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The Structure of Racemic μ-Amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] Tetranitrate Hydrate

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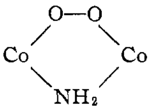
Racemic μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate hydrate, DL-[(en)$_2$Co-μ-(NH$_2$,O$_2$)-Co(en)$_2$]-(NO$_3$)$_4$·H$_2$O, forms monoclinic crystals with lattice constants a = 8.781 (1), b = 23.968 (2), c = 12.498 (2) Å, and β = 95.80 (1)°. There are four formula units per cell; the space group is $P2_1/n$. The observed and calculated densities are 1.72 (1) and 1.706 g/cm^3. The structure has been solved by Patterson and Fourier methods and refined by least-squares calculations based on visually collected data. The final R index for 2312 reflections is 0.075. The two cobalt atoms are octahedrally coordinated; the central five-membered ring of the cation is slightly puckered. The O–O distance of 1.35 Å is typical for a

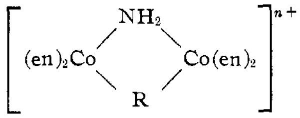


superoxo group. One of the ethylenediamine rings and one of the nitrate groups show disorder.

Introduction

One of the more remarkable properties of cobalt is its ability to form O$_2$-bridged dinuclear ammine complexes. Much of our knowledge in this field has been gained from X-ray crystallographic investigations during the past few years.[2-6] The complicated reduction–oxidation and interconversion reactions of these complexes were also recently clarified.[7] We now know that the cations of the green, paramagnetic salts are best described as containing a superoxo bridge, O$_2^-$, with the unpaired electron distributed equally between the two bridge oxygen atoms, and that the cations of the brown diamagnetic salts are best described as containing a peroxo bridge, O$_2^{2-}$. In both species the cobalt and oxygen atoms are connected in a nonlinear array: Co–O–O–Co; this array is approximately planar in the paramagnetic species but nonplanar in the diamagnetic species.

We have solved the structures of the three closely related cations



where R is a superoxo O$_2^-$ (n = 4), a hydroperoxo HO$_2^-$ (n = 4), and a peroxo group O$_2^{2-}$ (n = 3). These ethylenediamine complexes are of additional interest because of the many isomers that can be expected to exist if one takes into account the possible configurations about the cobalt atoms and the possible conformations of the ethylenediamine chelate groups.

The present paper is concerned with the superoxo-bridged complex μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate hydrate, DL-[(en)$_2$Co-μ-(NH$_2$,O$_2$)-Co(en)$_2$](NO$_3$)$_4$·H$_2$O. A preliminary report has been published.[8]

Experimental Section

Racemic μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate hydrate, DL-[(en)$_2$Co-μ-(NH$_2$,O$_2$)-Co(en)$_2$]-(NO$_3$)$_4$·H$_2$O, was prepared by the method of Werner.[9] Dark green, needle-shaped crystals were grown by slow addition of nitric acid to an aqueous solution of the crude product. The needle axis is parallel to the a axis. Preliminary oscillation and Weissenberg photographs taken about [100] and [010] showed the crystals to be monoclinic. The systematic absences $0k0$ for k odd and $h0l$ for $h + l$ odd lead to the space group $P2_1/n$. (The equivalent positions in $P2_1/n$, an alternative setting of $P2_1/c$, are $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$.) The unit-cell dimensions were obtained from a least-squares treatment of the measurements of 25 $0kl$ and $h0l$ reflections on Weissenberg photographs made in a Straumanis-type camera using Cu Kα radiation. The resulting values, their standard deviations, and related data are a = 8.781 (1), b = 23.968 (2), c = 12.498 (2) Å, β = 95.80 (1)°, (λ(Cu Kα_1) 1.54051 Å, λ(Cu Kα_2) 1.54433 Å), V = 2616.9 Å^3 at 26 ± 2°; $F(000)$ = 1396. The density measured by flotation in a carbon tetrachloride–1,2-dibromoethane mixture is 1.72 ± 0.01 g/cm^3. It agrees well with that calculated for the monohydrate salt and Z = 4, d_x = 1.706 g/cm^3, indicating clearly that the actual compound is not anhydrous as was assumed by Werner[9] (and for which d_x would be 1.661 g/cm^3).

Intensity data were collected visually from multiple-film Weissenberg photographs taken with Fe Kα radiation (λ 1.9373 Å; MnO$_2$ filter). The layers 0–5 around a and 0–6 around c were recorded. For both sets of films prismatic crystal fragments were used with almost square cross sections and diameters of about 0.14 mm. The intensity data were processed by a subprogram of the CRYRM system.[10] This processing included assignment of an estimated standard deviation to each individual observation, correction for Lorentz and polarization factors, evaluating of film and pack factors, and the scaling together of the different observations to give a single value of F_o^2 and $\sigma(F_o^2)$ for each reflection. No absorption correction was applied (μ = 45.5 cm^{-1}); we estimate that the maximum error in the relative value of F_o^2 would not exceed 5% for any reflection. A total of 2812 independent reflections were obtained, of which 466 were too weak to be measured.

Determination and Refinement of the Structure

The coordinates of the cobalt atoms were determined from a three-dimensional Patterson map. A three-dimensional electron

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TABLE I

POSITIONAL AND THERMAL PARAMETERS OF THE HEAVY ATOMS[a]

Atom	x	y	z	β_{11} or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	30,033 (13)	9,401 (4)	26,619 (10)	1,204 (21)	123 (2)	595 (13)	26 (10)	230 (26)	48 (8)
Co(1′)	26,010 (14)	19,155 (4)	8,442 (10)	1,195 (21)	147 (2)	596 (13)	−5 (10)	155 (26)	104 (8)
O(1)	3,119 (6)	1,700 (2)	3,049 (5)	207 (11)	12 (1)	78 (5)	2 (5)	9 (12)	4 (4)
O(1′)	2,641 (6)	2,089 (2)	2,305 (5)	179 (10)	16 (1)	90 (6)	18 (5)	66 (12)	21 (4)
O(2)	6,724 (6)	2,129 (2)	3,069 (4)	175 (10)	22 (1)	70 (6)	32 (5)	45 (12)	−20 (4)
O(3)	7,838 (6)	1,568 (2)	2,037 (4)	134 (9)	19 (1)	73 (5)	−6 (5)	59 (11)	−28 (4)
O(4)	9,194 (7)	2,076 (2)	3,176 (6)	183 (12)	34 (2)	133 (8)	−18 (7)	−44 (14)	−47 (5)
O(6)	8,218 (7)	683 (2)	6,017 (6)	216 (14)	31 (2)	128 (8)	−31 (7)	−56 (16)	49 (5)
O(7)	6,993 (7)	1,134 (2)	4,718 (5)	283 (14)	14 (1)	88 (6)	−13 (6)	−36 (14)	12 (4)
O(8)	723 (9)	3,332 (3)	2,318 (7)	326 (19)	40 (2)	179 (11)	18 (10)	71 (22)	−51 (7)
O(9)	−1,552 (9)	3,635 (3)	2,151 (7)	283 (17)	49 (2)	185 (10)	102 (9)	148 (20)	−8 (7)
O(10)	−773 (9)	3,097 (3)	943 (7)	283 (17)	43 (2)	141 (9)	43 (9)	32 (19)	−56 (7)
O(11)	7,594 (8)	1 (3)	94 (6)	248 (15)	57 (2)	112 (8)	−92 (9)	56 (16)	−67 (6)
O(12)	8,953 (9)	738 (3)	411 (6)	382 (19)	23 (2)	167 (10)	−26 (8)	139 (20)	−25 (6)
O(13)	9,386 (8)	20 (3)	1,387 (6)	292 (17)	38 (2)	136 (9)	22 (9)	−44 (18)	21 (6)
O(14)	5,839 (9)	1,191 (3)	−538 (6)	279 (15)	35 (2)	140 (8)	69 (7)	−24 (16)	−55 (6)
N(1)	2,695 (7)	1,124 (2)	1,170 (5)	145 (11)	13 (1)	51 (6)	4 (5)	−15 (13)	3 (4)
N(2)	2,967 (7)	139 (2)	2,330 (5)	166 (12)	14 (1)	66 (6)	−14 (6)	−1 (14)	0 (4)
N(2′)	2,478 (7)	1,776 (2)	−697 (5)	116 (11)	20 (1)	70 (7)	−17 (6)	−87 (14)	23 (4)
N(3)	3,161 (8)	824 (2)	4,242 (5)	183 (13)	16 (1)	69 (7)	3 (6)	59 (15)	3 (4)
N(3′)	2,606 (7)	2,729 (2)	632 (5)	134 (12)	17 (1)	80 (7)	7 (6)	67 (14)	13 (4)
N(4)	811 (7)	951 (2)	2,782 (6)	110 (11)	22 (1)	95 (8)	14 (6)	45 (15)	16 (5)
N(4′)	4,799 (7)	1,979 (2)	943 (6)	120 (11)	17 (1)	69 (6)	−6 (6)	−22 (13)	11 (4)
N(5)	5,217 (7)	865 (2)	2,659 (6)	141 (12)	22 (1)	74 (7)	−7 (6)	17 (14)	13 (5)
N(5′)	337 (8)	1,920 (2)	628 (7)	156 (13)	18 (1)	114 (9)	3 (6)	49 (16)	27 (5)
N(6)	7,924 (7)	1,924 (3)	2,761 (6)	121 (12)	19 (1)	88 (8)	−5 (6)	9 (15)	11 (5)
N(7)	7,191 (8)	728 (3)	5,299 (7)	140 (13)	23 (2)	109 (9)	−23 (7)	−23 (16)	20 (6)
N(8)	−585 (10)	3,347 (4)	1,807 (8)	185 (16)	35 (2)	138 (12	21 (10)	53 (23)	5 (8)
N(9)	8,637 (9)	249 (3)	622 (7)	207 (16)	27 (2)	84 (9)	3 (8)	79 (19)	−20 (6)
C(2′)	939 (11)	1,589 (3)	−1,085 (7)	220 (18)	24 (2)	65 (9)	−7 (9)	−62 (21)	25 (6)
C(3)	1,668 (12)	930 (4)	4,643 (8)	209 (19)	32 (2)	93 (11)	26 (10)	106 (22)	2 (7)
C(3′)	4,142 (11)	2,936 (3)	992 (8)	196 (18)	16 (2)	126 (11)	4 (8)	8 (22)	15 (7)
C(4)	476 (10)	731 (4)	3,824 (8)	109 (15)	39 (2)	113 (12)	3 (9)	65 (21)	47 (8)
C(4′)	5,293 (9)	2,537 (3)	604 (8)	128 (14)	23 (2)	108 (10)	−13 (8)	2 (18)	35 (7)
C(5′)	−168 (10)	1,932 (3)	−551 (8)	130 (15)	26 (2)	96 (10)	−8 (8)	−77 (20)	39 (7)
O(5)	6,095 (14)	415 (5)	5,401 (11)	6.1 (3)					
O(5)′	6,564 (12)	263 (4)	4,820 (9)	4.5 (2)					
C(2)	4,621 (22)	−36 (8)	2,022 (15)	5.2 (4)					
C(2)′	4,502 (19)	−122 (6)	2,572 (13)	3.4 (3)					
C(5)	5,783 (21)	275 (7)	2,701 (15)	5.2 (4)					
C(5)′	5,543 (21)	312 (7)	2,082 (15)	4.7 (4)					

[a] The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Isotropic temperature factors are in Å^2. x, y, z, and β_{ij} values for the cobalt atoms have been multiplied by 10^5; for other atoms, by 10^4.

density synthesis based on the cobalt atoms showed almost all remaining nonhydrogen atoms, including the water oxygen atom; a few atoms were located on stereochemical grounds. Four cycles of full-matrix least-squares refinement of the coordinates and the individual isotropic temperature factors resulted in an R index of 0.137 ($R = \Sigma|F_o - |F_c||/\Sigma F_o$). At this stage of the structure determination relatively large temperature factors for some of the atoms suggested disorder in the regions of one of the ethylenediamine groups (N(2)–C(2)–C(5)–N(5)) and of the N(7) nitrate group.

The positions of the hydrogen atoms of the ethylenediamine groups (except those on the carbon atoms of the disordered en group) were then calculated, assuming sp^3 bond configurations and C–H and N–H bond distances of 0.9 Å. The water hydrogen atoms were positioned by considering the potential hydrogen bonding. The hydrogen atoms were included in the subsequent structure factor calculations with B values of the heavy atoms to which they were bonded. No attempts were made to refine their parameters.

In subsequent least-squares cycles the parameters—a scale factor, a secondary extinction factor,[11] positional and anisotropic (or isotropic) temperature parameters—were apportioned among six matrices of nearly equal size. After two cycles of refinement, examination of the anisotropic temperature parameters for the atoms of the disordered ethylenediamine group and an inspection of a ΔF map in this region of the structure indicated that the disorder was caused by a superposition of two conformers of the chelate ring $\overline{\text{CoNCCN}}$. Thus, the ring appeared almost planar, but the C–C bond distance was unrealistically short (1.30 Å), and the carbon atoms had highly anisotropic temperature factors, with rms amplitudes of about 0.50 Å in directions nearly perpendicular to the N–Co–N plane (Figure 2). Similarly, the disordered oxygen atom O(5) of the nitrate group N(7) had an unreasonably large rms amplitude of about 0.7 Å in a direction almost perpendicular to the plane of the ion. Each of the atoms C(2), C(5), and O(5) was then split into two half-populated atoms, the coordinates of which were obtained on stereochemical grounds: 50% of the disordered en ring was given a δ conformation and the other 50% was given a λ conformation, and the split oxygen atoms were positioned above and below the plane defined by the remaining three atoms of the nitrate group.

The refinement was then continued—with isotropic temperature factors for the split atoms and with anisotropic temperature factors for the other nonhydrogen atoms—until Δ/σ was less than 0.3 for all 341 parameters. The final R index for 2312 reflections of nonzero weight was 0.075. The goodness of fit $[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, where $m = 2312$ and $s = 341$, was 2.0. The parameter g of the secondary extinction correction had a final value of $(5.9 \pm 0.5) \times 10^{-6}$. As usual for visual data, it is possible that this "extinction" parameter corrects in part for systematic errors in estimated intensities.

A final three-dimensional ΔF map had no positive peak greater than 0.8 e/Å^3 and no negative peak greater than −0.4 e/Å^3. Observed and calculated structure factors are available as indicated in ref 12. The final atomic parameters are listed in

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[11] A. Larson, *Acta Crystallogr.*, **23**, 664 (1967).

[12] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE II

POSITIONAL PARAMETERS CHOSEN FOR THE HYDROGEN ATOMS[a]

	Atom	*x*	*y*	*z*
N(1)	H(2)	181	96	89
	H(3)	348	97	84
N(2)	H(4)	248	−4	284
	H(5)	245	9	169
N(3)	H(6)	386	107	456
	H(7)	347	47	440
N(4)	H(8)	33	74	226
	H(9)	46	130	272
N(5)	H(10)	567	94	332
	H(11)	555	111	218
N(2′)	H(12)	316	151	−83
	H(13)	269	209	−105
N(3′)	H(14)	192	289	103
	H(15)	237	281	−7
N(4′)	H(16)	519	191	162
	H(17)	516	172	50
N(5′)	H(18)	−3	161	92
	H(19)	−2	222	95
C(3)	H(22)	155	129	476
	H(23)	161	73	526
C(4)	H(24)	−45	86	398
	H(25)	46	36	380
C(2′)	H(28)	84	122	−94
	H(29)	79	164	−181
C(3′)	H(30)	427	297	171
	H(31)	427	328	70
C(4′)	H(32)	625	261	92
	H(33)	529	255	−11
C(5′)	H(34)	−16	229	−78
	H(35)	−112	179	−67
O(14)	H(36)	584	136	−126
	H(37)	687	105	−24

[a] All values have been multiplied by 10^3. The hydrogen atoms bonded to the disordered carbon atoms C(2) and C(5) were not included.

Tables I and II. The esd's listed in Table I are *pro forma* values, calculated in the usual way from the diagonal elements of the inverses of the normal equation matrices; since the refinement was blocked matrix, these values are almost certainly too small. In the discussion that follows, we have somewhat arbitrarily increased the esd's in the bond distances and angles by 50% over the values that were calculated from the *pro forma* esd's of the atomic coordinates.

All calculations were carried out on an IBM 7094 computer using subprograms operating under the CRYRM[10] system. Atomic-form factors for the heavier atoms were taken from ref 13. The scattering curve for cobalt was corrected for the real part of anomalous dispersion by subtracting 1.74 electrons.[14] The form factor for hydrogen was that calculated by Stewart, Davidson, and Simpson.[15] The quantity minimized in the least-squares calculations was $\Sigma w(F_o^2 - F^*{}_c^2)^2$ with weights, w, taken equal to $1/\sigma^2\,(F_o^2)$ and $F^*{}_c^2$ as defined by Larson's eq 3.[11]

Unobserved reflections were included in the least-squares calculations only if F_c exceeded the threshold value of F_o.

Discussion

An illustration of one of the cation antipodes that are present in the crystal is shown in Figure 1. Bond lengths and angles are listed in Table III.

The O–O distance of the O_2 bridge (1.353 ± 0.011 Å) seems to be slightly larger than that in other μ-superoxo complexes (1.312 ± 0.014,[2] 1.317 ± 0.012,[4] 1.320 ± 0.005[5] Å). This enlargement, if real, might be related to the distortion from planarity of the five-membered central ring; the two oxygen atoms lie 0.06 and 0.22 Å from, and on opposite sides of, the Co–N–Co plane, and the torsion angle Co(1)–O(1)–O(1′)–Co(1′) is 23.4°. Nevertheless, the near planarity of the central ring (as compared with the considerable puckering in the corresponding μ-amido-μ-peroxo cation[6]) and the short O–O bond distance (compared with the O–O distance of 1.46 Å in the μ-amido-μ-peroxo cation[6]) indicate that the present compound is a μ-superoxo complex with a Co^{3+}–O_2^-–Co^{3+} arrangement and not, as formulated by Werner,[9] a Co^{3+}–O_2^{2-}–Co^{4+} arrangement. The equivalence of the two cobalt atoms in cations of the present type has been demonstrated from epr studies,[16] and ^{17}O epr splitting as measured in the related μ-amido-μ-superoxo-octaammine cation indicated that the unpaired electron is concentrated in the region of the O_2 group.[17]

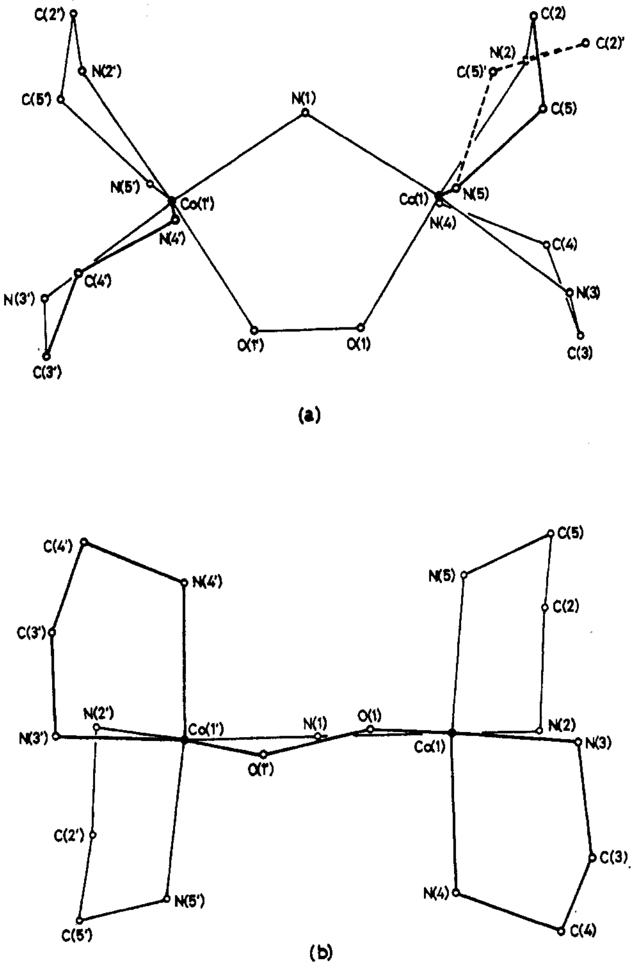

Figure 1.—Two projections of the ΔΔ isomer of the $[(en)_2Co\text{-}\mu\text{-}(NH_2,O_2)\text{-}Co(en)_2]^{4+}$ cation: (a) perpendicular to the Co(1), N(1), Co(1′) plane; (b) parallel to the plane named in (a) and perpendicular to the Co(1)–Co(1′) axis. For clarity in (b) only the λ conformer of the disordered ethylenediamine group is shown.

With the exception of the O–O distance, the dimensions of the central five-membered ring compare well with those of the corresponding μ-amido-μ-superoxo-octaammine complex[5] (given in parentheses). The average values are d(Co–N) = 1.924 (1.922) Å, d(Co–O) = 1.877 (1.867) Å, ∠(N–Co–O) = 91.2° (91.5°), ∠(Co–N–Co) = 115.4° (114.9°), and ∠(Co–O–O) = 119.2° (120.8°). The eight Co–N(en) bonds range from 1.928 to 1.984 Å in length, with a mean

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(13) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

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

(16) I. Bernal, E. A. V. Ebsworth, and J. A. Weil, *Proc. Chem. Soc., London*, 57 (1959).

(17) J. A. Weil and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 3341 (1967).

TABLE III

BOND DISTANCES AND BOND ANGLES[a]

Atoms	Distance, Å	Atoms	Distance, Å
Co(1)–Co(1′)	3.276 (3)	O(1)–O(1′)	1.353 (11)
–O(1)	1.885 (8)	Co(1′)–O(1′)	1.870 (9)
–N(1)	1.908 (9)	–N(1)	1.940 (8)
–N(2)	1.963 (8)	–N(2′)	1.947 (11)
–N(3)	1.984 (12)	–N(3′)	1.967 (9)
–N(4)	1.946 (9)	–N(4′)	1.928 (9)
–N(5)	1.952 (11)	–N(5′)	1.979 (11)
N(2)–C(2)	1.596 (32)	N(2′)–C(2′)	1.459 (16)
–C(2)′	1.489 (26)		
N(3)–C(3)	1.472 (19)	N(3′)–C(3′)	1.465 (17)
N(4)–C(4)	1.462 (19)	N(4′)–C(4′)	1.480 (15)
N(5)–C(5)	1.498 (29)	N(5′)–C(5′)	1.496 (19)
–C(5)′	1.550 (29)		
C(2)–C(5)	1.464 (40)	C(2′)–C(5′)	1.482 (18)
C(2)′–C(5)′	1.551 (36)	C(3′)–C(4′)	1.507 (18)
C(3)–C(4)	1.466 (20)		
N(6)–O(2)	1.258 (14)	N(8)–O(8)	1.257 (20)
–O(3)	1.241 (14)	–O(9)	1.206 (18)
–O(4)	1.236 (13)	–O(10)	1.232 (19)
N(7)–O(5)	1.237 (21)	N(9)–O(11)	1.227 (17)
–O(5)′	1.354 (20)	–O(12)	1.240 (15)
–O(6)	1.211 (15)	–O(13)	1.232 (16)
–O(7)	1.217 (14)		

Atoms	Angle, deg	Atoms	Angle, deg
Co(1)–N(1)–Co(1′)	115.5 (6)		
Co(1)–O(1)–O(1′)	118.9 (7)	Co(1′)–O(1′)–O(1)	119.5 (6)
O(1)–Co(1)–N(1)	91.5 (3)	O(1′)–Co(1′)–N(1)	90.9 (3)
–N(2)	176.7 (3)	–N(2′)	176.4 (4)
–N(3)	83.3 (4)	–N(3′)	84.9 (3)
–N(4)	89.7 (3)	–N(4′)	90.0 (4)
–N(5)	93.6 (3)	–N(5′)	92.9 (4)
N(1)–Co(1)–N(2)	91.2 (4)	N(1)–Co(1′)–N(2′)	92.1 (4)
–N(3)	173.2 (5)	–N(3′)	175.2 (4)
–N(4)	91.6 (4)	–N(4′)	92.5 (3)
–N(5)	93.6 (4)	–N(5′)	93.1 (3)
N(2)–Co(1)–N(3)	94.1 (5)	N(2′)–Co(1′)–N(3′)	92.1 (4)
–N(4)	92.0 (4)	–N(4′)	91.8 (4)
–N(5)	84.5 (4)	–N(5′)	84.9 (4)
N(3)–Co(1)–N(4)	84.0 (5)	N(3′)–Co(1′)–N(4′)	85.1 (3)
–N(5)	91.1 (5)	–N(5′)	89.5 (3)
N(4)–Co(1)–N(5)	173.7 (4)	N(4′)–Co(1′)–N(5′)	173.6 (4)
Co(1)–N(2)–C(2)	108.3 (12)	Co(1′)–N(2′)–C(2′)	109.7 (7)
–C(2)′	111.9 (11)		
Co(1)–N(3)–C(3)	109.9 (9)	Co(1′)–N(3′)–C(3′)	108.0 (7)
Co(1)–N(4)–C(4)	110.7 (9)	Co(1′)–N(4′)–C(4′)	111.9 (8)
Co(1)–N(5)–C(5)	114.5 (12)	Co(1′)–N(5′)–C(5′)	109.2 (9)
–C(5)′	108.1 (12)		
N(2)–C(2)–C(5)	108.9 (22)	N(2′)–C(2′)–C(5′)	108.0 (10)
N(2)–C(2)′–C(5)′	101.3 (18)		
N(3)–C(3)–C(4)	107.7 (13)	N(3′)–C(3′)–C(4′)	108.2 (10)
N(4)–C(4)–C(3)	108.1 (12)	N(4′)–C(4′)–C(3′)	104.9 (11)
N(5)–C(5)–C(2)	104.6 (22)	N(5′)–C(5′)–C(2′)	106.9 (10)
N(5)–C(5)′–C(2)′	104.1 (21)		
O(2)–N(6)–O(3)	120.0 (11)	O(8)–N(8)–O(9)	118.4 (15)
–O(4)	120.4 (10)	–O(10)	117.8 (14)
O(3)–N(6)–O(4)	119.6 (11)	O(9)–N(8)–O(10)	123.6 (15)
O(5)–N(7)–O(6)	113.5 (14)	O(11)–N(9)–O(12)	120.9 (13)
–O(7)	118.8 (13)	–O(13)	120.9 (12)
O(5)′–N(7)–O(6)	119.6 (12)	O(12)–N(9)–O(13)	118.2 (12)
–O(7)	111.5 (13)		
O(6)–N(7)–O(7)	124.3 (12)		

[a] These values contain no corrections for thermal motion.

value of 1.958 Å. While the rms deviation of the individual values from this mean value is 0.017 Å and thus is somewhat larger than the average internal esd of about 0.010 Å, we do not feel that there are any real differences between the individual values; on this basis, the esd in the mean value itself is about 0.004 Å. Mean values and standard deviations for other distances of the Co–en chelate rings (the disordered en ring not included) are d(N–C) = 1.472 (0.007) Å and d(C–C) = 1.485 (0.011) Å. These values are in good agreement with those found in other ethylenediamine chelate complexes.[18] The puckering of the chelate rings is described in Table IV; again, agreement with other Co–en complexes is good.[18] The "bite" distances N···N range from 2.630 (14) to 2.650 (15) Å, with an average of 2.637 (8) Å.

TABLE IV

PUCKERING OF THE ETHYLENEDIAMINE RINGS[a]

Plane defined by atoms	Atom	Dev from plane, Å	α, deg	β, deg
Co(1), N(2), N(5)	C(2)	0.31	26.4	46.6
	C(5)	0.34		
	C(2)′	0.40	32.5	56.9
	C(5)′	0.43		
Co(1), N(3), N(4)	C(3)	0.29	25.7	48.3
	C(4)	0.35		
Co(1′), N(2′), N(5′)	C(2′)	0.40	26.8	50.2
	C(5′)	0.27		
Co(1′), N(3′), N(4′)	C(3′)	0.41	27.1	50.4
	C(4′)	0.27		
		Av 0.33	Av 26.5	Av 49.6
		σ 0.07	σ 0.8	σ 1.2

[a] α and β are as used by K. N. Raymond, P. W. R. Carfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968). α is the angle between the N–metal–N plane and the C–metal–C plane; β is the torsion angle between the nitrogen atoms across the C–C bond.

If one takes into account the possible configurations of the en groups about the cobalt atoms and the possible conformations of the ethylenediamine rings themselves (and regards the central ring as planar), then there exist 36 possible isomers for the μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] cation. Because of the positional disorder of the one ethylenediamine group there are two pairs of antipodes in the present crystal, which can be described by the symbols

$$ {}^{\lambda}_{\lambda}\Delta^{NH_2}_{O_2}\Delta^{\lambda}_{\lambda} \qquad {}^{\delta}_{\delta}\Lambda^{NH_2}_{O_2}\Lambda^{\delta}_{\delta} $$

$$ {}^{\lambda}_{\lambda}\Delta^{NH_2}_{O_2}\Delta^{\delta}_{\lambda} \qquad {}^{\delta}_{\delta}\Lambda^{NH_2}_{O_2}\Lambda^{\delta}_{\lambda} $$

Details of the isomerism in polynuclear complexes and the symbolism used here will be described elsewhere.[19] The first pair of antipodes fits into the scheme developed in a preceding paper,[20] where it was shown that in complexes with a ΔΔ configuration the intramolecular nonbonded H···H interactions favor a λ conformation for all the en groups. The disorder of the one en group in the present case seems to represent a compromise between intramolecular H···H interactions and crystal packing (see below).

As in other dinuclear cobalt complexes with ethylenediamine ligands, the thermal vibrations of the cobalt atoms are moderately small and nearly isotropic (with rms amplitudes of *ca.* 0.22 Å) and the largest vibrations are exhibited by the carbon atoms with rms amplitudes up to 0.37 Å (not including the disordered C atoms). The ellipsoids of thermal motion are shown in Figure 2.

The bond distances and angles within the nitrate groups are given in Table III. Excluding the disordered nitrate group N(7), the average distance for the nine N–O bonds is 1.237 (6) Å with an rms deviation of 0.016 Å. The thermal motions of the atoms of the nitrate groups are relatively high, particularly for the

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(18) U. Thewalt, to be published.

(19) U. Thewalt, K. A. Jensen, and C. E. Schäffer, to be submitted for publication.

(20) U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **10**, 1789 (1971).

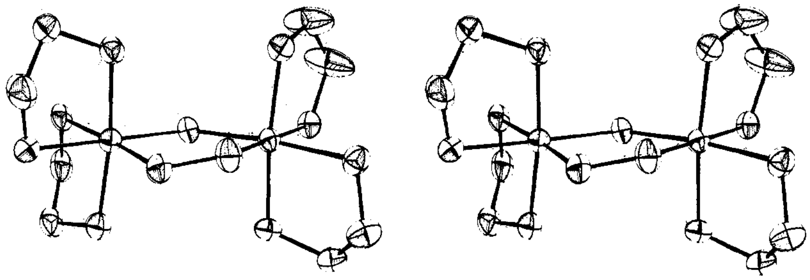


Figure 2.—A stereoscopic view of the ΔΔ isomer of the cation. The temperature parameters used for the carbon atoms of the disordered ethylenediamine group are those obtained before introducing split atoms; for other atoms the final parameters were used. The ellipsoids are drawn at the 20% probability levels.

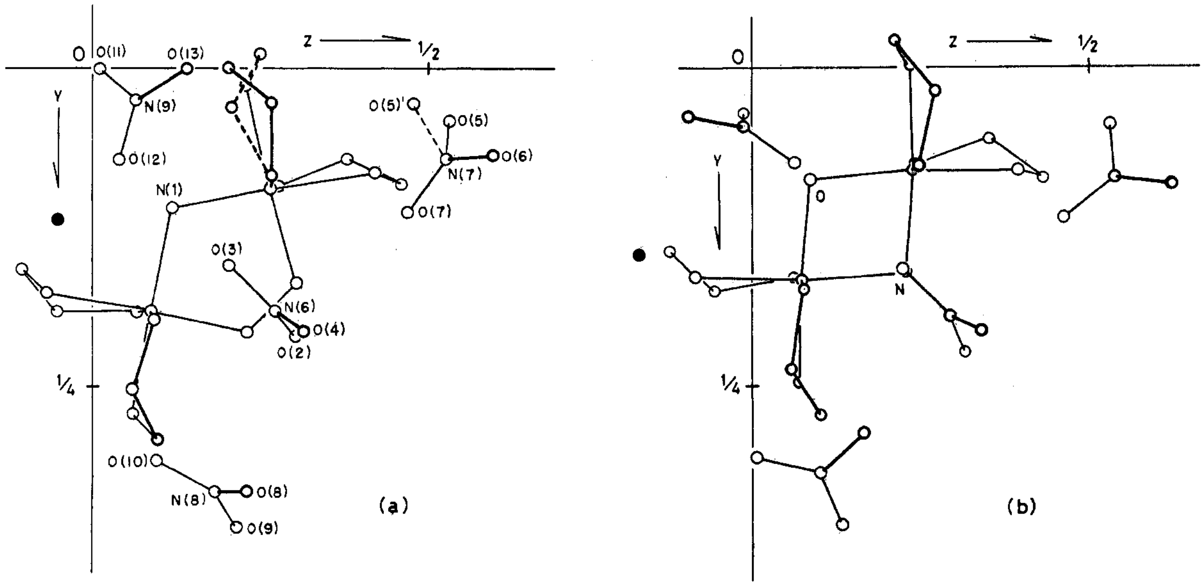
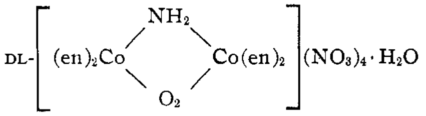


Figure 3.—A comparison of a-axis projections of the structures of (a) $[(en)_2Co\text{-}\mu\text{-}(NH_2,O_2)\text{-}Co(en)_2](NO_3)_4\cdot H_2O$ (this work) and (b) $[(en)_2Co\text{-}\mu\text{-}(NH_2,OH)\text{-}Co(en)_2](NO_3)_4\cdot H_2O$.[20]

nitrate group containing N(8), where some kind of positional disorder cannot be excluded. Therefore not much significance should be attributed to the observed nonplanarity of this group (N(8) is 0.03 Å from the plane of its oxygen ligands). The remaining two nitrate groups are planar within experimental error.

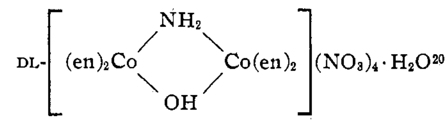
The nitrate group containing N(7) apparently takes on two orientations in the crystal, both with about equal probability. The difference between the two orientations is manifested primarily in the position of O(5). We have represented O(5) as two half-atoms, having isotropic temperature factors and being separated by 0.94 Å; these two positions are nearly symmetric with respect to the plane of the other three atoms of the nitrate group. Consistent with this picture, the longest axes of the temperature ellipsoids of the other atoms are roughly perpendicular to the plane of the average nitrate group. The rms amplitudes of the motion of these atoms (up to 0.38 Å) were not large enough, however, as to require separated half-atoms. The resulting bond lengths and angles (and their esd's) for the nonplanar model are, of course, not very meaningful.

The crystal structures of the two salts



$$\text{DL-}\left[(en)_2Co\begin{matrix}NH_2\\ \\ O_2\end{matrix}Co(en)_2\right](NO_3)_4\cdot H_2O$$

(this work) and



$$\text{DL-}\left[(en)_2Co\begin{matrix}NH_2\\ \\ OH\end{matrix}Co(en)_2\right](NO_3)_4\cdot H_2O^{20}$$

are surprisingly similar. The cell dimensions are given below

	μ-(NH_2,O_2) complex	μ-(NH_2,OH) complex
Space group	$P2_1/n$	$P2_1/n$
a, b, c, Å	8.78, 23.97, 12.50	8.31, 23.93, 12.40
β, deg	95.8	90.7

Views of both structures as seen along the a axis are shown in Figure 3. A major difference between the two structures is in the relative positions of the bridging groups. The similar overall crystal packing of the two compounds evidently is caused by the similar size and charge distribution of the cations. On the other hand, the differences are large enough that the compounds form separate crystals from a mixed solution—a property, by the way, that made it possible for us to isolate the nitrate salt of the μ-(NH_2,OH) cation.[20]

A study of the nonbonded distances in the structure indicates that the disorder of the nitrate group N(7) is coupled with the conformational disorder of the

TABLE V

NONBONDED CONTACTS ≦3.25 Å[a]

D	A	H	*d*, Å	Angle, deg
N(1)	O(11b)		3.12	
N(2)	O(5a)		3.16	
	O(6a)	H(4)	3.11	163
	O(11b)	H(5)	3.04	150
N(3)	O(5)		2.99	
	O(5a)	H(7)	3.06	171
	O(5a)′	H(7)	2.86	155
N(4)	O(13c)	H(8)	3.02	161
	O(3c)	H(9)	3.06	125
	O(4c)	H(9)	3.11	156
N(5)	O(5)′	H(10)	3.18	128
	O(7)	H(10)	2.94	172
	O(3)	H(11)	3.02	135
N(2′)	O(14)	H(12)	3.25	146
	O(9d)		3.06	
	O(2e)	H(13)	3.08	146
N(3′)	O(8)	H(14)	3.16	166
	O(2e)	H(15)	3.23	171
	O(7e)		2.98	
	O(10)		3.16	
N(4′)	O(2)	H(16)	3.02	151
	O(3)	H(16)	3.04	121
	O(14)	H(17)	2.86	175
C(2)	0(11b)		3.12	
C(2)′	O(5a)		2.73	
C(3′)	O(7e)		3.23	
C(4′)	O(4e)		3.23	
C(5)	O(5)′		2.67	
C(5′)	O(12c)		3.23	
O(5)	O(5a)		2.87	
O(5)′	O(5a)′		3.10	
O(2)	O(7)		3.14	
O(3)	O(12)		3.07	
O(14)	O(8d)	H(36)	2.90	177
O(14)	O(12)	H(37)	3.07	178

[a] Hydrogen atoms that are possibly involved in the contacts are indicated together with the angle at the H atom. Symmetry code: no letter, coordinates as given in Tables I and II; (a) $1 - x, -y, 1 - z$; (b) $1 - x, -y, -z$; (c) $-1 + x, y, z$; (d) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (e) $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$.

ethylenediamine group N(2)···N(5). The two compatible sets of atoms are C{(2), C(5), O(5)} and {C(2)′, C(5)′, O(5)′}. For this arrangement, there is only one relatively short, but still acceptable, C···O distance (C(2)···O(11b) = 3.12 Å) (for symmetry code, see Table V). In a structure with either {C(2), C(5), O(5)′} or {C(2)′, C(5)′, O(5)}, on the other hand, there would be unrealistic short nonbonded distances (C(2)′···O(5a) = 2.73 Å and C(5)···O(5)′ = 2.67 Å)).

The shortest nonbonded distances are listed in Table V. Most N-bonded hydrogen atoms seem to participate in the three-dimensional hydrogen-bond network, although some of the donor···acceptor (D···A) distances are rather long and some of the D–H···A angles deviate considerably from 180°, suggesting only weak interactions. The angles at the hydrogen atoms are certainly not very accurate, since the hydrogen atom positions were assumed (see above).

The water oxygen atom O(14) has two close nitrate oxygen neighbors O(12) and O(8d) at distances 3.07 and 2.90 Å; the angle O(12)···O(14)···O(8d) is 116°, suggesting that these contacts represent hydrogen bonds. (As indicated above, the water hydrogen atoms were positioned on this assumption.) In addition, there is one close contact (N(4′)–H(17)···O(14); N–H···O = 175°) of 2.86 Å in which the water oxygen atom seems to act as hydrogen-bond acceptor. This bond makes angles of 108 and 116° with the O(14)···O(12) and O(14)···O(8d) bonds. A fourth contact (N(2)′–H(12)···O(14); ∠N–H···O = 146°) of 3.25 Å probably does not represent a hydrogen bond.

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