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Oxygen-Carrying Cobalt Complexes. 10. Structures of *N*,*N'*-Ethylenebis(3-*tert*-butylsalicylideniminato)cobalt(II) and Its Monomeric Dioxygen Adduct[1]

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The crystal structures of the title compound and its dioxygen adduct with pyridine as the axial base have been determined by X-ray diffraction. The unoxygenated compound crystallizes in the monoclinic space group $C2/c$, with four molecules in a cell with dimensions a = 23.201 (7) Å, b = 13.880 (2) Å, c = 7.017 (1) Å, and β = 98.10 (2)°. The structure was refined by full-matrix least squares, using 1985 reflections, to an R index of 7.2%. The structure is normal but shows a disordered ethylene bridge and a very regular rigid-body thermal motion. The oxygenated complex crystallizes from acetonitrile at −17 °C as monomers in the monoclinic space group $P2_1/c$, with four molecules in the cell with dimensions a = 14.77 (2) Å, b = 9.94 (1) Å, c = 19.63 (1) Å, and β = 105.00 (4)°. The structure was refined by using full-matrix least squares to an R index of 7.9% for 1714 data having $F^2 > 3\sigma(F_2)$. The O–O distance is 1.350 (11) Å and the Co–O–O angle is 116.4 (5)°, both compatible with a $Co^{III}–O_2^-$ formulation. The ethylene bridge in this complex is also disordered. Crystals of the dioxygen complex do not form at room temperature, but the crystals grown at −17 °C are stable for periods of days at 25 °C.

Of the compounds studied as models for the oxygen-carrying proteins such as hemoglobin and myoglobin—principally the iron picket-fence porphyrin complexes[2] and the CoSalen derivatives[3,4]—only the cobalt complexes have furnished sufficiently good crystals to allow accurate determinations of the metal–dioxygen geometry. It has been assumed that this geometry is dependent upon the electron density at the cobalt atom and that the extent of electron transfer from metal to dioxygen will vary from compound to compound. The changes in metal–dioxygen geometry, then, should tell us something concerning the bonding between the metal atom and the oxygen molecule. In turn, the variations may also provide a means of determining the electron distribution in these complexes. For these reasons we have synthesized many derivatives of *N*,*N'*-ethylenebis(salicyldeniminato)cobalt(II) ("CoSalen") and attempted to prepare crystals of the oxygen adducts of these derivatives for structural studies. Originally we believed it was necessary to provide steric hindrance in the molecules, to prevent μ-peroxo dimers from forming,[3] but subsequent work[4b] has showed that monomeric adducts could be crystallized with sterically unhindered chelates. However, every compound which we had been able to crystallize had tetramethyl substitution on the ethylene bridge in the CoSalen group. The possibility occurred to us that this substitution might be necessary to the oxygen-carrying ability of the compounds; to test this possibility, we synthesized several complexes with no substitution on the bridge. One of these—the 3-*tert*-butyl compound—provided suitable crystals of the oxygenated material, disproving our hypothesis. We report here the structure of the unoxygenated complex and that of the oxygenated material, with pyridine as the axial base. A recent, comprehensive review of this field is available.[5]

Experimental Section

3-*tert*-Butylphenol was purchased from Aldrich Chemical Co. and it was converted to 3-*tert*-butylsalicylaldehyde by the method of Duff.[6] The yield was 5.2%. Approximately 3 g (17 mmol) of 3-*tert*-butylsalicylaldehyde in 50 mL of ethanol was mixed with 0.51 g (8.5 mmol) of ethylenediamine; the Schiff base separated as yellow crystals, yield 99%. Cobalt acetate (1.49 g, 8.4 mmol) was dissolved in water and added to a slurry of 3.2 g (8.4 mmol) of the ligand and about 0.01 g of sodium hydroxide in ethanol. The red complex Co(3-*t*-Bu-Salen) formed instantly, apparently in high yield.

Table I. Crystallographic Data and Data Collection Parameters for Unoxygenated and Oxygenated Forms of Co(3-*t*-BuSalen)

formula	$Co(C_{24}H_{30}N_2O_2)$	$Co(C_{24}H_{30}N_2O_2)\cdot O_2\cdot C_5H_5N$
fw	437.43	548.52
space group	$C2/c(C_{2h}^6)$	$P2_1/c(C_{2h}^5)$
a, Å	23.201 (7)	14.77 (2)
b, Å	13.880 (2)	9.94 (1)
c, Å	7.017 (1)	19.63 (1)
β, deg	98.10 (2)	105.00 (4)
V, Å^3	2237.1 (8)	2784 (6)
Z	4	4
ρ_{calcd}, g·cm^{-1}	1.299	1.309
abs coeff, cm^{-1}	8.2	6.8
no. of reflctns measd	4227	5126
no. of unique reflctns	1985	4943
radiation	Mo K$\bar{\alpha}$	
monochromator	graphite crystal	
max 2θ, deg	50	
scan mode	θ:2θ	
scan width	1.0° below 2θ (Kα_1) to 1.0° above 2θ (Kα_2)	
scan speed, deg·min^{-1}	2.02	
bkgd time/scan time	1.0	

Crystals of the unoxygenated material were obtained by dissolving about 0.05 g of the cobalt complex in 50 mL of acetone. The solution was filtered into a 100-mL beaker which was then covered with a paper tissue to retard evaporation. The beaker was set aside at room temperature; after a week, large, well-developed ruby red crystals had formed which were used for further experiments. Crystals which grew faster were badly twinned. For the oxygenated complex, we obtained the best crystals as follows: Acetonitrile (Spectrograde, 25 mL) was placed in a 50-mL volumetric flask and 2 drops (0.03 mL) of reagent grade pyridine were added. The flask was placed in a cold bath at −18 °C; after 24 h, 50–53 mg of powdered Co(3-*t*-Bu-Salen) was added gently, with no stirring or shaking, and a slow stream of O_2 was passed over the surface of the solution. After 4 days the solvent had evaporated; the crystalline material was scraped out and provided the crystals for the experiment. It was not possible to grow oxygenated crystals at room temperature, but the crystals prepared at −18 °C were stable for days at 25 °C.

X-ray Data Collection. The Unoxygenated Complex. Preliminary Weissenberg photographs of a crystal of Co(3-*t*-Bu-Salen) showed the space group to be either Cc or $C2/c$ (systematic absences hkl, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$). Space group $C2/c$, with each molecule lying on a crystallographic twofold axis, was confirmed by the structure solution and refinement. Cell dimensions were determined by least-squares fit to the setting angles of 15 reflections on

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Table II

Atomic Parameters for the Unoxygenated Compound[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0	5574.7 (5)	7500	72.7 (5)	32.1 (3)	41.8 (3)	0	2.5 (3)	0
O(1)	556 (1)	6539 (1)	7552 (3)	46 (1)	42 (1)	64 (1)	6 (1)	9 (1)	−2 (1)
N(1)	539 (2)	4599 (2)	7423 (4)	117 (3)	42 (2)	42 (2)	20 (2)	2 (2)	−1 (1)
C(1)	1115 (2)	6484 (3)	7439 (5)	53 (2)	71 (3)	53 (2)	14 (2)	7 (2)	0 (2)
C(2)	1454 (2)	7342 (3)	7455 (5)	43 (2)	107 (3)	64 (2)	−4 (2)	5 (2)	3 (2)
C(3)	2040 (2)	7230 (5)	7285 (7)	54 (3)	152 (6)	102 (4)	−15 (4)	9 (2)	7 (4)
C(4)	2302 (3)	6345 (7)	7112 (9)	59 (4)	219 (9)	124 (5)	40 (5)	15 (4)	10 (5)
C(5)	1992 (3)	5547 (6)	7137 (7)	93 (5)	161 (6)	97 (3)	72 (5)	10 (3)	3 (5)
C(6)	1391 (2)	5577 (4)	7302 (4)	68 (3)	96 (3)	58 (2)	36 (3)	6 (2)	2 (3)
C(7)	1087 (3)	4703 (4)	7340 (6)	116 (4)	79 (4)	49 (2)	52 (4)	2 (3)	2 (2)
C(8)	302 (3)	3617 (3)	7414 (12)	209 (8)	38 (2)	117 (4)	21 (3)	25 (6)	18 (3)
C(9)	1187 (2)	8330 (3)	7656 (6)	58 (2)	76 (3)	83 (3)	−29 (2)	8 (2)	1 (2)
C(10)	1635 (3)	9163 (5)	7698 (10)	97 (4)	119 (5)	113 (5)	−61 (4)	14 (4)	5 (4)
C(11)	942 (3)	8391 (4)	9565 (8)	90 (4)	77 (3)	112 (4)	−29 (3)	38 (4)	−20 (3)
C(12)	714 (2)	8529 (3)	5964 (8)	82 (3)	59 (3)	117 (4)	−17 (3)	2 (3)	8 (3)

Atomic Parameters for the H Atoms in the Unoxygenated Compound[b]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(3)	223 (1)	783 (2)	721 (5)	7 (1)	H(10)C	197 (2)	903 (3)	880 (6)	9 (1)
H(4)	269 (2)	639 (3)	698 (7)	12 (2)	H(11)A	74 (2)	897 (3)	973 (5)	8 (1)
H(5)	212 (2)	497 (3)	712 (6)	8 (1)	H(11)B	126 (2)	829 (3)	1068 (6)	9 (1)
H(7)	130 (2)	408 (3)	723 (5)	8 (1)	H(11)C	62 (1)	799 (2)	959 (4)	6 (1)
H(8)A	52 (2)	331 (4)	829 (8)	13 (2)	H(12)A	52 (2)	916 (3)	612 (5)	9 (1)
H(8)B	31 (3)	330 (5)	623 (10)	23 (3)	H(12)B	41 (1)	807 (2)	585 (4)	6 (1)
H(10)A	144 (2)	976 (3)	769 (7)	10 (2)	H(12)C	87 (1)	851 (2)	479 (5)	6 (1)
H(10)B	179 (2)	911 (3)	648 (5)	7 (1)					

[a] Positional parameters are multiplied by 10^4. Anisotropic thermal parameters are multiplied by 10^3. The estimated standard deviation for the last digit is given in parentheses. The anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + \cdots + 2U_{23}b^*c^*kl)]$. [b] Positional parameters have been multiplied by 10^3.

a locally modified Syntex P2$_1$ diffractometer. The results are given in Table I along with the details of the data collection. Two equivalent sets of data (h, k, $\pm l$ and h, $-k$, $\pm l$) were measured with subsequent averaging to produce the unique set of data. Five check reflection intensities were measured every 100 reflections; they showed no systematic variations throughout the data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The Oxygenated Complex. Preliminary Weissenberg photographs of a crystal of the oxygenated form showed systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, which established the space group as $P2_1/c$. Cell dimensions were taken as the average of the values obtained for two different crystals. The cell dimensions for each crystal were determined as for the unoxygenated complex. The final values are reported in Table I along with the details of the data collection. For every 100 reflections the intensities of six check reflections were measured. A significant loss in intensity was observed which necessitated the use of two different crystals to measure the data. The first crystal was used to measure 2555 intensities after which the average check reflection intensity had decreased by 6.7%. The remaining 2569 intensities were measured by using a second crystal and the average check reflection intensity had decreased by 12.2% at the end of this data collection. For each crystal the decay was approximately linear; the data were corrected according to the equation $F_c = F_o(1.0 + k)n$ where F_o is the observed structure factor magnitude, F_c = corrected structure factor magnitude, n = sequence number during data collection, and k = decay constant. For crystal 1, $k = 8.4 \times 10^{-6}$, and for crystal 2, $k = 11.7 \times 10^{-6}$. The two data sets were merged by scaling to the intensities of the check reflections. The data were corrected for Lorentz and polarization effects, but no correction was made for absorption. In the reduced data set only 1714 reflections had $F_o^2 > 3\sigma(F_o^2)$.

Solution and Refinement of the Structures. The Unoxygenated Complex. The structure of the unoxygenated complex was solved by using MULTAN.[7] The E map with the highest figure of merit showed the cobalt, oxygen, and nitrogen atoms of the compound. The rest of the molecule was located by successive structure factor and Fourier calculations. The only troublesome feature of the solution was the configuration of the ethylenediamine bridge portion of the molecule (see the Description of the Structure). Hydrogen atoms were located in a difference map at a late stage of refinement and included in subsequent calculations. The least-squares refinement converged at an R index of 0.072 (R_w = 0.071) $\{R = \sum||F_o| - |F_c||/\sum|F_o|;\ R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}\}$ and a goodness of fit, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$, of 1.13, where N_o is 1985 reflections and N_p is 192, the number of parameters refined. In the final cycle no nonhydrogen parameter shifted by more than 0.2 times its standard deviation. A final difference map showed no excursion greater than 0.5 e/Å^3. The final parameters are given in Table II.

The Oxygenated Complex. The structure was again solved with MULTAN[7] and conventional structure factor and Fourier map methods. The Co atom, all N atoms, 3 O atoms, and 19 C atoms were located from an E-map calculation. These atoms were used in a structure factor calculation (R = 39.3%) and a subsequent Fourier map yielded the positions of the remaining nonhydrogen atoms. The structure was refined by full-matrix, least-squares techniques which minimized $\sum w(F_o^2 - kF_c^2)^2$. The Co, N, and O atoms were included in the refinement with anisotropic temperature parameters while carbon atoms were included with isotropic thermal parameters. The hydrogen atoms were placed at calculated positions, 1 Å from the atoms they were bonded to. The isotropic temperature factor for an H atom was taken as 1.5 times the value of B (Å^2) for the C atom to which it is attached. The number of variables was limited to 189 because of the low number of data with $F_o^2 > 3\sigma(F_o^2)$. The R value based on the final parameters (Table III) is 0.167 for all 4943 data and 0.079 for those data with $F_o^2 > 3\sigma(F_o^2)$. The corresponding weighted residuals are 0.150 and 0.123. The goodness-of-fit is 1.49. In the final cycle of least-squares refinement no parameter shifted by more than 0.5 its standard deviation. A final difference map showed several peaks between 1.0 and 1.3 e Å^{-3} and a moderately high background level. A listing of observed and calculated structure factors for both compounds is available.[8]

Results

Figure 1 shows a representation of the oxygenated complex with the atom numbering system that is used for both struc-

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(8) Supplementary material.

Table III. Atomic Parameters for the Oxygenated Compound[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1293.3 (8)	6039 (1)	6851.6 (5)	52.9 (7)	42.9 (6)	49.1 (6)	0.1 (7)	16.7 (5)	2.4 (6)
O(1)	1982 (3)	5609 (4)	7783 (2)	47 (4)	59 (4)	49 (3)	2 (3)	24 (3)	6 (3)
O(2)	2340 (3)	5445 (4)	6538 (2)	64 (4)	62 (3)	32 (3)	4 (3)	23 (3)	2 (2)
O(3)	781 (5)	4309 (5)	6782 (3)	140 (6)	37 (4)	96 (5)	1 (4)	50 (5)	−6 (3)
O(4)	1010 (7)	3478 (8)	6310 (5)	255 (11)	116 (8)	213 (10)	−77 (8)	39 (9)	4 (7)
N(1)	236 (4)	6597 (6)	7146 (3)	58 (5)	57 (4)	51 (4)	4 (4)	4 (4)	7 (4)
N(2)	578 (4)	6442 (6)	5928 (3)	56 (5)	42 (4)	77 (5)	4 (4)	22 (4)	−1 (4)
N(3)	1822 (4)	7920 (6)	6998 (3)	69 (5)	61 (4)	52 (4)	−17 (4)	29 (4)	−6 (4)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	1654 (5)	5487 (7)	8330 (4)	4.0 (2)	C(16)	2836 (7)	5952 (9)	4603 (5)	7.2 (2)
C(2)	2275 (5)	4960 (7)	8973 (4)	3.8 (2)	C(17)	1968 (6)	6224 (9)	4655 (4)	6.8 (2)
C(3)	1921 (6)	4847 (8)	9573 (4)	4.9 (2)	C(18)	1763 (5)	6017 (8)	5323 (4)	4.5 (2)
C(4)	1024 (6)	5293 (8)	9573 (4)	5.1 (2)	C(19)	865 (6)	6356 (8)	5356 (4)	5.3 (2)
C(5)	442 (5)	5804 (8)	8981 (4)	5.0 (2)	C(20)	4160 (6)	4701 (8)	6454 (4)	5.3 (2)
C(6)	729 (5)	5920 (8)	8358 (4)	4.3 (2)	C(21)	4402 (6)	5770 (9)	7015 (5)	7.7 (2)
C(7)	115 (6)	6487 (8)	7766 (4)	5.1 (2)	C(22)	5081 (6)	4439 (9)	6213 (5)	8.0 (3)
C(8)	3257 (5)	4477 (7)	8998 (4)	4.3 (2)	C(23)	3856 (6)	3396 (9)	6687 (4)	6.7 (2)
C(9)	3771 (6)	3860 (9)	9721 (4)	7.7 (2)	C(24)	−391 (7)	6734 (9)	5921 (5)	6.5 (2)
C(10)	3228 (6)	3369 (9)	8448 (4)	6.2 (2)	C(25)	1845 (6)	8649 (9)	7576 (4)	5.9 (2)
C(11)	3826 (6)	5675 (8)	8850 (4)	6.4 (2)	C(26)	2221 (6)	9912 (9)	7760 (4)	5.6 (2)
C(12)	−435 (6)	7258 (9)	6581 (5)	7.0 (2)	C(27)	2569 (6)	10468 (8)	7256 (5)	6.3 (2)
C(13)	2475 (5)	5569 (7)	5904 (4)	4.3 (2)	C(28)	2598 (6)	9830 (9)	6636 (5)	6.5 (2)
C(14)	3403 (5)	5245 (7)	5833 (4)	4.4 (2)	C(29)	2191 (6)	8543 (9)	6539 (4)	5.6 (2)
C(15)	3535 (6)	5454 (8)	5160 (5)	6.2 (2)					

[a] Positional parameters are multiplied by 10^4. Anisotropic thermal parameters are multiplied by 10^3. The estimated standard deviation for the last digit is given in parentheses. The anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + \cdots + 2U_{23}b^*c^*kl)]$.

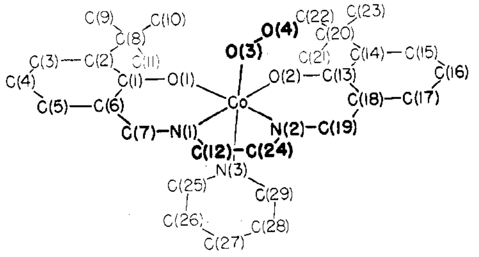

Figure 1. The atom numbering system for both molecules.

Table IV. Bond Distances (Å)[a]

	unoxygenated	oxygenated
Co–O(1), Co–O(2)	1.855 (2)	1.897 (5), 1.900 (5)
Co–N(1), Co–N(2)	1.849 (3)	1.883 (6), 1.890 (6)
O(1)–C(1), O(2)–C(13)	1.314 (4)	1.293 (9), 1.316 (9)
C(1)–C(2), C(13)–C(14)	1.427 (5)	1.453 (10), 1.449 (10)
C(2)–C(3), C(14)–C(15)	1.389 (7)	1.411 (10), 1.400 (11)
C(3)–C(4), C(15)–C(16)	1.384 (9)	1.397 (11), 1.386 (12)
C(4)–C(5), C(16)–C(17)	1.323 (10)	1.353 (11), 1.339 (13)
C(5)–C(6), C(17)–C(18)	1.416 (8)	1.398 (11), 1.436 (12)
C(6)–C(7), C(18)–C(19)	1.405 (6)	1.394 (11), 1.386 (11)
C(1)–C(6), C(13)–C(18)	1.422 (5)	1.448 (11), 1.409 (11)
N(1)–C(7), N(2)–C(19)	1.290 (6)	1.280 (10), 1.303 (10)
N(1)–C(12), N(2)–C(24)	1.469 (7)	1.441 (11), 1.457 (11)
C(2)–C(8), C(14)–C(20)	1.521 (5)	1.516 (10), 1.525 (11)
C(8)–C(9), C(20)–C(21)	1.552 (8)	1.554 (12), 1.506 (12)
C(8)–C(10), C(20)–C(22)	1.530 (7)	1.536 (11), 1.573 (12)
C(8)–C(11), C(20)–C(23)	1.524 (6)	1.528 (11), 1.483 (12)
C(12)–C(24)	1.424 (9)	1.414 (13)
Co–O(3)		1.870 (6)
Co–N(3)		2.018 (6)
O(3)–O(4)		1.350 (11)
N(3)–C(25), N(3)–C(29)		1.339 (10), 1.322 (10)
C(25)–C(26), C(28)–C(29)		1.383 (12), 1.405 (12)
C(26)–C(27), C(27)–C(28)		1.346 (12), 1.382 (12)

[a] Chemically equivalent bonds are listed on the same line.

tures. Bond distances for the two complexes are given in Table IV and selected bond angles are listed in Table V. Because the unoxygenated molecule lies on a twofold axis passing through the cobalt atom and the center of the C–C (en) bond, only half the molecule constitutes the asymmetric unit and thus only half as many distances and angles are listed in these tables, compared to the oxygenated complex.

The Unoxygenated Complex. The geometry of the unoxygenated compound is normal, all distances save one being within 3σ of the average found for other CoSalen complexes with four-coordinate cobalt.[9] The C–C distance in the ethylenediamine bridge is short—1.424 (9) Å—suggesting that the ordered model we have used is not entirely appropriate. Ethylenediamine ligands by themselves sometimes exhibit a λ–δ disorder which can be modeled by a planar metal–en ring with a short C–C distance. The thermal ellipsoids of the disordered carbon atoms in such cases are elongated perpendicular to the metal–en ring. In this case, the apparent thermal motion of these two atoms combines this perpendicular motion with a rigid body motion of the entire molecule in the plane of the molecule (vide infra). The five-atom cobalt–en grouping is nearly planar, again suggesting that the en carbon atoms are disordered and that the short C–C distance is simply a reflection of that disorder. The isotropic thermal parameters of the hydrogen atoms attached to these carbon atoms are the largest of those observed in the structure, another indication that there is disorder in the bridging atoms. The probable locations of the disordered atoms are so near to one another that we chose to represent them by this disordered, anisotropic model rather than by two ordered half-occupancy C–C groups. It should be understood, then, that the short C–C distance does not represent a measurement of the distance between two single-bonded carbon atoms.

The most remarkable feature of this structure is the pattern of thermal motion. Figure 2 shows an ORTEP drawing of the molecule perpendicular to the Salen plane. The twofold axis lies in this plane and passes through the cobalt atom and between C(12) and C(12′). It appears from this striking drawing that the entire molecule is undergoing an oscillation about an axis perpendicular to the plane of the molecule and

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Table V. Bond Angles for the Two Compounds (Deg)

	unoxygenated	oxygenated		unoxygenated	oxygenated
O(1)–Co–O(2)	87.6 (1)	87.9 (2)	C(2)–C(8)–C(10), C(14)–C(20)–C(22)	109.7 (3)	110.7 (6), 109.2 (6)
O(1)–Co–O(3), O(2)–Co–O(3)		88.2 (2), 92.2 (2)	C(2)–C(8)–C(11), C(14)–C(20)–C(23)	110.5 (3)	108.5 (6), 109.9 (7)
O(1)–Co–N(1), O(2)–Co–N(2)	93.4 (1)	92.9 (2), 93.1 (2)	C(9)–C(8)–C(10), C(21)–C(20)–C(22)	105.9 (4)	106.1 (6), 106.1 (7)
O(1)–Co–N(2), O(2)–Co–N(1)	177.1 (1)	178.4 (2), 178.5 (2)	C(9)–C(8)–C(11), C(21)–C(20)–C(23)	106.7 (4)	108.6 (6), 115.2 (7)
O(1)–Co–N(3), O(2)–Co–N(3)		88.9 (2), 91.0 (2)	C(10)–C(8)–C(11), C(22)–C(20)–C(23)	110.9 (4)	110.0 (6), 107.6 (7)
N(1)–Co–O(3), N(2)–Co–O(3)		86.6 (3), 90.6 (3)	C(3)–C(4)–C(5), C(15)–C(16)–C(17)	119.7 (6)	120.7 (7), 123.0 (9)
N(1)–Co–N(2)	85.8 (1)	86.0 (3)	C(4)–C(5)–C(6), C(16)–C(17)–C(18)	121.3 (6)	120.9 (7), 118.2 (8)
N(1)–Co–N(3), N(2)–Co–N(3)		90.3 (2), 92.3 (3)	C(5)–C(6)–C(7), C(17)–C(18)–C(19)	118.6 (4)	118.9 (7), 116.0 (7)
N(3)–Co–O(3)		175.6 (3)	C(5)–C(6)–C(1), C(17)–C(18)–C(13)	119.3 (4)	120.7 (7), 119.6 (7)
Co–O(1)–C(1), Co–O(2)–C(13)	130.3 (2)	126.8 (4), 127.8 (4)	C(6)–C(7)–N(1), C(18)–C(19)–N(2)	126.8 (4)	127.3 (7), 125.8 (7)
O(1)–C(1)–C(2), O(2)–C(13)–C(14)	120.0 (3)	117.9 (6), 116.7 (6)	C(7)–N(1)–C(12), C(19)–N(2)–C(24)	118.3 (4)	122.2 (7), 122.9 (7)
O(1)–C(1)–C(6), O(2)–C(13)–C(18)	120.9 (3)	124.3 (7), 122.0 (7)	N(1)–C(12)–C(24), N(2)–C(24)–C(12)	111.8 (5)	110.6 (7), 110.0 (7)
C(1)–C(2)–C(3), C(13)–C(14)–C(15)	116.9 (4)	117.9 (6), 115.1 (7)	Co–N(3)–C(25), Co–N(3)–C(29)		123.1 (5), 123.3 (5)
C(1)–C(2)–C(8), C(13)–C(14)–C(20)	121.5 (3)	121.7 (6), 121.2 (7)	N(3)–C(25)–C(26), N(3)–C(29)–C(28)		129.2 (8), 124.9 (8)
C(2)–C(3)–C(4), C(14)–C(15)–C(16)	123.7 (5)	122.1 (7), 122.7 (8)	C(25)–C(26)–C(27), C(29)–C(28)–C(27)		112.7 (8), 115.3 (8)
C(2)–C(8)–C(9), C(14)–C(20)–C(21)	113.1 (4)	113.0 (6), 108.7 (7)	C(26)–C(27)–C(28)		124.3 (8)

Table VI. Selected Dimensions of Oxygenated Cobalt Complexes

compd	Co–O, Å	O–O, Å	Co–base, Å	Co–O–O, deg
Co(3-*t*-Bu-Saltmen), *N*-benzylimidazole[3]	1.877 (7)	1.273 (10)	1.974 (8)	117.5 (5)
Co(3-F-Saltmen), *N*-methylimidazole[4a]	1.881 (2)	1.320 (3)	2.004 (3)	117.4 (2)
CoSaltmen, *N*-benzylimidazole[4b]	1.889 (2)	1.277 (3)	2.011 (2)	120.0 (2)
Co(3-MeO-Saltmen), aquo (av values)[1]	1.877 (15)	1.25 (2)	2.048 (5)	117 (1)
Co(3-*t*-Bu-Salen), pyridine[b]	1.870 (6)	1.350 (11)	2.018 (6)	116.4 (5)
average	1.879 (7)	1.294 (40)	2.011 (27)[a]	117.7 (1.4)

[a] Excluding H_2O. [b] This work.

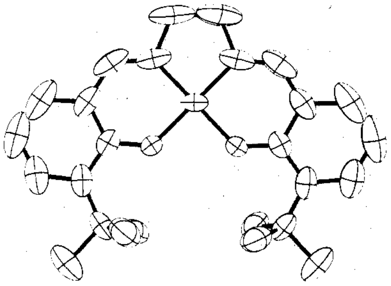

Figure 2. A view of the unoxygenated compound perpendicular to the CoSalen plane showing the very regular rigid-body motion of the molecule. The drawing was prepared by ORTEP.

passing through the twofold axis 2.0 Å from the cobalt atom. A rigid-body analysis of the motion of the Schomaker–Trueblood method[10] confirms this motion, with root-mean-square amplitude 4.3°, and reveals a second smaller component perpendicular to it. The stereo drawing in Figure 3 provides a visualization of this composite motion. The detailed analysis shows that the two carbon atoms of the en bridge are not fit adequately by this rigid-body treatment, still another reason for believing them to be disordered pairs of C–C atoms rather than an ordered group with the apparent thermal motion shown in the figure.

The Oxygenated Complex. The CoSalen portion of this molecule is normal, the sole exception being the C–C bond in the ethylenediamine bridge. This is even shorter (1.414 (13) Å) than in the unoxygenated complex and we believe it is short for the same reasons as given above for that structure. Figure 4 is an ORTEP drawing of the oxygenated complex.

The cobalt–dioxygen geometry is qualitatively the same as we have found in other oxygenated complexes:[3,4] the cobalt–oxygen bond is nearly perpendicular to the CoSalen plane, the Co–O–O angle is about 120° and the Co–O–O plane approximately bisects an in-plane O–Co–N angle. Quantitatively there are some differences between this molecule and others that have been studied. The most outstanding of these is the long O–O distance in the bound dioxygen group, 1.350 (11) Å. This will be discussed later. The cobalt–N(pyridine) distance of 2.02 Å falls within the wide range (1.96–2.18 Å) found for a variety of cobalt–pyridine complexes. The in-plane, Co–O and Co–N distances are just those expected for a six-coordinate CoSalen complex.

The dioxygen group in this molecule is positioned between a Co–O and a Co–N bond, pointing away from the en bridge and slightly toward one of the 3-*tert*-butyl groups. This geometry can best be described by the two torsion angles O(4)–O(3)–Co–O(2) = 27 (1)° and O(4)–O(3)–Co–N(2) = 67 (1)°. This is the same relative positioning as observed in the other CoSalen–dioxygen adducts but different from the arrangement in Co(bzacen)(py)(O_2),[11] where the Co–O–O plane bisects the N–Co–N angle of the Schiff base ligand. Either arrangement allows for good overlap between π^* orbitals on the dioxygen group and $d\pi$ orbitals on the cobalt atom. The pyridine ligand is closely coplanar with the Co–O–O plane, the angle between the two being 18 (1)°. Again, this arrangement allows for π overlap between the cobalt atom and the ligand.

Discussion

It has been our intention in collecting data on oxygen-carrying cobalt complexes to use the data to understand the influence of a change in axial base or a change in substitution on the in-plane ligand, on the metal–dioxygen geometry. From these changes we expect to be able to infer the electronic state of the bound dioxygen and gain some insight into the nature of the bonding. It has not been possible so far to prepare a rational series of compounds to examine these effects; the molecules of interest can be synthesized, but crystals are difficult to grow. Thus we must attempt to learn what we can from the data available; eventually we may have a complete

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[10] Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *24*, 63.

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

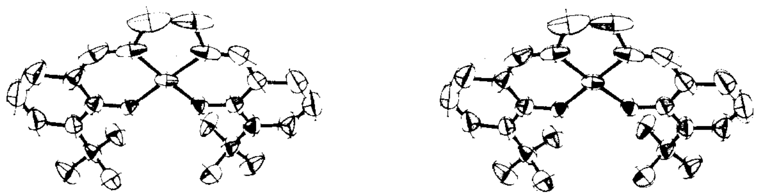

Figure 3. A stereoview of the unoxygenated compound showing the two components of the rigid-body motion. The drawings were prepared by ORTEP.

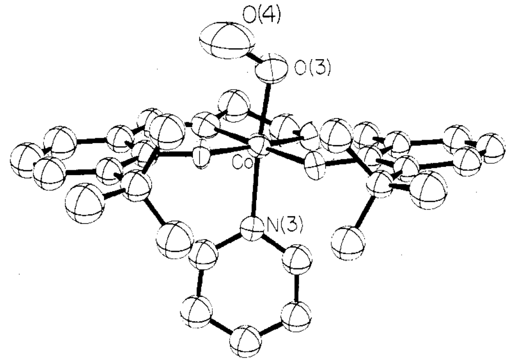

Figure 4. An ORTEP drawing of the oxygenated complex.

series of substituted complexes all with the same axial base or a complete series of one complex with a wide range of axial bases, whose dimensions will give precise answers to our questions.

Some pertinent dimensions of the five known structures of monomeric oxygenated CoSalen complexes are given in Table VI. The only dimension which shows significant changes is the O–O distance, which varies from 1.25 (2) to 1.35 (1) Å. It does not appear that this variation is correlated with in-plane substitution. We can postulate that, as the dioxygen molecule binds to the metal center, electron density is transferred from the metal to π^* antibonding orbitals of the O_2. Thus, if in-plane substituents on the ligand are affecting the O–O distance, electron-donating groups should give longer O–O distances and electron-withdrawing groups, shorter ones. Such is not the case; the longest distance and the shorter ones come with large alkyl substituents on the ligand, whereas 3-fluoro substitution gives an intermediate or even slightly long distance. It appears from these limited data that in-plane substituents do not exert any large influence on the O_2 group.

So far as the axial bases are concerned, it may be another story. The bases involved have pK_a's (for $BH^+ + H_2O \rightleftarrows B + H_3O^+$) ranging from 0 (water) to 7 (*N*-methylimidazole).[12] Figure 5 shows the correlation between O–O distance and pK_a; it is obvious that the correlation is not a particularly good one, but the trend appears to be real. If there are minor effects due to in-plane substitution, they might act to shift the O–O distances; however, the shifts are not all in directions to improve the correlation. For example, the O–O distance in the 3-*t*-Bu-Salen–pyridine complex, 1.350 (11) Å, appears to be long; the substituents on the Salen ligand might cause this, but a similar effect would be observed for three of the other complexes. Unless the tetramethyl substituents on the ethylenediamine bridge are acting as electron-withdrawing groups (highly unlikely), it is not possible to force these five compounds into any monotonic sequence. Either, then, there is some other reason for the variation in the O–O distances or the errors we have estimated for these determinations are far too small. We prefer the first explanation and we will continue to collect more data to obtain some insight into the underlying causes of the varying O_2 bond length.

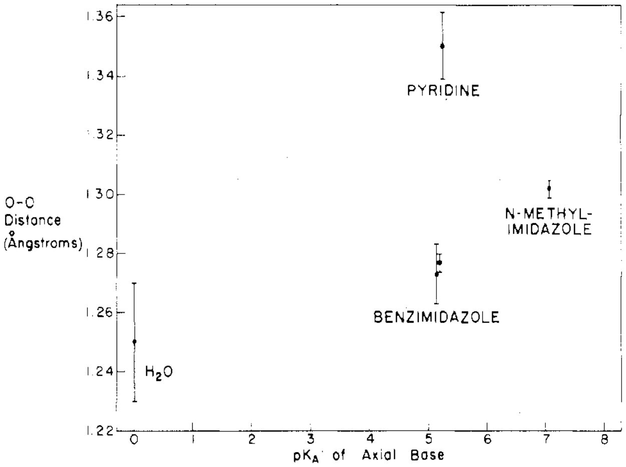

Figure 5. The O–O distance in monomeric Co–O_2 complexes vs. pK_a of the axial base.

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Registry No. Co(3-*t*-Bu-Salen), 72152-15-9; Co(3-*t*-Bu-Salen)·O_2·C_5H_5N, 72251-86-6; 3-*tert*-butylsalicylaldehyde, 24623-65-2; ethylenediamine, 107-15-3; 3-*t*-Bu-SalenH_2, 72138-54-6.

Supplementary Material Available: Listings of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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(12) Taken from Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1150.