial positions. In the observed conformation of the quinquedentate ligand, the salicylidene rings are bent away from the axial position occupied by the secondary amine nitrogen, and apparently this bending restricts the sixth coordination site to preferential coordination by ligands which are planar in the vicinity of the ligating atom. Thus, Co(saldpt)Cl reacts selectively with heterocyclic nitrogen donor ligands in preference to more basic phosphorus ligands.

Introduction

In these laboratories we have been concerned with the stereochemistry of interligand interactions. We have found that the complexes chloro [*N,N'*-bis(salicylidene)dipropylenetriamine]cobalt(III), Co(saldpt)Cl, and chloro [*N,N'*-bis(3-methoxysalicylidene)dipropylenetriamine]cobalt(III), Co-(3-MeOsaldpt)Cl, exhibit an unusual pattern of reactivity toward neutral ligands in nonaqueous solvents. In particular, the complexes react selectively with heterocyclic nitrogen donor ligands in preference to more basic phosphorus ligands. Comparison of proton magnetic resonance spectral changes for both Co(saldpt)Cl and Co(3-MeOsaldpt)Cl which occur on addition of a variety of ligands, L, revealed the following order of stability: P(OMe)$_3$ ~ P(O-*i*-Pr)$_3$ < PBu$_3$ < MePPh$_2$ < 3,5-(Me)$_2$py ~ 4-*t*-Bupy < 1-methylimidazole. The spectral changes were consistent with the formation of only one complex for each ligand L, although small concentrations of other isomers could not be definitely ruled out. The similarity in chemical shifts of the analogous L complexes of the two ligand systems and the observation of magnetic nonequivalence of the methyl groups of the [Co(3-MeOsaldpt)(P(O-*i*-pr)$_3$)]$^+$ complex, as well as the observed similarity in order of stability for both systems, suggest that in each case the conformation of the quinquedentate ligand is the same.

Complexes of saldptH$_2$ with cobalt have been widely studied, particularly as homogeneous catalysts,[1] as oxygen carriers,[2-3] and as models for vitamin B$_{12}$.[4] The nonbifurcated saldpt can adopt four different geometries. The only structural study involving this ligand in a cobalt complex is that of a peroxo dimer species.[3] However, there is no evidence to suggest that the observed conformation of the quinquedentate ligand persists in solution. Therefore, an X-ray structural analysis seemed desirable. It was hoped that such a study, in addition to revealing the gross geometry of the complex, would indicate the reasons for the planar ligand selectivity noted above.

In addition, the multidentate ligand systems found in several biological systems (heme, B$_{12}$ for example) are quinquedentate and are arranged about the metal in a square-pyramidal fashion with extended unsaturation in the "planar" base. The design and synthesis of such ligand systems require considerable expertise in organic preparation and large investment in time. An example of such a synthesis can be found in the elegant work reported by Collman, Robinson, Rodley, and their coworkers,[5] who have synthesized and studied the structure of some complexes of the ligand *N,N'*-bis[salicylidene(2-(2'-pyridyl)ethyl)]ethylenediamine. In contrast to the specifically designed ligand of Collman, *et al.*,[5] only two of the isomers of the ligand saldpt would represent model systems. It appeared clear to us that if the prevalent isomer were one of the two which could serve as a model biological system, then such ligands would be of interest because of their ease of preparation.

Experimental Section

Preparation of [Co(saldpt)(1-methylimidazole)]Br. The complex Co(saldpt) was prepared essentially by following the syntheses outlined by Sacconi and Bertini[6] except that 0.1 mol of cobalt acetate (150 ml of H$_2$O) and Schiff's base (200 ml of EtOH) were used. All operations were performed under nitrogen; yield 45%. The light olive green complex (7 g) was recrystallized by first dissolving it in N$_2$-purged THF (110 ml). After filtration, addition of hexane (60 ml, N$_2$ purged), in a glove bag, resulted in the formation of a considerable amount of dark crystals on the walls of the beaker. More hexane (40 ml) was added and the product was collected and washed with 9:1 hexane–THF and hexane and dried under vacuum over CaSO$_4$; yield 5.8 g (83%).

The complex Co(saldpt)I was prepared by dissolving the above product in THF (340 ml, N$_2$ purged) containing iodine (1.86 g). This solution was purged with N$_2$ for 15 min, sealed, and allowed to react for 1 day. The dark product formed was collected in air and washed with THF and hexane. It was then dried in a vacuum desiccator over CaSO$_4$ for 2 weeks; yield 5.4 g (71%).

The Co(saldpt)I (0.73 g) was suspended in methylene chloride (40 ml) and 1-methylimidazole (0.14 ml) was added. The solution was filtered to remove a small amount of undissolved material. The solution was transferred to an uncovered beaker and crystals began

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(5) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley, and W. T. Robinson, *J. Amer. Chem. Soc.*, 95, 1036 (1973).

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Table I. Crystal Data for [Co(saldpt)(1-methylimidazole)]Br·H$_2$O

$a = 16.195$ (9) Å	Space group $P2_12_12_1$
$b = 17.401$ (12) Å	$Z = 4$
$c = 8.888$ (4) Å	$d_m = 1.52$ (1) g cm^{-3}
$V = 2504.7$ Å^3	$d_c = 1.53$ g cm^{-3}
$F(000) = 1184$ e	$\mu = 24.4$ cm^{-1}
Mol wt 576.39	λ(Mo Kα) 0.71069 Å

to form. Benzene (10–15 ml) was added; the beaker was then covered and allowed to stand for 1.5 hr. The beaker was uncovered and the product was collected after 15 min. After washing with benzene and drying under vacuum, the product weighed 0.73 g (86% yield).

This [Co(saldpt)(1-methylimidazole)]I was dissolved in methylene chloride (80 ml) and toluene (75 ml) was added. The solution was placed in a covered beaker. The black-green crystals which formed were collected leaving a pale green filtrate. The product was washed with toluene and dried, a process which converted it to a lettuce green color; yield 0.685 g, 94%.

Half of this material was converted to the bromide salt as follows. The product was dissolved in warm water (175 ml) and a concentrated solution of LiBr (25 ml) was added. This solution was allowed to stand in a large evaporating dish for 2 days. The dark green crystals which formed were collected and washed with water and air-dried. The crystals were dissolved in methanol and a concentrated aqueous solution of LiBr was added. After 1 week, the needlelike clusters which formed were collected and washed with water. These crystals were dissolved in methanol (30 ml), the solution was filtered, and 30 ml of water was added. After 2 weeks, the green rodlike crystals which had formed at the bottom of the beaker were collected and washed with water. The crystal structure study, showing one water of crystallization, was performed on these freshly prepared crystals. The compound was not analyzed until 1 year later and indicates two waters of crystallization. *Anal.* Calcd for BrCoO$_4$N$_5$C$_{24}$H$_{33}$ (dihydrate): C, 48.6; H, 5.6. Found: C, 48.6; H, 5.4. The difference in the degree of hydration between the chemical and the X-ray analysis can be attributed to the large interval in time between the respective analyses.

Collection and Reduction of the X-Ray Intensity Data. Preliminary Weissenberg and precession photographs of crystals of [Co(saldpt)(1-methylimidazole)] bromide indicated an orthorhombic lattice. The observed systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) are consistent with the space group $P2_12_12_1$. Accurate unit cell dimensions were obtained from the complete angular settings of 15 reflections measured on a diffractometer. The density was measured by flotation methods, and it indicated that there were four formula units per unit cell. Complete crystal data are given in Table I.

Intensity measurements were made on a Syntex $P\bar{1}$ computer-controlled diffractometer with the incident beam of the spectrometer monochromatized by a highly oriented graphite crystal. The crystal used in data collection was an orthorhombic prism with dimensions 0.30 × 0.32 × 0.50 mm. The long axis of the prism was tilted relative to the ϕ axis of the diffractometer. Intensity data were collected with Mo Kα radiation by the θ–2θ scan technique. Individual scan speeds were determined by a rapid scan at each Bragg peak, and the rate of scanning varied from a minimum of 1°/min to a maximum of 24°/min. Three standards were measured after each 100 reflections during the course of the experiment, and their intensities showed no unusual fluctuations or decay with time. All reflections in the hkl octant to $2\theta = 42°$ were surveyed; these totaled 1492 independent reflections of which 1428 had intensities greater than zero. Those reflections which had negative intensities were assigned a F and a $w(F)$ equal to zero. The reflections with positive intensities were assigned observational variances based on the formula

$$\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$$

where S, B_1, and B_2 are the scan and background counts, T_S and T_B are the scan and individual background counting times ($T_B = \frac{1}{4}T_S$ for all relfections), and p was taken equal to 0.03 and represents the error proportional to the diffracted beam intensity.[7] The intensities and their standard deviations were corrected for Lorentz and polarization effects, but no correction for absorption was applied ($\mu = 24.4$ cm^{-1}); maximum and minimum transmission factors estimated to be 0.49 and 0.46, respectively. The corrected intensities were placed on an approximate absolute scale by the method of Wilson.[8]

(7) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(8) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

Table II[a]

Final Heavy-Atom Positional ($\times 10^4$) and Thermal Parameters

Atom	x	y	z	B, Å^2
Br	2355 (1)	−1124 (1)	914 (2)	
Co	−434 (1)	−1518 (1)	−1751 (1)	
O(1)	−1188 (4)	−690 (3)	−1723 (8)	3.9 (1)
O(2)	319 (4)	−2347 (3)	−1835 (7)	3.7 (1)
O(3)	1493 (6)	129 (6)	−6589 (12)	
N(1)	−1600 (5)	−2736 (5)	−5035 (10)	3.8 (2)
N(2)	−1044 (4)	−1928 (4)	−3445 (9)	3.1 (1)
N(3)	−1104 (5)	−2091 (4)	−367 (9)	3.6 (2)
N(4)	218 (4)	−1105 (4)	−64 (8)	3.3 (2)
N(5)	269 (5)	−930 (4)	−3063 (9)	4.1 (2)
C(1)	−1892 (6)	−3450 (6)	−5693 (12)	5.1 (2)
C(2)	−1240 (6)	−2645 (6)	−3666 (11)	3.5 (2)
C(3)	−1268 (6)	−1528 (6)	−4722 (11)	3.5 (2)
C(4)	−1606 (6)	−2029 (6)	−5676 (13)	4.3 (2)
C(5)	−676 (6)	−2677 (5)	561 (11)	4.1 (2)
C(6)	−6 (6)	−2292 (6)	1476 (11)	4.1 (2)
C(7)	−17 (6)	−1428 (6)	1445 (11)	4.8 (2)
C(8)	246 (7)	−253 (6)	28 (12)	5.3 (2)
C(9)	677 (7)	85 (6)	−1341 (13)	5.4 (3)
C(10)	282 (6)	−78 (5)	−2838 (11)	4.3 (2)
C(11)	754 (6)	−1233 (5)	−4036 (11)	3.6 (2)
C(12)	901 (5)	−2020 (5)	−4253 (11)	3.2 (2)
C(13)	696 (6)	−2550 (5)	−3106 (11)	3.2 (2)
C(14)	918 (6)	−3321 (5)	−3297 (12)	4.0 (2)
C(15)	1323 (6)	−3547 (6)	−4592 (11)	4.2 (2)
C(16)	1527 (6)	−3039 (6)	−5710 (14)	4.7 (2)
C(17)	1333 (6)	−2287 (6)	−5525 (12)	3.9 (2)
C(18)	−1871 (6)	−1966 (5)	−109 (11)	3.4 (2)
C(19)	−2355 (5)	−1360 (5)	−713 (10)	3.1 (2)
C(20)	−1983 (5)	−754 (5)	−1515 (11)	3.5 (2)
C(21)	−2520 (6)	−189 (6)	−2100 (11)	4.3 (2)
C(22)	−3347 (6)	−226 (6)	−1845 (14)	4.9 (2)
C(23)	−3701 (6)	−801 (6)	−1030 (13)	5.1 (2)
C(24)	−3203 (6)	−1365 (6)	−459 (12)	4.5 (2)

Anisotropic Thermal Parameters ($\times 10^4$)[b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	62 (1)	64 (1)	250 (3)	13 (1)	9 (1)	26 (1)
Co	35 (1)	25 (1)	80 (2)	2 (1)	0 (1)	−2 (1)
O(3)	98 (6)	95 (5)	252 (19)	−18 (4)	−1 (9)	−4 (9)

[a] Estimated standard deviations are in parentheses. [b] Defined by the ellipsoid equation: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Solution and Refinement of the Structure. The positions of the cobalt and bromine atoms were determined from an unsharpened Patterson synthesis. A Fourier map based on the phases derived from the Co and Br atoms allowed the positioning of the remaining 32 heavy atoms in the asymmetric unit ($R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.29$). Six cycles of isotropic least squares, the quantity minimized being $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_o)]^2$, reduced R to 0.14. Three further cycles of refinement, adding to the parameter list anisotropic thermal parameters for the cobalt and bromine atoms, further lowered the R value to 0.080. In these three cycles of refinement corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$, Cromer[9]) were applied to the form factors for Co and Br. Inversion of the structure and refinement to convergence gave an R of 0.094. On this basis we have assumed that the structure as originally obtained from the Patterson map describes the correct absolute configuration.

At this stage a difference Fourier was computed and coordinates for the 31 hydrogen atoms were obtained. Inclusion of the contributions of the hydrogen atoms to the calculated structure factors lowered R to 0.073. Four further cycles of refinement were computed, adding to the parameter list: (1) anisotropic thermal parameters for the water oxygen, O(3), which showed a large isotropic temperature factor of about 10 Å^2 and (2) coordinates of the hydrogen atoms. The hydrogen atoms were assigned the isotropic temperature of the atom to which they were attached. The final R indices are 0.064 (including zeros) and 0.058 (excluding zeros). The final weighted R value $[(\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}]$ and goodness-of-fit $[(\Sigma w(F_o - F_c)^2/(n - p))^{1/2}]$ for $n = 1428$ observations of

(9) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table III. Final Hydrogen Parameters $(\times 10^3)^a$

Atom	x	y	z	B, Å^2
H(1)[C(1)]	−200 (5)	−395 (5)	−491 (10)	5.2
H(2)[C(1)]	−243 (5)	−336 (5)	−622 (9)	5.2
H(3)[C(1)]	−149 (5)	−376 (5)	−634 (10)	5.2
H(4)[C(2)]	−121 (5)	−306 (4)	−300 (10)	3.6
H(5)[C(3)]	−117 (5)	−93 (4)	−482 (9)	3.6
H(6)[C(4)]	−188 (5)	−194 (5)	−656 (10)	4.6
H(7)[C(5)]	−55 (5)	−312 (4)	1 (9)	3.9
H(8)[C(5)]	−119 (5)	−202 (4)	105 (10)	3.9
H(9)[C(6)]	54 (5)	−244 (4)	122 (9)	4.2
H(10)[C(6)]	−16 (5)	−257 (4)	247 (9)	4.2
H(11)[C(7)]	−55 (5)	−140 (4)	162 (9)	5.1
H(12)[C(7)]	34 (5)	−117 (5)	220 (9)	5.1
H(13)[N(4)]	76 (4)	−132 (4)	−24 (8)	3.3
H(14)[C(8)]	59 (5)	−20 (5)	109 (11)	5.5
H(15)[C(8)]	−30 (5)	−12 (5)	8 (10)	5.5
H(16)[C(9)]	128 (5)	−8 (5)	−134 (10)	5.1
H(17)[C(9)]	60 (5)	58 (5)	−121 (10)	5.1
H(18)[C(10)]	62 (5)	9 (4)	−373 (10)	4.6
H(19)[C(10)]	−26 (5)	10 (4)	−289 (10)	4.6
H(20)[C(11)]	107 (4)	−89 (4)	−475 (9)	3.3
H(21)[C(14)]	71 (5)	−374 (4)	−257 (9)	4.0
H(22)[C(15)]	141 (5)	−401 (5)	−449 (10)	4.5
H(23)[C(16)]	192 (5)	−327 (5)	−664 (10)	4.7
H(24)[C(17)]	153 (5)	−184 (5)	−607 (9)	4.2
H(25)[C(18)]	−210 (4)	−235 (4)	45 (9)	3.5
H(26)[C(21)]	−227 (5)	20 (5)	−259 (9)	4.6
H(27)[C(22)]	−366 (5)	16 (5)	−238 (10)	4.7
H(28)[C(23)]	−435 (5)	−83 (5)	−74 (10)	5.2
H(29)[C(24)]	−342 (5)	−191 (5)	−11 (10)	4.4
H(30)[O(3)]	202 (7)	21 (7)	−588 (14)	9.6
H(31)[O(3)]	179 (7)	−27 (7)	−700 (15)	9.6

^{a} Estimated standard deviations are in parentheses.

nonzero weight and $p = 245$ are 0.050 and 1.8, respectively. The scattering curves for Br, Co, O, N, and C were taken from the compilation of Hanson, Herman, Lea, and Skillman.[10] The scattering curve for H was that of Stewart, Davidson, and Simpson.[11] Final atomic coordinates and thermal parameters are given in Tables II and III. A list of structure factor amplitudes is available.[12] In the final cycle of refinement, no shift over error exceeded 0.6 for any parameter. The largest $|F_c|$ for a reflection with $|F_o| = 0$ was about 9 e.

The structure factor and Fourier calculations were done using the X-RAY 67 series of programs;[13] the least-squares calculations were performed using an extensively modified version of ORFLS;[14] the illustrations were prepared with the aid of ORTEP.[15] All remaining calculations were done with locally written programs.

Discussion

Our principal aim in this structural analysis was an elucidation of the conformation of the quinquedentate saldpt ligand and the relationship of the molecular conformation to the unusual stability of complexes with heterocyclic ligands in the sixth coordination site. The overall conformation of the monomeric [Co(saldpt)(1-methylimidazole)]⁺ cation is illustrated in Figure 1. The octahedral coordination about the cobalt atom consists of the quinquedentate saldpt ligand arranged such that the oxygen and nitrogen atoms of the salicylidene rings occupy trans positions in the equatorial plane with the secondary amine nitrogen N(4) and the imidazole ligand in axial positions, Figure 1.

In the conformation adopted by the saldpt ligand, the

(10) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

(13) "X-RAY 67" system of programs by J. M. Stewart, University of Maryland, 1967.

(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS," Report ORNL-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

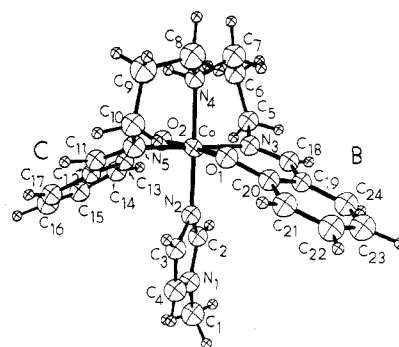(15) C. K. Johnson, "ORTEP," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Figure 1. A perspective view of the [Co(saldpt)(1-methylimidazole)]⁺ cation. The thermal ellipsoids are drawn at the 40% probability level.

Table IV. Some Least-Squares Planes and Deviations (Å)^a

(a) Benzene Ring Planes

(i) C(19)–C(24) [−0.1180X − 0.5297Y − 0.8399Z = 2.2200]

C(19)	0.016	C(22)	0.006
C(20)	−0.015	C(23)	−0.005
C(21)	0.004	C(24)	−0.007

Other Atoms

C(18)	0.032	N(3)	0.193
O(1)	−0.070	Co	0.570

(ii) C(12)–C(17) [−0.8765X − 0.1718Y − 0.4498Z = 1.0151]

C(12)	0.010	C(15)	0.003
C(13)	0.001	C(16)	0.008
C(14)	−0.007	C(17)	−0.015

Other Atoms

C(11)	−0.103	N(5)	0.106
O(2)	−0.033	Co	0.755

(b) Equatorial Plane of the Complex [−0.4897X − 0.3877Y − 0.7809Z = 2.5747]

Co	0.009	N(3)	−0.033
O(1)	0.029	N(5)	−0.034
O(2)	0.029		

(c) Imidazole Ring [0.8996X − 0.1724Y − 0.4005Z = 0.2944]

N(1)	−0.004	C(3)	0.002
N(2)	−0.005	C(4)	0.001
C(2)	0.006		

Other Atoms

Co	0.157	C(1)	0.021

^{a} In each of the planes, the X, Y, and Z are coordinates (Å) referred to the axes a, b, and c. Each of the atoms used to define the plane have been equally weighted. Estimated positional uncertainties: Co, 0.001 Å; O(N), 0.006 Å; C, 0.009 Å.

salicylidene rings are bent away from the axial position occupied by N(4). This bending is similar to that found in some penta- and hexacoordinate complexes with the ligand bis(salicylidene)ethylenediamine[16] and recalls the buckling of the corrin nucleus in vitamin B_{12}.[17] The angles between the normal to the equatorial plane [Co, O(1), O(2), N(3), N(5)] and the normals to the benzene rings B and C are 23.2 (3) and 32.1 (3)°, respectively. The equations of these least-squares planes are given in Table IV. This asymmetry in the bending is apparently directly attributable (see below) to the difference in the conformations of the six-membered rings linking the salicylidene rings to the secondary amine nitrogen N(4): a boat conformation for the chain to ring B and a chair conformation to ring C, Figure 1. Table V contains the sets of observed torsion angles for both the boat and chair ring conformations. The steric restrictions

(16) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).

(17) C. Brink-Shoemaker, D. W. J. Cruickshank, D. C. Hodgkin, M. J. Kamper, and D. Pilling, *Proc. Roy. Soc., Ser. A*, **278**, 1 (1964).

Table V. Torsion Angles (deg)[a]

(a) [Co(saldpt)(1-methylimidazole)]Br

Boat		Chair	
C(7)-N(4)-Co-N(3)	4.2	C(8)-N(4)-Co-N(5)	56.9
N(4)-Co-N(3)-C(5)	-61.6	N(4)-Co-N(5)-C(10)	-59.8
Co-N(3)-C(5)-C(6)	58.6	Co-N(5)-C(10)-C(9)	67.4
N(3)-C(5)-C(6)-C(7)	9.6	N(5)-C(10)-C(9)-C(8)	-60.6
C(5)-C(6)-C(7)-N(4)	-69.2	C(10)-C(9)-C(8)-N(4)	61.0
C(6)-C(7)-N(4)-Co	53.4	C(9)-C(8)-N(4)-Co	-63.9

(b) [Co(saldpt)(peroxo)][b]

Boat		Chair	
C(20)-N(3)-Co-N(2)	-10.4	C(17)-N(3)-Co-N(1)	37.3
N(3)-Co-N(2)-C(18)	-54.7	N(3)-Co-N(1)-C(15)	-36.5
Co-N(2)-C(18)-C(19)	71.6	Co-N(1)-C(15)-C(16)	53.0
N(2)-C(18)-C(19)-C(20)	-13.2	N(1)-C(15)-C(16)-C(17)	-65.7
C(18)-C(19)-C(20)-N(3)	-54.7	C(15)-C(16)-C(17)-N(3)	69.0
C(19)-C(20)-N(3)-Co	63.2	C(16)-C(17)-N(3)-Co	-56.4

[a] A positive torsion angle corresponds to a right-handed screw. Estimated standard deviations are about 0.2–0.4°. [b] The numbering used here is the same as in ref 3, Figure 3. The order of the torsion angles is as given in part (a).
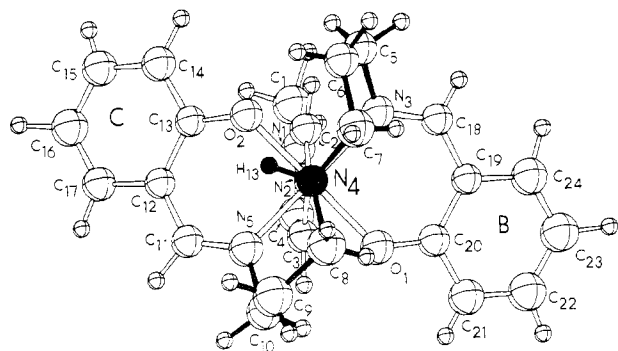

Figure 2. A projection view of the [Co(saldpt)(1-methylimidazole)]⁺ down the N(4)-Co bond. The thermal ellipsoids are drawn at the 50% probability level.
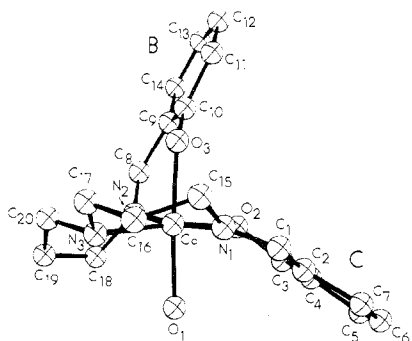

Figure 3. A perspective view of half of the μ-peroxo-[Co(saldpt)]₂ dimer. All of the atoms have been assigned an isotropic temperature factor of 3.0 A².

at the sixth coordination site due to the bending of the salicylidene rings would appear to explain several results: (1) the unusual stability of the heterocyclic ligand complexes; (2) the observation[4] that straight-chain alkyl complexes, [Co(saldpt)R], are more stable than branched-chain alkyl complexes; (3) the chemical shift nonequivalence of the methyl groups in the triisopropyl phosphite complexes noted above. Figure 2 is a projection view of the complex cation down the N(4)-Co bond and serves to illustrate further not only the differences in the propylene chain conformations but also the unique positioning of the secondary amine hydrogen atom, H(13).

The oxygen carrier properties of saldpt complexes of

Table VI. Heavy-Atom Interatomic Distances (A) and Angles (deg)[a]

(a) Primary Coordination Sphere about the Co Atom

Distances

Co-O(1)	1.889	Co-N(3)	1.920
Co-O(2)	1.891	Co-N(4)	1.970
Co-N(2)	1.937	Co-N(5)	1.924

Angles

O(1)-Co-O(2)	178.5	O(2)-Co-N(4)	87.8
O(1)-Co-N(2)	87.8	O(2)-Co-N(5)	90.0
O(1)-Co-N(3)	91.3	N(2)-Co-N(3)	91.0
O(1)-Co-N(4)	93.3	N(2)-Co-N(4)	178.2
O(1)-Co-N(5)	89.2	N(2)-Co-N(5)	91.5
O(2)-Co-N(2)	91.0	N(3)-Co-N(4)	90.3
O(2)-Co-N(3)	89.6	N(3)-Co-N(5)	177.4
		N(4)-Co-N(5)	87.2

(b) Salicylidene Rings

Distances

O(1)-C(20)	1.306	O(2)-C(13)	1.332
N(3)-C(18)	1.282	N(5)-C(11)	1.282
C(18)-C(19)	1.419	C(11)-C(12)	1.402
C(19)-C(20)	1.408	C(12)-C(13)	1.414
C(19)-C(24)	1.392	C(12)-C(17)	1.408
C(20)-C(21)	1.412	C(13)-C(14)	1.399
C(21)-C(22)	1.360	C(14)-C(15)	1.382
C(22)-C(23)	1.362	C(15)-C(16)	1.370
C(23)-C(24)	1.368	C(16)-C(17)	1.356

Angles

Co-O(1)-C(20)	125.1	Co-O(2)-C(13)	122.1
Co-N(3)-C(18)	125.0	Co-N(5)-C(11)	123.6
N(3)-C(18)-C(19)	126.4	N(5)-C(11)-C(12)	126.8
C(18)-C(19)-C(20)	120.8	C(11)-C(12)-C(13)	119.8
C(18)-C(19)-C(24)	118.6	C(11)-C(12)-C(17)	121.1
C(20)-C(19)-C(24)	120.6	C(13)-C(12)-C(17)	118.7
O(1)-C(20)-C(19)	123.9	O(2)-C(13)-C(12)	123.1
O(1)-C(20)-C(21)	119.7	O(2)-C(13)-C(14)	118.4
C(19)-C(20)-C(21)	116.4	C(12)-C(13)-C(14)	118.5
C(20)-C(21)-C(22)	120.8	C(13)-C(14)-C(15)	119.7
C(21)-C(22)-C(23)	122.5	C(14)-C(15)-C(16)	122.3
C(22)-C(23)-C(24)	118.4	C(15)-C(16)-C(17)	118.6
C(19)-C(24)-C(23)	121.1	C(12)-C(17)-C(16)	122.1

(c) Propylene Chains

Distances

N(3)-C(5)	1.484	N(5)-C(10)	1.498
C(5)-C(6)	1.513	C(10)-C(9)	1.503
C(6)-C(7)	1.504	C(9)-C(8)	1.521
C(7)-N(4)	1.503	C(8)-N(4)	1.486

Angles

Co-N(3)-C(5)	116.7	Co-N(5)-C(10)	117.0
N(3)-C(5)-C(6)	109.3	N(5)-C(10)-C(9)	108.1
C(5)-C(6)-C(7)	115.1	C(10)-C(9)-C(8)	116.1
C(6)-C(7)-N(4)	112.8	C(9)-C(8)-N(4)	110.8
C(7)-N(4)-Co	114.0	C(8)-N(4)-Co	115.0
		C(7)-N(4)-C(8)	109.4

(d) Imidazole Ring

Distances

N(1)-C(1)	1.452	N(2)-C(2)	1.302
N(1)-C(2)	1.359	N(2)-C(3)	1.380
N(1)-C(4)	1.356	C(3)-C(4)	1.334

Angles

C(1)-N(1)-C(2)	126.7	Co-N(2)-C(3)	126.0
C(1)-N(1)-C(4)	127.2	C(2)-N(2)-C(3)	107.2
C(2)-N(1)-C(4)	105.9	N(1)-C(2)-N(2)	110.6
Co-N(2)-C(2)	126.5	N(2)-C(3)-C(4)	107.5
		N(1)-C(4)-C(3)	108.8

[a] Bond length esd's: Co-N(O), 0.006–0.008 A; C-C(N,O), 0.01 A. Bond angle esd's: N-Co-N(O), 0.4°; C-C-C(N,O), 0.6°.

cobalt are of considerable interest. Bailes and Calvin[2] reported that [Co^IIsaldpt] takes up 1 mol of dioxygen per mole of complex in the solid state. In a later report by Lindblom, Schaefer, and Marsh,[3] a dimeric cobalt(III) peroxide complex,

μ-peroxo-bis [N,N'-bis(salicylidene)dipropylenetriamineco-balt(III)], was described. The dimer was prepared by O_2 oxidation of [Co^{II}saldpt] in toluene solution. This difference in the metal-to-O_2 ratio would seem to be explicable solely on the basis of solution *vs.* solid-state oxidation of the [Co^{II}saldpt] complex. Half of the peroxo dimer[3] is illustrated in Figure 3. It is immediately obvious from a comparison of Figures 1 and 3 that the conformations of the saldpt ligand in the peroxo and the 1-methylimidazole complexes are very different. In particular, the saldpt ligand in the peroxo complex has a conformation in which the salicylidene rings are in cis positions about the cobalt atom with the peroxo group trans to an oxygen atom of one of the salicylidene rings. An important feature is that in the dimer the halves are arranged so that the secondary amine nitrogen and its associated propylene linkages eclipse a salicylidene ring of the opposite half. The six-membered propylene rings in the peroxo complex are found in a boat and a chair conformation as we have found in the 1-methylimidazole complex, Table V. The bending of the salicylidene rings is also similar to that in the 1-methylimidazole complex: for the boat conformation 24.5 (3)° *vs.* 23.2 (3)°; for the chair conformation 32.9 (3)° *vs.* 32.1 (3)°. This suggests that the bending is primarily a function of the conformation of the associated propylene ring system.

It seems clear that the cis arrangement of the salicylidene rings is necessary for dimer formation to occur. Otherwise, if a conformation similar to that observed in the 1-methylimidazole complex were adopted, severe nonbonded repulsion between the salicylidene rings would occur, thus destabilizing the dimer. Such considerations have been recently exploited in the synthesis of model iron heme complexes.[18] It is likely that the saldpt ligand conformation found in this study will predominate in [Co(saldpt)(O_2)].[2] Also, the adopted conformation can be considered as a reasonable model for B_{12} studies in that the buckling of the corrin nucleus is mimicked.[17] However, the ligand system suffers from the obvious drawback that the ligating oxygen atoms are present in the equatorial system.

Heavy-atom distances and angles for the [Co(saldpt)(1-methylimidazole)]+ cation are given in Table VI. The parameters in the saldpt ligand are in good agreement with those found in the peroxo dimer[3] and in the complex [Ni(N-Me-saldpt)].[19] The cobalt to nitrogen distances in the equatorial plane average 1.922 (5) Å; the Co–N(imidazole) distance is only slightly longer at 1.937 (6) Å, while the Co–N(4), the secondary amine, distance is significantly longer at 1.970 (6) Å. The 1-methylimidazole ligand is quite planar, Table IV, and its bond lengths and angles are in good agreement with other observations.[20] A complete

Figure 4. An illustration of the hydrogen bonding among the complex cation, the bromide anion, and the water of crystallization. The twofold screw axis parallel to the crystallographic *c* axis is indicated in the figure.

Table VII. Distances and Angles in the Hydrogen Bonds, D–H···A

D	H	A	D···A, Å	H···A, Å	∠D–H···A, deg
N(4)	H(13)	Br[a]	3.569	2.81	137
O(3)	H(30)	Br[b]	3.381	2.47	143
O(3)	H(31)	Br[c]	3.410	2.54	157

[a] x, y, z. [b] $1/2 - x, -y, -1/2 + z$. [c] $x, y, -1 + z$.

list of bond lengths and angles involving the hydrogen atoms has been deposited.[12] The average C–H distance is 0.99 (9) Å, the N(4)–H(13) distance is 0.96 (9) Å, and the two O(water)–H distances average to 0.99 (9) Å.

The crystal packing is dominated by a series of hydrogen bonds involving the water of crystallization, the bromide anion, and the secondary amine nitrogen hydrogen, N(13), of the saldpt ligand. These hydrogen bonds are arranged about a twofold screw axis parallel to the crystallographic *c* axis, Figure 4 and Table VII. All of the potential hydrogen-bond donors are involved in these hydrogen bonds. There are no unusually short contacts in the crystal structure.

Supplementary Material Available. A listing of structure factor amplitudes and a complete list of bond lengths and angles involving the hydrogen atoms 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-74-2089.

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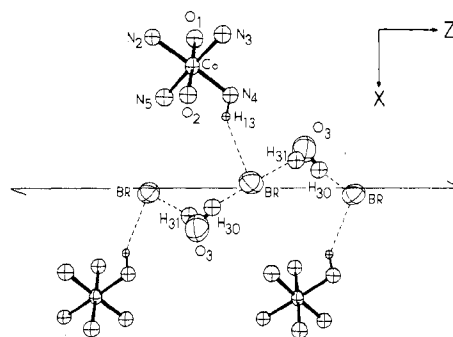(20) H. C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).