

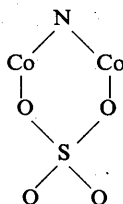
The Crystal Structure of Racemic μ -Amido- μ -sulfato-bis[bis(ethylenediamine)cobalt(III)] Tribromide*

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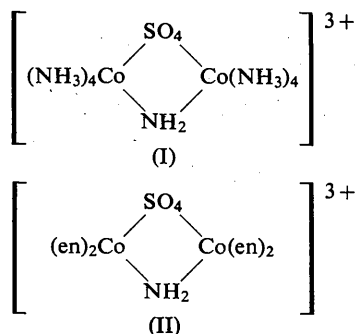
The crystal structure of racemic μ -amido- μ -sulfato-bis[bis(ethylenediamine)cobalt(III)] tribromide, DL-[(en)₂Co· μ (NH₂,SO₄)·Co(en)₂]Br₃, has been solved from three-dimensional X-ray diffraction data. The salt crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 11.258 (1), *b* = 17.095 (1), *c* = 12.495 (1) Å and β = 106.79 (1)°. The observed density is 2.05 g.cm⁻³, and that calculated for four formula units in the cell is 2.049 g.cm⁻³. The structure was solved using Patterson and Fourier methods and refined by least-squares calculations. The final conventional *R* index is 0.066 for the 2944 independent reflections of non-zero weight. The cation contains a six-membered puckered central ring of the form



The endocyclic S–O bonds (uncorrected average 1.493 Å) appear to be slightly longer than the *exo* S–O bonds (uncorrected average 1.442 Å) and the S–O bonds in free sulfate ions. The cation has essentially C₂ symmetry. The configurations and conformations of the two cation antipodes in the crystal are described by the symbols $\frac{2}{3}A\lambda A_2^2$ and $\frac{1}{2}A\delta A_2^2$.

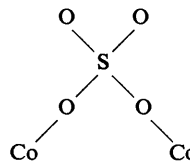
Introduction

Salts of the sulfato-bridged cations (I) and (II) were prepared and formulated



as doubly bridged dinuclear cobalt cations by Werner (1910) more than sixty years ago. As in other bridged cobalt complexes, the geometry of the central part, particularly the geometry of the sulfato bridge, was of considerable interest. Nakamoto, Fujita, Tanaka & Kobayashi (1957) concluded on the basis of the infrared spectrum of the nitrate salt of (I), that the

μ -sulfato group in these cations is bonded to the cobalt atoms *via* two of its oxygen atoms:



To obtain full confirmation of this arrangement, the crystal structure of DL-[(en)₂Co· μ (NH₂,SO₄)·Co(en)₂]Br₃ was investigated by single-crystal X-ray diffraction techniques. It would also be of interest to compare the cations of this salt with related cations in respect of configurations and conformations of the cobalt atoms and of the ethylenediamine rings.

Experimental

Of the two methods described by Werner for the preparation of DL-[(en)₂Co· μ (NH₂,SO₄)·Co(en)₂]Br₃ (Werner, 1910; Werner, Kuh & Wüst, 1914), we used that described in his 1914 paper. By this method an aqueous solution of racemic μ -amido- μ -superoxo-bis[bis(ethylenediamine)cobalt(III)] tetranitrate hydrate (Tetraäthylendiamin- μ -amino-peroxo-kobalti-kobalte-Nitrat in Werner's nomenclature) was treated with an excess of sulphur dioxide in aqueous solution. The reaction, which is completed within a few seconds,

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probably involves direct addition of an SO₂ molecule to the superoxo bridge (Garbett & Gillard, 1968). The nitrate salt obtained in this way was transformed into the bromide by precipitating from an ammonium bromide solution. The bromide salt was purified by recrystallization from hot water.

Analysis of DL-[(en)₂Co.μ(NH₂, SO₄).Co(en)₂]Br₃

Calculated: Co, 16.6; Br, 33.8; S, 4.5; N, 17.8; C, 13.5; H, 4.8

Found: Co, 17.4; Br, 33.8; S, 4.3; N, 17.8; C, 13.5; H, 5.2

Table 1. Observed and calculated structure factors

The columns are *k*, 10*F*_o, and 10*F*_c. Values of 10*F*_o reported as '—' indicate unobserved reflections; asterisks indicate zero-weight reflections.

-12 k 2	1 162	-9 k 35	12 277 -249	4 232 177	3 1644 1600	10 91 71	4 650 601	16 317 -326	6 276 -223	15 216 197	2 1405 1432
0 147 -142	2 215 -104	0 98 35	13 5 0	5 1396 1375	4 515 -474	11 106 66	5 826 -801	17 111 98	7 501 533	-3 k 8	3 1303 1332
1 368 377	3 663 -342	3 663 -342	18 5 0	6 950 938	6 87 112	0 k 11	6 1135 -1108	18 111 98	8 1011 938	-3 k 8	4 1638 1626
2 134 77	4 862 -901	2 755 -786	19 17 -260	7 850 386	7 87 112	0 k 11	7 1161 1101	19 111 98	9 1011 938	-3 k 8	5 1938 1926
-12 k 2	5 1417 -840	4 418 -420	20 132 131	8 171 -260	8 276 -249	1 212 -34	8 1409 457	20 111 98	10 1011 938	-3 k 8	6 2238 2226
1 161 205	6 516 -465	5 533 -486	21 276 259	9 213 -111	9 213 131	2 142 -34	9 1409 457	21 111 98	11 1011 938	-3 k 8	7 2538 2526
2 132 122	7 516 -465	6 265 -252	22 352 171	10 98 -25	10 313 131	3 57 10	10 1409 457	22 111 98	12 1011 938	-3 k 8	8 2838 2826
3 249 246	8 197 143	7 214 -117	23 190 -93	11 205 12	11 515 -568	4 242 148	11 1409 457	23 111 98	13 1011 938	-3 k 8	9 3138 3126
-12 k 2	9 429 -466	8 149 -46	24 501 -536	12 205 12	12 515 -568	5 242 148	12 1409 457	24 111 98	14 1011 938	-3 k 8	10 3438 3426
0 546 -253	10 117 -420	9 149 -46	25 269 -253	13 308 -291	13 421 -394	6 272 -207	13 1409 457	25 111 98	15 1011 938	-3 k 8	11 3738 3726
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3 19 354	13 403 -474	12 150 187	28 905 1021	16 162 -110	16 162 -110	9 252 230	16 1409 457	28 111 98	18 1011 938	-3 k 8	14 4638 4626
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1 101 205	15 403 -474	14 150 187	30 1021 1021	18 162 -110	18 162 -110	11 252 230	18 1409 457	30 111 98	20 1011 938	-3 k 8	16 5238 5226
2 132 122	16 403 -474	15 150 187	31 1021 1021	19 162 -110	19 162 -110	12 252 230	19 1409 457	31 111 98	21 1011 938	-3 k 8	17 5538 5526
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Table 1 (cont.)

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1 1620 1615	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
2 2237 2301	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
3 1376 1317	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
4 439 485	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
5 418 385	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
6 1094 1077	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
7 2022 2116	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
8 382 389	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
9 108 159	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
10 1275 1228	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
11 291 296	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
12 404 340	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
13 688 -682	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
14 160 166	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
15 462 -462	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
16 488 -482	3 210 299	4 971 -167	1 311 -342	2 050 -889	6 937 606	8 939 944	6 150 466	4 324 279	6 424 556
17 129 -144	3 210 299	4 971 -167	1 311 -342						

Dark red monoclinic crystals, in the shape of short prisms with prominent forms {100} and {011} and with volumes up to several cubic millimeters, were grown by slow evaporation of an aqueous solution at room temperature.

We did not observe the needle-like crystals described by Werner. The space group $P2_1/c$ was indicated by systematic absences on Weissenberg photographs ($h0l, l=2n+1; 0k0, k=2n+1$). Cell parameters were obtained from a least-squares treatment of measurements for 38 reflections on zero-level Straumanis-type Weissenberg photographs, taken about the a and b axes with Cu $K\alpha$ radiation at $23 \pm 2^\circ\text{C}$. The results with other crystal data are:

$\text{Co}_2\text{C}_8\text{H}_{34}\text{N}_9\text{O}_4\text{SBr}_3$	M.W. 710.08
$a = 11.258 (1) \text{ \AA}$	Space group $P2_1/c$
$b = 17.095 (1)$	$F(000) = 1408$
$c = 12.495 (1)$	$\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$
$\beta = 106.79 (1)^\circ$	$\lambda(\text{Cu } K\alpha_2) = 1.54433$
$V = 2302.2 \text{ \AA}^3$	$\mu(\text{Co } K\alpha) = 148 \text{ cm}^{-1}$
$D_m = 2.05 \text{ g.cm}^{-3}$	$D_x = 2.049 \text{ g.cm}^{-3}$

The observed density was measured by flotation in a carbon tetrachloride-1,2-dibromoethane mixture. It agrees well with the calculated density, assuming four formula units in the unit cell.

Intensity data were collected on a Datex-automated General Electric XRD-5 diffractometer, using iron fil-

tered cobalt radiation, a NaI(Tl) scintillation counter and a pulse-height analyzer. The intensities were measured at a takeoff angle of 3° using a $\theta-2\theta$ scan at a scanning speed of $4^\circ.\text{min}^{-1}$. The measurements were made in the range $2\theta = 7^\circ$ to 154° . Background was counted for 15 sec at each end of the scan. The scan range was adjusted to account for $\alpha_1-\alpha_2$ splitting. The crystal used was ground into a sphere of 0.12 mm diameter and was mounted with \mathbf{b} parallel to the φ axis of the diffractometer. The 081 reflection was monitored periodically during the data collection process; there was no significant deviation in its intensity over the period of data collection. The individual reflections were assigned intensity values, I_{obs} , and standard deviations, $\sigma(I_{\text{obs}})$, according to the formulas

$$I_{\text{obs}} = [S - (B_1 + B_2)T_s/2t]/Lp$$

$$\sigma(I_{\text{obs}}) = [S + (B_1 + B_2) \cdot (T_s/2t)^2 + (0.017S)^2]^{1/2}/Lp$$

where S = total scan count, T_s = scanning time, B_1 and B_2 = background counts, t = time spent counting the background, and Lp = Lorentz-polarization correction factor.

The term $(0.017S)^2$ in the second equation was introduced to compensate for errors not due to counting statistics (Busing & Levy, 1957). Of the 3093 recorded independent reflections, 142 had net intensities I_{obs} equal to or below background level; they were assigned intensities and weights of zero. All reflections which were

Table 2. Positional and thermal parameters of the non-hydrogen atoms and their standard deviations

Values for the Co, Br and S atoms have been multiplied by 10^5 ; for other atoms by 10^4 . The standard deviations are given in parentheses, and refer to the last decimal position of respective values. The temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	-20179(10)	15191(7)	20370(9)	267(10)	158(4)	217(9)	-48(11)	93(15)	-18(10)
Co(1')	12248(10)	13549(6)	30102(9)	267(10)	132(4)	217(8)	-8(10)	71(15)	-8(10)
Br(1)	43418(8)	19289(5)	-5072(8)	530(8)	287(4)	633(7)	221(8)	159(12)	190(9)
Br(2)	323(9)	7784(5)	-14141(8)	1024(11)	235(4)	692(8)	117(10)	-310(15)	-204(9)
Br(3)	48637(8)	3258(6)	29747(9)	553(8)	467(5)	954(9)	324(10)	653(14)	595(11)
S	-4318(16)	17335(11)	45440(15)	389(16)	197(7)	153(12)	-42(17)	156(23)	-56(15)
O(1)	-1489(4)	1401(3)	3658(4)	48(5)	42(3)	17(4)	-23(6)	11(7)	-4(5)
O(1')	568(4)	1968(3)	4031(4)	43(4)	19(2)	25(4)	-11(5)	33(7)	-15(4)
O(2)	-815(5)	2427(4)	5008(5)	84(6)	36(3)	101(6)	-33(7)	142(11)	-62(7)
O(2')	17(5)	1140(4)	5384(5)	65(6)	52(3)	51(5)	9(7)	30(9)	62(6)
N(1)	-383(5)	1271(3)	1881(4)	36(5)	17(2)	17(4)	-9(5)	-2(8)	0(5)
N(2)	-2639(5)	1495(3)	428(5)	31(5)	20(2)	31(4)	-3(6)	12(8)	-4(6)
N(2')	1937(5)	877(3)	1936(5)	41(5)	18(2)	41(5)	-4(6)	12(9)	-8(6)
N(3)	-3648(5)	1844(4)	2175(5)	42(5)	26(3)	41(5)	-17(6)	20(9)	4(6)
N(3')	2843(5)	1372(3)	4151(5)	29(5)	18(2)	34(5)	-7(6)	2(8)	-1(5)
N(4)	-1663(5)	2643(3)	2050(5)	45(5)	17(2)	37(5)	-13(6)	20(9)	-3(6)
N(4')	1030(5)	339(3)	3673(5)	36(5)	16(2)	33(5)	2(6)	5(8)	5(6)
N(5)	-2517(5)	407(4)	1971(5)	33(5)	22(2)	47(5)	-3(6)	21(9)	14(6)
N(5')	1618(5)	2358(3)	2423(5)	38(5)	18(2)	28(5)	-13(6)	5(8)	4(5)
C(2)	-2845(7)	664(5)	28(6)	62(8)	30(3)	36(6)	9(9)	-12(12)	-25(8)
C(2')	2128(7)	1478(5)	1139(6)	76(8)	39(4)	29(6)	-3(10)	29(12)	1(8)
C(3)	-3573(8)	2673(5)	2522(8)	65(8)	34(4)	96(9)	0(9)	83(15)	-44(10)
C(3')	2841(7)	822(5)	5048(7)	65(8)	29(3)	37(6)	10(9)	1(12)	5(8)
C(4)	-2805(8)	3100(5)	1904(8)	72(9)	16(3)	90(9)	23(8)	17(14)	-6(9)
C(4')	2214(8)	94(5)	4478(7)	73(8)	18(3)	66(8)	12(8)	10(13)	26(8)
C(5)	-3326(7)	226(5)	827(7)	56(8)	21(3)	71(8)	-12(8)	1(13)	-20(8)
C(5')	2490(7)	2225(5)	1770(7)	58(7)	37(4)	35(6)	-32(8)	38(11)	10(8)

measured above background were treated as observed. An absorption correction was applied to the data assuming a spherical crystal with $\mu R=0.89$.

The data were then placed approximately on the absolute scale by a Wilson plot, giving a final set of F_o^2 and $\sigma(F_o^2)$ values on which the determination and the refinement of the structure were based.

Determination and refinement of the structure

The approximate positional parameters of the two cobalt and the three bromine atoms were obtained from a three-dimensional sharpened Patterson map. The first structure factor calculation gave $R=0.38$. (R is defined throughout as $\sum||F_o|-|F_c||/\sum|F_o|$, where the sums are over reflections with $w \neq 0$). The remaining non-hydrogen atoms were located from a three-dimensional electron density map. The R index for the complete trial structure was 0.25. At this point refinement was started by least-squares procedures. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weights w taken equal to $1/\sigma^2(F_o^2)$. F_c^* is derived from F_c by correcting for the effect of secondary extinction [Larson, 1967; equation (3)]. The atomic scattering factors used for Co^{2+} , O, N, C, and Br^- were those listed in *International Tables for X-ray Crystallography* (1962). The curve for Co^{2+} was corrected for the real part of the anomalous scattering by subtracting 2.2 electrons over the whole $\sin \theta/\lambda$ range (Saravia & Caticha-Ellis, 1966). The form factor curve used for hydrogen was that of Stewart, Davidson & Simpson (1965). Two cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of all non-hydrogen atoms, based on the 1717 reflections with lowest values of $\sin \theta/\lambda$, reduced R to 0.124.

At this point the coordinates of the hydrogen atoms of the ethylenediamine groups and the $\mu\text{-NH}_2$ group were calculated assuming N-H and C-H distances of 0.9 Å and H-C-H and H-N-H angles of 109.5°. The hydrogen atoms were included in the structure factor calculations but not the refinement in the subsequent least-squares cycles; in these calculations the hydrogens were assigned isotropic temperature factors equal to those of the atoms to which they were bonded. In the subsequent anisotropic refinement the complete set of data was used (except reflections with $w=0$). A total of 245 parameters were adjusted: a scale factor, a sec-

ondary extinction parameter, and three positional and six thermal parameters for each of the non-hydrogen atoms. Because of the limited core storage of the computer all 245 parameters could not be refined at the same time; therefore they were included in three matrices of about equal dimensions, the positional and thermal parameters of a given atom being in one matrix.

Four cycles of anisotropic refinement brought R to 0.067. After the second cycle the hydrogen positions were readjusted using the improved heavy atom coord-

Table 3. Positional parameters assigned to the hydrogen atoms

All values have been multiplied by 10^3 .

		x	y	z
N(1)	H(2)	-43	77	163
	H(3)	-31	159	130
N(2)	H(4)	-210	176	11
	H(5)	-338	178	19
N(3)	H(6)	-387	153	269
	H(7)	-425	178	152
N(4)	H(8)	-130	278	149
	H(9)	-107	279	271
N(5)	H(10)	-294	30	247
	H(11)	-185	8	212
N(2')	H(12)	267	64	229
	H(13)	142	49	155
N(3')	H(14)	303	187	443
	H(15)	346	123	385
N(4')	H(16)	76	-3	312
	H(17)	43	36	403
N(5')	H(18)	196	271	299
	H(19)	92	260	197
C(2)	H(20)	-210	46	1
	H(21)	-336	65	-67
C(3)	H(22)	-320	272	329
	H(23)	-435	289	241
C(4)	H(24)	-328	315	118
	H(25)	-269	361	218
C(5)	H(26)	-413	38	75
	H(27)	-335	-29	66
C(2')	H(28)	276	132	83
	H(29)	144	154	55
C(3')	H(30)	237	103	549
	H(31)	361	74	552
C(4')	H(32)	274	-16	412
	H(33)	211	-28	499
C(5')	H(34)	327	222	223
	H(35)	245	265	129

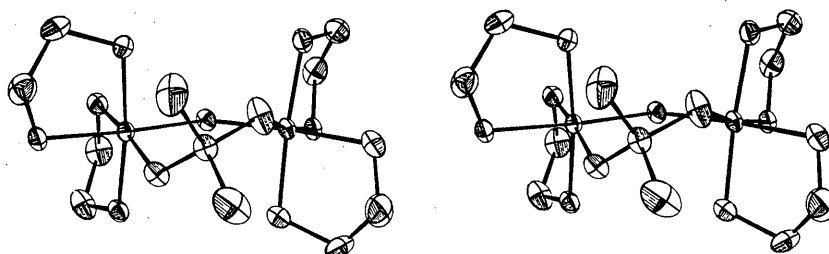


Fig. 1. A stereoscopic view of one of the cation antipodes (the $\frac{1}{2}\delta\delta\frac{1}{2}$ isomer) in DL-[(en)₂Co·μ(NH₂, SO₄)·Co(en)₂]Br₃.

dinates. Seven medium strong reflections which apparently were incorrectly measured were then given zero weight. Two more cycles of least-squares concluded the refinement. In the last cycle the shift/error ratios for all parameters were less than 0.5. The final R index for the 2944 reflections of non-zero weight was 0.066 and the goodness of fit $[\sum w(F_o^2 - F_c^2)^2 / (m-s)]^{1/2}$ was 1.54. The parameter g of the secondary extinction had a final value of $(1.16 \pm 0.07) \times 10^{-6}$. The two maximum deviations from zero in a final difference Fourier synthesis were $+1.3$ and $-1.6 \text{ e.}\text{\AA}^{-3}$; these excursions were located close to Br(3). Since no chemical significance could be attributed to these regions and since Br(3) exhibits a large anisotropy in its temperature factor, we assume that some kind of positional disorder is associated with this atom. All other deviations were less than $\pm 0.6 \text{ e.}\text{\AA}^{-3}$.

The observed and calculated structure factors are listed in Table 1. The final heavy-atom parameters and their estimated standard deviations are listed in Table 2. The assumed hydrogen parameters are given in Table 3. The average estimated standard deviations in the final positional coordinates are: Co, 0.001; Br, 0.001; S, 0.002; O, 0.005; N, 0.006; C, 0.009 Å. These errors correspond to the following average e.s.d.'s in bond lengths: Co-N, Co-O and S-O, 0.006; C-N, 0.011, C-C, 0.013 Å. The e.s.d.'s in bond angles are about 0.3° at Co; 0.4° at S and the bridging N(1), and up to 0.7° at the other lighter atoms.

All calculations were carried out on an IBM 7094 computer using subprograms of the *CRYRM* system (Duchamp, 1964).

Discussion

The cation

A stereo view of one of the cation antipodes is shown in Fig. 1. (For simplicity of expression, properties which are equal for both cation antipodes, such as bond

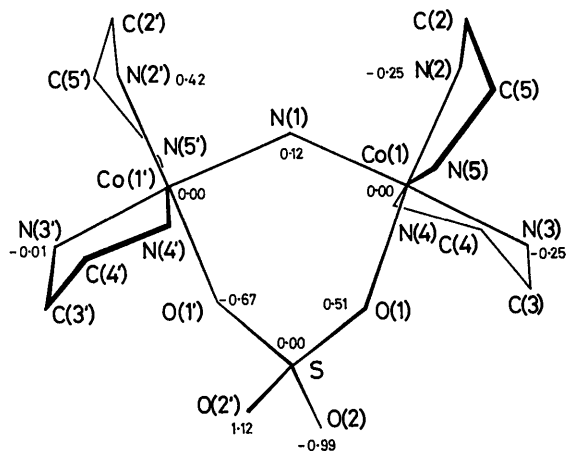


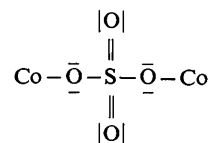
Fig. 2. A view of one of the cation antipodes (the $\frac{1}{2}4s4s^2$ isomer) in DL-[(en)₂Co.μ(NH₂, SO₄).Co(en)₂]Br₃ perpendicular to the Co(1), Co(1'), S plane. The deviations from this plane (Å) are given for some of the atoms.

lengths, are discussed in terms of 'the cation' in the following discussion.) The cation consists of two octahedrally coordinated cobalt atoms which are connected by an amido and a sulfato bridge. As predicted by Nakamoto, Fujita, Tanaka & Kobayashi (1957), the sulfato group is involved in the bridge with two of its oxygen atoms, so that a six-membered cation central ring is formed.

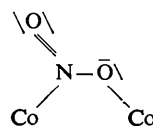
The central ring is considerably puckered. Details of the puckering are indicated in Fig. 2. The four atoms Co(1), Co(1'), S and N(1) are nearly coplanar, while the two bridging sulfato oxygen atoms are displaced by about 0.5 Å to opposite sides of this plane.

The bond distances and angles for the cation are listed in Table 4. The geometry of the bridging sulfato group is close to that of the free sulfato ion. All six O-S-O angles deviate by less than 3° from the tetrahedral angle. The average (uncorrected) lengths of the exocyclic and endocyclic S-O bonds are 1.442 and 1.493 Å respectively. In view of the relatively high thermal motions of atoms O(1), O(2), and O(2'), all of which have their maximum root-mean-square amplitudes approximately perpendicular to the respective S-O bonds, as can be seen from Fig. 1, corrections to the bond lengths due to thermal motion should be applied.

Assuming a 'riding motion' (Busing & Levy, 1964) for these oxygen atoms the average bond lengths become 1.47 Å (*exo*) and 1.50 Å (*endo*). The average corrected S-O bond length as found in several inorganic sulfates is close to 1.48 Å (Larson, 1965). The deviations from this value possibly reflect the change of bond order of the S-O bonds when the free sulfato ion forms a bridge between the cobalt atoms. This situation is illustrated by the following valence bond scheme:



An analogous effect has been observed for the μ -NO₂ bridge in the

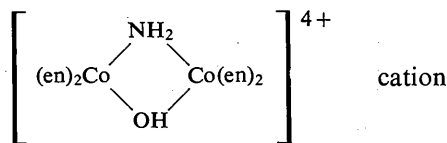


arrangement.

There, the bridge N-O bond distance (1.31 Å) approaches the N-O single bond distance, whereas the *exo* N-O bond is slightly shorter than the N-O bond distance in the nitrite ion (Thewalt & Marsh, 1970a; Thewalt, 1970).

There are two groups of Co-N(en) bonds with different bond distances: (a) the bonds *trans* to the sulfato oxygen atoms, 1.932 and 1.929 Å, and (b) the remaining six bonds with a mean of 1.967 Å and ranging from 1.962 to 1.978 Å. The standard deviation of these six

bond lengths, as calculated from the spread of the individual values, is $\sigma=0.006$ Å. These values compare well with 1.960 ± 0.009 Å for the



(hereafter called the $\mu(\text{NH}_2, \text{OH})$ cation) (Thewalt & Marsh, 1970*b*). Mean values and standard deviations for the other bond distances and angles of the Co-(en) chelate rings are given below. For comparison corresponding values for the $\mu(\text{NH}_2, \text{OH})$ cation are given in parentheses.

N-C	1.479 ± 0.013	(1.476 ± 0.009) Å
C-C	1.493 ± 0.016	(1.485 ± 0.013) Å
N-Co-N	85.2 ± 0.7	$(84.5 \pm 0.6)^\circ$

Since most C and N atoms of the (en) rings exhibit relatively high thermal vibrations, the bond lengths and angles are of relatively low precision.

The (en) chelate rings are all in the unstrained *gauche* form. The deviations of the carbon atoms of each ring from the respective N-Co-N plane and the dihedral angles α and β are listed in Table 5 (α and β are as used by Raymond, Corfield & Ibers, 1968: α =angle between the (N-metal-N) plane and the (C-metal-C) plane; β =torsion angle between the nitrogen atoms across the C-C bond). The mean values are $26.3 \pm 0.8^\circ$ for α and $49.1 \pm 1.3^\circ$ for β ; the average deviation of a C atom from its N-Co-N plane is 0.33 ± 0.07 Å. The corresponding values for the $\mu(\text{NH}_2, \text{OH})$ cation are $26.3 \pm 1.4^\circ$, $48.9 \pm 2.8^\circ$, and 0.33 ± 0.09 Å. Within one complex cation both cobalt atoms have identical configurations and the four ethylenediamine chelate rings have identical conformations. Additional chirality of

Table 4. Distances and angles in the cation

These values contain no corrections for thermal motion. Error assignments are described in the text.

Distances			
Co(1)-Co(1')	3.510 Å	Co(1')-O(1')	1.953 Å
O(1)	1.949	N(1)	1.953
N(1)	1.953	N(2)	1.932
N(2)	1.929	N(3')	1.963
N(3)	1.972	N(4')	1.963
N(4)	1.962	N(5')	1.965
N(5)	1.978	N(2')-C(2')	1.490
N(2)-C(2)	1.500	N(3')-C(3')	1.463
N(3)-C(3)	1.478	N(4')-C(4')	1.479
N(4)-C(4)	1.469	N(5')-C(5')	1.465
N(5)-C(5)	1.489	C(2')-C(5')	1.493
C(2)-C(5)	1.471	C(3')-C(4')	1.506
C(3)-C(4)	1.503	S-O(1')	1.502
S-O(1)	1.484	O(2')	1.443
O(2)	1.440		
Angles			
Co(1)-N(1)-Co(1')	128.0°	Co(1')-O(1')-S	127.4°
Co(1)-O(1)-S	132.4	O(1')-Co(1')-N(1)	93.7
O(1)-Co(1)-N(1)	93.9	-N(2)	172.5
-N(2)	172.2	-N(3')	88.0
-N(3)	87.2	-N(4')	95.1
-N(4)	95.3	-N(5')	86.8
-N(5)	86.7	N(1)-Co(1')-N(2')	87.2
N(1)-Co(1)-N(2)	87.7	-N(3')	176.6
-N(3)	176.2	-N(4')	92.7
-N(4)	91.1	-N(5')	93.2
-N(5)	92.9	N(2')-Co(1')-N(3')	91.5
N(2)-Co(1)-N(3)	91.8	-N(4')	92.2
-N(4)	92.4	-N(5')	85.8
-N(5)	85.6	N(3')-Co(1')-N(4')	84.3
N(3)-Co(1)-N(4)	85.2	-N(5')	89.8
-N(5)	90.8	N(4')-Co(1')-N(5')	173.7
N(4)-Co(1)-N(5)	175.4	Co(1')-N(2')-C(2')	110.0
Co(1)-N(2)-C(2)	110.0	N(2')-C(2')-C(5')	107.8
N(2)-C(2)-C(5)	107.9	C(2')-C(5')-N(5')	107.6
C(2)-C(5)-N(5)	107.7	C(5')-N(5')-Co(1')	109.4
C(5)-N(5)-Co(1)	109.1	Co(1')-N(3')-C(3')	109.9
Co(1)-N(3)-C(3)	108.7	N(3')-C(3')-C(4')	105.8
N(3)-C(3)-C(4)	107.9	C(3')-C(4')-N(4')	107.1
C(3)-C(4)-N(4)	106.9	C(4')-N(4')-Co(1')	110.5
C(4)-N(4)-Co(1)	110.5	O(1')-S-O(2)	107.5
O(1)-S-O(2)	110.3	-O(2')	110.5
-O(2')	108.1	O(2)-S-O(2')	111.7
-O(1')	108.8		

the cation is caused by the puckering of the six-membered central ring. The general configuration and conformation of the cation, shown in Figs. 1 and 2 can be expressed by the symbol $\lambda\delta\lambda\delta\lambda$ and those of its antipode by $\delta\lambda\lambda\delta\delta$. Here λ and δ refer to configurations about the metal atoms and λ and δ to ring conformations. The λ , δ , and λ symbols are used in accord with a recent IUPAC (1970) proposal; they are put together in an obvious way to represent the dinuclear complex cations. Details of this symbolism for polynuclear complexes will be discussed elsewhere.

Table 5. Puckering of the ethylenediamine rings

Plane defined by atoms	Atom	Deviation from plane	α	β
Co(1), N(2), N(5)	C(2)	0.32 Å	26.0	48.3°
	C(5)	0.32		
Co(1), N(3), N(4)	C(3)	0.37	26.4	49.7
	C(4)	0.29		
Co(1'), N(2'), N(5')	C(2')	0.28	25.5	47.9
	C(5')	0.36		
Co(1'), N(3'), N(4')	C(3')	0.46	27.3	50.7
	C(4')	0.23		

If one takes into account the possible configurations about the cobalt atoms and the possible conformations of the five rings in the cation, one finds that there are 36 pairs of optical antipodes. As in the case of the $\mu(\text{NH}_2, \text{OH})$ complex the actually observed cations possess a twofold non-crystallographic axis. It goes through S and N(1). Most other possible isomers, on the other hand, do not have any element of symmetry (except the identity). The $\lambda\delta\lambda\delta\lambda$ and $\delta\lambda\lambda\delta\delta$ conformations were observed for the $\mu(\text{NH}_2, \text{OH})$ cation, and it appeared that

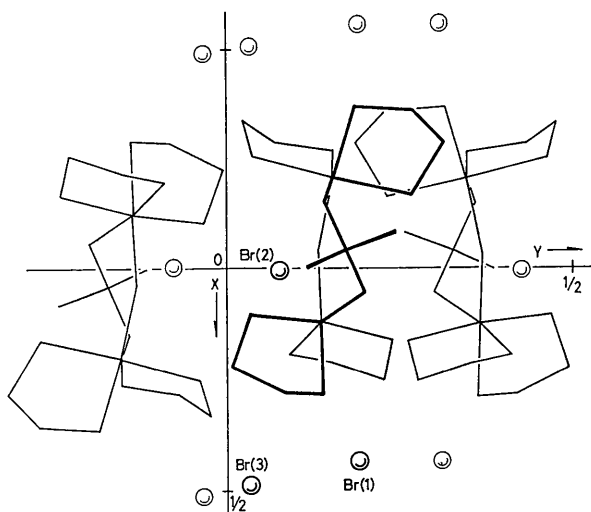


Fig. 3. A portion of the structure viewed along the c axis. The cation with the coordinates of Table 2 and its closest cation and anion neighbors are shown.

these particular conformations are a consequence of nonbonded interactions between amine hydrogen atoms of the ethylenediamine rings *cis* to the central ring (Thewalt & Marsh, 1970*b*). It is somewhat surprising that in the $\mu(\text{NH}_2, \text{SO}_4)$ cation the same conformational pattern is observed, since the $\text{N}\cdots\text{N}$ distances between the relevant NH_2 groups are considerably longer than in the $\mu(\text{NH}_2, \text{OH})$ cation and therefore could be expected to allow other overall conformations. [$i\mu(\text{NH}_2, \text{SO}_4)$: $\text{N}(4)\cdots\text{N}(5')=3.62$; $\text{N}(4')\cdots\text{N}(5)=3.95$ Å; $\mu(\text{NH}_2, \text{OH})$: 3.26 and 3.26 Å].

The ellipsoids of thermal vibration for the atoms of the cation are shown in Fig. 1. The thermal vibrations are in general agreement with those that would be expected on the basis of the cation geometry. The vibration amplitudes of the cobalt atoms are moderately small and nearly isotropic (0.12 to 0.15) Å. The vibrations of the sulfur atom are also relatively small. The largest vibrations are exhibited by the two *exo* oxygen atoms O(2) and O(2') with maximum r.m.s. amplitudes (0.32 and 0.31 Å, respectively) roughly perpendicular to the respective S–O bonds and by some of the carbon atoms of the ethylenediamine rings (r.m.s. amplitudes up to 0.29 Å).

The overall structure

Fig. 3 shows the crystal structure projected down the c axis. The shortest distances between the non-hydrogen atoms of the cation and atoms of surrounding cations and bromide anions are listed in Table 6. All amine hydrogen atoms of the ethylenediamine rings and of the $\mu\text{-NH}_2$ group seem to participate in the three-

Table 6. Short contacts, $D\cdots A$, between the non-hydrogen atoms of the cation and surrounding anions and cations

Hydrogen atoms not too far from the $D\cdots A$ line and angles $D\text{--}H\text{--}A$ are also given. Symmetry code: no letter, coordinates as given in Tables 2 and 3; (a) $-x, -y, -z$; (b) $-x, -y, 1-z$; (c) $-1+x, y, z$; (d) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (e) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

D	A	H	$d(DA)$	$\langle(DHA)\rangle$
N(1)	Br(2,a)	H(2)	3.59 Å	164°
		H(3)	3.16	157
N(2)	O(2,d)	H(4)	2.92	157
		H(5)	3.34	154
N(3)	Br(3,c)	H(6)	3.39	146
		H(7)	3.46	164
N(4)	O(2,d)	H(8)	2.97	154
		H(9)	3.53	135
N(5)	Br(3,c)	H(10)	3.52	148
		H(11)	3.68	151
N(2')	Br(2,a)	H(12)	3.31	163
		H(13)	3.54	153
N(3')	Br(1,e)	H(14)	3.32	147
		H(15)	3.53	159
N(4')	Br(2,a)	H(16)	3.33	168
		H(17)	3.03	136
N(5')	Br(1,e)	H(18)	3.60	138
		H(19)	3.46	146
C(2')	Br(2)	H(29)	3.58	142
C(4')	O(2'b)	H(33)	3.32	122

dimensional hydrogen bond network. Some of the donor...acceptor distances are rather long, however, and some of the donor-H...acceptor angles deviate considerably from 180°, suggesting weak interactions. The angles at the hydrogen atoms are certainly not accurate, since the hydrogen atom positions were calculated on rather simplified assumptions (see above). The majority of hydrogen bonds are of the form N-H...Br, ranging from 3.31 to 3.68 Å. In several other structure determinations, distances for Br...N hydrogen bonds have been found to be around 3.3 Å. It is of interest that there also seem to be hydrogen bonds of the type N-H...O (sulfato) between neighboring cations, e.g. N(2)-H(4)...O(2d), 2.92 Å. This indicates that despite the +3 overall charge on the cations, the oxygen atoms are still negative enough to be hydrogen bond acceptors. The shortest intermolecular distances involving carbon atoms of the en groups (last two lines in Table 6) may be regarded as an accidental result of the molecular packing rather than hydrogen bonding.

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The Crystal Structure of 1,6:2,3-Dianhydro-β-D-gulopyranose

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The crystal structure of 1,6:2,3-dianhydro-β-D-gulopyranose, C₆O₄H₈, has been determined from X-ray diffraction data measured on an automatic diffractometer. The phase problem was solved by combining the minimum function and direct methods. $R=0.031$. The crystal data are: $P2_12_12_1$, $Z=8$, $D_m=1.55$ g.cm⁻³; the lattice parameters $a=6.825$ (15), $b=10.274$ (5), $c=17.618$ (20) Å changed during exposure. The twofold dehydration and formation of additional intramolecular five- and three-membered rings force changes in the conformation of the pyranose ring. Above all, the existence of the epoxy ring shortens the bond C(2)-C(3) from 1.53 to 1.46 Å. The crystal packing is determined by two independent hydrogen-bonding systems, which form infinite chains around the screw axes parallel to the a and b axes, respectively.

Introduction

Several anhydro sugars have been reported recently, since they are considered as possible intermediates in some metabolisms (Isaacs & Kennard, 1970) and since they can be used in the synthesis of derivatives (Carvalho & Schuerch, 1959).

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The dehydration of pyranoses to form the anhydrides results in the formation of additional intramolecular rings. For example, the dicyclic ring system of 1,6-anhydro-β-D-glucopyranose (I) is the anhydride of D-glucopyranose (II), and the tricyclic ring system of 1,6:2,3-dianhydro-β-D-gulopyranose (III) is the dianhydride of β-D-gulopyranose (IV). The structure of (I) is known from an X-ray crystal structure analysis by Park, Kim & Jeffrey (1971). The structure of (III) was determined to investigate the conformation of the mol-