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The Crystal Structure of the Oxygen-Inactive Form of Bis(salicylaldehyde)ethylenediiminecobalt(II)

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The crystal and molecular structure of bis(salicylaldehyde)ethylenediiminecobalt(II) [$Co(C_7H_5O)_2(C_2H_4N_2)$] has been determined using three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares methods to a conventional *R* factor of 4.9% for the 1616 nonzero reflections. The salt crystallizes in the monoclinic space group $C2/c$ with eight molecules in a unit cell of dimensions a = 26.380 (5), b = 7.105 (5), c = 14.470 (5) Å, β = 97.96 (2)° at 25°. The coordination geometry around the Co is five-coordinate (square pyramidal), with average Co–O and Co–N bond distances of 1.920 (4) and 1.897 (5) Å, respectively. In addition, the molecules exist in dimeric form, with two cobalt–oxygen bonds of length 2.259 (4) Å bonding the two units of the dimer.

Introduction

The oxygen-carrying complex bis(salicylaldehyde)ethylenediiminecobalt(II) has been the subject of an extensive series of investigations over the past 35 years.[1-10] These have demonstrated that this compound exists in several crystalline modifications some of which can absorb oxygen. Although the physical properties of these polymorphs have been well delineated, very little is known about the structures of the solids or about the manner in which the oxygen is bound in the active modifications.

The only structural work on these systems known to us at the initiation of this work was that of Hughes, *et al.*[11] Structures for several forms of bis(salicylaldehyde)ethylenediiminecobalt(II) were proposed based upon cell dimensions, packing considerations, and inspection of X-ray diffraction photographs. Initial observations in our laboratories indicated that some of these proposed structures could not be correct and consequently the mechanisms proposed for reversible oxygenation were most likely incorrect.

Preparation of Crystals and Collection and Reduction of the X-Ray Data

Bis(salicylaldehyde)ethylenediiminecobalt(II), Co(salen), was prepared in a manner similar to that reported by Bailes and Calvin.[12] An aqueous solution of cobalt acetate was added to a water–ethanol solution of the sodium salt of the preformed Schiff base. A brown gelatinous precipitate formed immediately. This precipitate was converted to the crystalline inactive form of the complex by maintaining the reaction flask at ~40° for 2 days. At the end of this period dark red-brown crystals were collected, washed with water and alcohol, and then dried *in vacuo*. The dried material was not capable of absorbing O_2. A typical crystal in the shape of a rectangular plate measuring 0.05 × 0.15 × 0.50 mm, the long axis being the b axis, was used for data collection. On the basis of zero- and first-layer Weissenberg and precession photographs, taken with Ni-filtered Cu Kα radiation (λ 1.5418 Å) at 25°, the material was assigned to the monoclinic system. Reflections of the types hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n$ were systematically absent. Space groups with this pattern of absences are C_2/c and C_c. The former was later shown to be correct. The unit cell dimensions were computed from settings on an automatic single-crystal diffractometer (see below). They are a = 26.380 (5), b = 7.105 (5), c = 14.470 (5) Å, and β = 97.96 (2)° at 25°. The density calculated on the basis of eight molecules per unit cell is 1.593 (5) g/cm^3. The observed density found by flotation is 1.60 g/cm^3.

Intensity data were collected with a Philips Automatic Intergrating Linear Reciprocal-Space Exploring Diffractometer (PAILRED) using Mo Kα radiation. The incident beam was monochromatized by means of a graphite single crystal. The diameter of the beam collimator was 0.5 mm and the receiving collimator had a 3.5° aperture. The takeoff angle was 3.0°. Data were collected using the Weissenberg geometry, the crystal being mounted along b. The peaks of the 1792 reflections with 2θ(Mo Kα) < 50° were each scanned using a range of 3.2° (ω) centered on the Bragg angle. The scanning rate was 1°/min. Background counts at each end of the scan were taken for 24 sec. The intensities of four standard reflections, measured after completing data collection for each Weissenberg layer, remained essentially constant throughout, showing only deviations from the mean due to counting statistics.

The intensities were corrected in the usual way for Lorentz and polarization effects, with the effect of the monochromator accounted for. Because the crystal was small (it was mounted along the "long" axis of the platelet and measured only 0.05 × 0.15 mm in cross section) and because the linear absorption coefficient (for Mo Kα) was only 13.1 cm^{-1} (producing an error of ~5% in F), intensity measurements were not corrected for absorption effects. Examination of the intensity data indicates that extinction did not affect the measured intensities appreciably and no correction was applied.

Solution of the Structure

A similarity between the cell parameters and space group of Co(salen) and that of Cu(salen)[13] had been noted during data collection. This prompted us to use the atomic coordinates and space group ($C2/c$) determined for the nonhydrogen atoms in the copper complex as a starting point. This choice of space group was confirmed in the course of the structure analysis. The structure based upon these coordinates was then refined by least-squares procedures using our version of the least-squares program of Busing, Martin, and Levy.[14] The atomic scattering factors used for all

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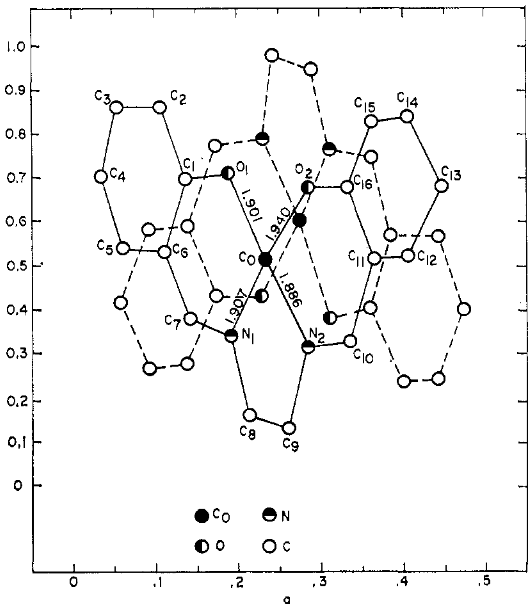

Figure 1.—Projection of a dimeric pair down [001].

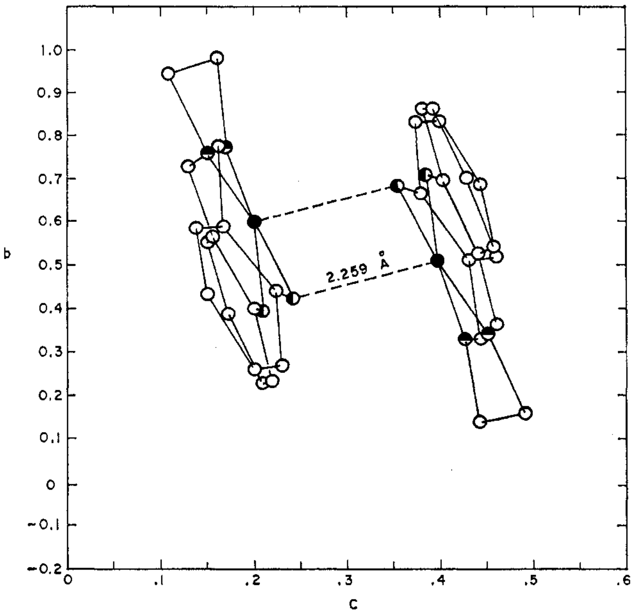

Figure 2.—Projection of a dimeric pair down [100].

atoms were those tabulated by Hanson, *et al.*[15] The scattering factor for Co was corrected for real and imaginary components of anomalous dispersion.[16] Throughout the refinement, all observed reflections were given a weight equal to unity ($w = 1$); the unobserved reflections were given zero weight. Each of the eight Weissenberg layers investigated was given an individual scale factor in the initial stages of the refinement. After four cycles of least-squares refinement in which individual isotropic temperature factors were used for the 21 nonhydrogen atoms, R_w was 9.8%. Anisotropic

$$R_w = \frac{\sum w|F_o - F_c|}{\sum w|F_o|}$$

temperature factors were then introduced. Because the calculated values of the scale factors for the various layers appeared to fall into two distinct groups, the eight scale factors were reduced to two. The first was for the zero and first layers, *i.e.*, $k = 0, 1$, while the second was for the layers with $k = 2, 3, 4, 5, 6, 7$. After three additional cycles of least squares R was reduced to 6.3%. At this point the estimated positions, based on geometry and calculated bond length, of the 14 hydrogen atoms were included in the calculations and after four additional cycles the discrepancy coefficient was 4.9%. A final difference Fourier map shows no peak higher than 0.4 $e^- \text{Å}^{-3}$.

Values of $10|F_o|$ and $10|F_c|$ (in electrons) for all 1616 reflections have been deposited with the ASIS National Auxiliary Publications Service.[17]

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR

$Co(C_7H_5O)_2(C_2H_4N_2)$[a]

Atom	x	y	z
Co	0.23422 (2)	0.20308 (1)	0.09749 (4)
O_1	0.1865 (1)	0.4051 (5)	0.0881 (3)
O_2	0.2832 (18)	0.3789 (6)	0.0549 (3)
N_1	0.1907 (2)	0.0367 (8)	0.1536 (4)
N_2	0.2842 (2)	0.0146 (8)	0.1273 (4)
C_1	0.1386 (2)	0.3966 (10)	0.1022 (4)
C_2	0.1077 (3)	0.5593 (11)	0.0799 (5)
C_3	0.0561 (3)	0.5604 (13)	0.0922 (5)
C_4	0.0338 (3)	0.4002 (14)	0.1294 (6)
C_5	0.0631 (3)	0.2419 (13)	0.1525 (6)
C_6	0.1157 (3)	0.2348 (11)	0.1395 (5)
C_7	0.1434 (2)	0.0651 (10)	0.1658 (5)
C_8	0.2164 (3)	−0.1367 (10)	0.1936 (5)
C_9	0.2617 (3)	−0.1720 (10)	0.1408 (5)
C_{10}	0.3333 (3)	0.0316 (10)	0.1426 (4)
C_{11}	0.3586 (2)	0.2102 (11)	0.1279 (4)
C_{12}	0.4127 (3)	0.2167 (13)	0.1561 (5)
C_{13}	0.4399 (3)	0.3783 (14)	0.1413 (6)
C_{14}	0.4144 (3)	0.5364 (13)	0.0982 (5)
C_{15}	0.3614 (3)	0.5326 (11)	0.0707 (5)
C_{16}	0.3330 (2)	0.3680 (10)	0.0849 (4)
H_1	0.123 (2)	0.678 (8)	0.046 (3)
H_2	0.032 (3)	0.686 (12)	0.072 (5)
H_3	−0.003 (2)	0.403 (10)	0.151 (4)
H_4	0.050 (2)	0.121 (11)	0.190 (4)
H_5	0.433 (3)	0.106 (13)	0.197 (5)
H_6	0.485 (3)	0.392 (17)	0.178 (6)

Atom	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Co	64 (1)	88 (2)	183 (5)	2 (4)	26 (2)	52 (7)
O_1	61 (7)	104 (10)	371 (26)	11 (21)	46 (10)	59 (40)
O_2	57 (7)	115 (9)	208 (21)	−9 (21)	15 (9)	75 (36)
N_1	87 (10)	98 (12)	231 (28)	−50 (27)	18 (13)	65 (45)
N_2	92 (10)	91 (11)	223 (28)	25 (27)	29 (13)	64 (44)
C_1	66 (11)	165 (16)	146 (32)	−4 (34)	25 (15)	−94 (57)
C_2	103 (13)	150 (17)	39 (43)	81 (38)	4 (19)	−111 (68)
C_3	84 (12)	228 (21)	447 (44)	52 (42)	44 (18)	−222 (78)
C_4	87 (12)	234 (23)	641 (55)	70 (45)	57 (21)	−134 (91)
C_5	80 (12)	211 (22)	533 (49)	−48 (41)	76 (19)	−150 (80)
C_6	75 (11)	161 (17)	301 (38)	−59 (35)	39 (16)	−103 (62)
C_7	75 (11)	139 (15)	276 (37)	−59 (34)	47 (16)	−118 (61)
C_8	118 (12)	88 (14)	426 (41)	1 (34)	71 (18)	222 (62)
C_9	115 (12)	102 (15)	335 (40)	3 (34)	48 (18)	88 (60)
C_{10}	99 (12)	121 (15)	229 (35)	71 (35)	21 (16)	13 (58)
C_{11}	68 (11)	145 (15)	263 (35)	70 (35)	24 (15)	−91 (60)
C_{12}	88 (12)	235 (20)	388 (42)	34 (44)	47 (18)	−204 (77)
C_{13}	86 (12)	265 (23)	472 (47)	−67 (45)	34 (19)	−294 (85)
C_{14}	109 (14)	204 (21)	452 (46)	−121 (44)	47 (20)	−247 (79)
C_{15}	79 (11)	170 (18)	282 (37)	−112 (36)	51 (16)	−146 (65)
C_{16}	67 (11)	124 (14)	217 (33)	−6 (32)	39 (14)	−130 (55)

[a] The estimated standard deviations from the least-squares refinements are given in parentheses in units of the last significant figure in the parameter value itself. The expression for the temperature factor is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

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(16) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.20.

(17) For this table, order NAPS Document No. NAPS-00830 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y., 10022, remitting $1.00 for microfiche or $3.00 for photocopies. Make checks or money orders payable to CCMIC-NAPS.

Description of the Structure

The projection of a portion of the unit cell viewed along [001] is shown in Figure 1. Figure 2 shows the projection along [100]. Interatomic distances and angles computed from the final atomic parameters of Table I are given in Tables II and III. Root-mean-square (rms) amplitudes of vibration appear in Table IV. Standard deviations of all bond lengths and bond angles reported have been computed by the function and error program (ORFFE) of Busing, Martin, and Levy.[14]

TABLE II
BOND DISTANCES (Å) AND BOND ANGLES (DEG) FOR $Co(C_7H_5O)_2(C_2H_4N_2)$

Bond	Distance	Atoms	Angle
Co–O_1	1.901 (4)	O_1–Co–O_2	88.0 (2)
Co–O_2	1.940 (4)	O_1–Co–N_2	92.5 (2)
Co–N_1	1.907 (5)	N_2–Co–N_1	84.6 (2)
Co–N_2	1.886 (5)	O_1–Co–N_1	93.9 (2)
O_1–C_1	1.311 (7)	O_1–C_1–C_2	117.5 (6)
O_2–C_{16}	1.325 (7)	O_2–C_{16}–C_{15}	116.2 (6)
N_1–C_7	1.301 (8)	O_1–C_1–C_6	124.1 (6)
N_2–C_{10}	1.289 (8)	O_2–C_{16}–C_{11}	124.5 (6)
N_1–C_8	1.484 (8)	Co–O_1–C_1	126.6 (4)
N_2–C_9	1.477 (8)	Co–O_2–C_{16}	123.1 (4)
C_1–C_2	1.426 (10)	C_1–N_1–C_7	127.4 (5)
C_2–C_3	1.399 (10)	Co–N_2–C_{10}	128.5 (5)
C_3–C_4	1.421 (12)	Co–N_1–C_8	114.2 (4)
C_4–C_5	1.379 (11)	Co–N_2–C_9	112.8 (4)
C_5–C_6	1.426 (9)	N_1–C_7–C_6	123.9 (6)
C_6–C_1	1.438 (10)	N_2–C_{10}–C_{11}	121.6 (6)
C_6–C_7	1.432 (10)	C_7–N_1–C_8	118.3 (5)
C_8–C_9	1.525 (10)	C_9–N_2–C_{10}	118.1 (5)
C_{10}–C_{11}	1.462 (10)	N_1–C_8–C_9	106.9 (5)
C_{11}–C_{12}	1.430 (9)	N_2–C_9–C_8	105.9 (5)
C_{12}–C_{13}	1.390 (12)	C_1–C_2–C_3	120.8 (7)
C_{13}–C_{14}	1.410 (12)	C_2–C_3–C_4	120.3 (7)
C_{14}–C_{15}	1.399 (10)	C_3–C_4–C_5	119.9 (6)
C_{15}–C_{16}	1.419 (9)	C_4–C_5–C_6	121.3 (7)
C_{16}–C_{11}	1.410 (9)	C_5–C_6–C_1	119.2 (6)
		C_6–C_1–C_2	118.4 (6)
		C_5–C_6–C_7	117.6 (6)
		C_1–C_6–C_7	123.2 (6)
		C_{10}–C_{11}–C_{12}	116.3 (6)
		C_{10}–C_{11}–C_{16}	123.6 (5)
		C_{11}–C_{12}–C_{13}	119.9 (7)
		C_{12}–C_{13}–C_{14}	120.2 (6)
		C_{13}–C_{14}–C_{15}	120.5 (7)
		C_{14}–C_{15}–C_{16}	120.1 (7)
		C_{15}–C_{16}–C_{11}	119.3 (6)

The crystal structure of Co(salen) consists of discrete five-coordinate dimers. The central cobalt atom of each molecule is bound by intramolecular bonds to two oxygens at 1.901 (4) and 1.940 (4) Å and two nitrogens at 1.886 (5) and 1.907 (5) Å, these four ligand atoms constituting a fairly planar arrangement. The cobalt atom lies ~0.15 Å above the mean basal plane. In addition, the cobalt atom is bound at 2.259 (4) Å to oxygen 2 of the nearest neighboring Co(salen) molecule. This then constitutes a dimer with each cobalt atom being five-coordinate and having distorted square-pyramidal geometry.

TABLE III
SOME ADDITIONAL INTERATOMIC DISTANCES (Å) AND INTERATOMIC ANGLES (DEG)

Atoms	Distance	Atoms	Distance	Atoms	Distance
O_1–O_2	2.668 (5)	Co–C_8'	3.323 (8)	O_1–O_2'	3.056 (6)
N_1–N_2	2.552 (7)	Co–C_9'	3.877 (7)	O_2–O_2'	2.826 (9)
O_1–N_1	2.782 (7)	Co–C_8	2.857 (7)	N_1–O_2'	3.248 (7)
O_2–N_2	2.764 (7)	Co–C_9	2.811 (7)	N_2–O_2'	3.071 (9)
Co–O_2	2.259 (4)	Co–O_2''	2.259 (4)	O_1–N_2	3.774 (7)
Co–O_2–	2.259 (4)	Co''–O_2	2.259 (4)	O_2–N_1	3.840 (7)

Atoms	Angle	Atoms	Angle
O_1–O_2–N_2	88.0 (2)	O_2–N_2–N_1	92.4 (2)
O_2–O_1–N_1	89.6 (2)	O_1–N_1–N_2	90.0 (4)

TABLE IV
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Co	0.129	0.149	0.156
O_1	0.139	0.161	0.200
O_2	0.139	0.142	0.177
N_1	0.141	0.161	0.184
N_2	0.141	0.159	0.181
C_1	0.116	0.152	0.208
C_2	0.171	0.188	0.227
C_3	0.161	0.203	0.257
C_4	0.164	0.240	0.267
C_5	0.154	0.217	0.253
C_6	0.152	0.171	0.213
C_7	0.145	0.161	0.205
C_8	0.130	0.191	0.229
C_9	0.155	0.184	0.205
C_{10}	0.154	0.161	0.199
C_{11}	0.139	0.165	0.204
C_{12}	0.163	0.196	0.255
C_{13}	0.170	0.203	0.277
C_{14}	0.176	0.199	0.256
C_{15}	0.144	0.165	0.227
C_{16}	0.127	0.157	0.189

The observed crystal and molecular structure differs from the one described by Martell and Calvin.[11] They suggested that this substance was inactive to oxygen uptake because of the absence of holes running through the crystal. The presence of an open structure was considered necessary for oxygen migration. Indeed, the correct crystal structure indicates the absence of any large voids but the Co(salen) monomer resembles the structure postulated by the Calvin group[11] for Co(salen)(active) more than the one they postulated for Co(salen)(inactive).

Several possibilities are suggested for the mode of oxygen coordination in the oxygenated complexes. For the 3:1 species it is possible that there is a 1:1 mixture of monomer and dimer. Lateral coordination of the oxygen could then occur to the monomeric unit while for electronic and steric reasons coordination sites upon the dimer would be unavailable. For the 2:1 species an oxygen-bridged dimer is the most likely possibility. Further structural work, supported in part by the NSF, is under way in an effort to clarify these points.[18]

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(18) Dr. Lucio Randaccio and his coworkers have independently solved the structure of Co(salen)(inactive) and their results are in good agreement with ours (private communication).