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The Absolute Configuration of the $(-)_{589}$-Oxalatobis(ethylenediamine)-cobalt(III) Ion as Determined by X-Ray Structure Analysis

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The absolute configuration of $(-)_{589}$-[Co ox $en_2]^+$ has been determined by the X-ray diffraction method. The crystals of $(-)_{589}$-[Co ox en_2]Br·H_2O are orthorhombic, with the space group $P2_12_12_1$, and the unit cell dimensions are: $a=16.67(1)$Å, $b=12.40(1)$Å, $c=6.183(7)$Å, and $Z=4$. The crystal structure was solved by the conventional Patterson and Fourier methods, and refined by the least-squares procedure to an R factor of 9.97%. The cobalt atom has an octahedral coordination, being chelated by an oxalate anion and two ethylenediamine molecules which are of the *ob-lel* conformation. The absolute configuration of the complex cation can be denoted as $\Delta(\delta\lambda)$.

In previous papers, the crystal structures of $(+)_{589}$-[$CoCl_2en_2$]Cl·$H_2O$$^{1)}$ and $(+)_{589}$-[$Co(CN)_2en_2$]Cl·$H_2O$$^{2)}$ have been reported. The absolute configurations of the complex cations in these compounds are consistent with those assigned spectroscopically.$^{3-7)}$ As a part of our X-ray studies of the absolute configurations of cobalt(III) complexes with C_2-symmetry, we have now determined the absolute crystal structure of $(-)_{589}$-[Co ox en_2]Br·H_2O (ox=oxalate anion).$^{8)}$

Experimental

The red plate-like crystals of $(-)_{589}$-[Co ox en_2]Br·H_2O were kindly provided by Dr. Jinsai Hidaka of Osaka University.

The unit cell dimensions were obtained by the least-squares refinement, using the θ values from zero-layer Weissenberg photographs on which powder lines of sodium chloride were super-imposed for calibration.

The crystal data are: FW=365.0; orthorhombic, $a=16.67(1)$Å, $b=12.40(1)$Å, $c=6.183(7)$Å; $Z=4$, $\mu=79.4\ \mathrm{cm}^{-1}$ (for Ni$K\alpha$); space group $P2_12_12_1$ from systematic absences.

The intensities were estimated visually from the Weissenberg photographs of the *hk*0—*hk*3 and *h*0*l*—*h*6*l* layers taken by means of the multiple-film and equi-inclination techniques. After they had been corrected for the Lp-factor, spot-shape,$^{9)}$ and absorption, they were placed on a common arbitrary scale by internal correlation. A total of 1185 reflections were obtained; however, 91 of these were too weak to be observed and were assumed to be zero. The crystal specimens used for the data collection were cylinders 0.35 mm in diameter, the cylindrical axes being parallel to the b and c axes respectively.

Determination of the Crystal Structure

The initial coordinates for the cobalt and bromine atoms were deduced from a three-dimensional Patterson function. From the first Fourier synthesis phased on

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TABLE 1. THE FINAL ATOMIC COORDINATES, TEMPERATURE FACTORS, AND THEIR e.s.d.'s.[a] TEMPERATURE FACTORS ARE OF THE FOFM: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.6844(1)	0.2936(2)	0.8988(4)	0.0026(1)	0.0041(1)	0.0227(6)	0.0009(2)	−0.0005(4)	−0.0002(7)
Co	0.4904(2)	0.4080(2)	0.4283(6)	0.0025(1)	0.0034(1)	0.0183(9)	0.0004(2)	0.0004(6)	0.0002(10)
H_2O	0.223 (1)	0.753 (2)	0.091 (3)	0.0057(9)	0.0206(27)	0.0319(60)	−0.0107(26)	0.0029(48)	−0.0087(90)
O_1	0.452 (1)	0.362 (1)	0.710 (2)	0.0028(5)	0.0024(7)	0.0182(40)	0.0018(11)	0.0011(25)	−0.0009(36)
O_2	0.542 (1)	0.268 (1)	0.416 (2)	0.0033(5)	0.0027(8)	0.0151(34)	0.0015(10)	−0.0005(27)	−0.0013(39)
O_3	0.449 (1)	0.215 (1)	0.918 (2)	0.0044(6)	0.0041(9)	0.0171(37)	0.0004(13)	0.0034(30)	−0.0009(47)
O_4	0.541 (1)	0.112 (1)	0.596 (3)	0.0034(5)	0.0025(7)	0.0184(38)	0.0005(10)	−0.0015(29)	0.0036(42)
N_1	0.427 (1)	0.543 (1)	0.444 (3)	0.0016(5)	0.0023(9)	0.0279(59)	0.0009(11)	−0.0008(32)	−0.0048(50)
N_2	0.396 (1)	0.345 (1)	0.284 (3)	0.0018(5)	0.0033(10)	0.0196(49)	−0.0010(12)	−0.0008(29)	−0.0021(45)
N_3	0.542 (1)	0.446 (1)	0.151 (3)	0.0032(6)	0.0034(10)	0.0136(45)	0.0000(14)	0.0007(29)	0.0013(43)
N_4	0.585 (1)	0.476 (1)	0.569 (3)	0.0018(5)	0.0031(9)	0.0160(44)	−0.0015(11)	−0.0032(19)	0.0018(48)
C_1	0.341 (1)	0.514 (2)	0.404 (4)	0.0020(6)	0.0053(14)	0.0260(64)	0.0021(16)	0.0025(42)	−0.0008(74)
C_2	0.340 (1)	0.434 (2)	0.213 (4)	0.0030(8)	0.0031(12)	0.0302(75)	0.0007(16)	−0.0037(43)	−0.0061(61)
C_3	0.607 (1)	0.530 (2)	0.192 (4)	0.0032(8)	0.0037(13)	0.0248(68)	−0.0029(17)	−0.0019(42)	0.0051(59)
C_4	0.649 (1)	0.495 (2)	0.401 (4)	0.0024(7)	0.0066(16)	0.0272(69)	−0.0010(18)	0.0028(47)	0.0039(63)
C_5	0.524 (1)	0.208 (1)	0.575 (3)	0.0022(6)	0.0033(10)	0.0056(37)	−0.0011(14)	−0.0035(29)	−0.0015(54)
C_6	0.470 (1)	0.265 (1)	0.756 (4)	0.0023(7)	0.0031(12)	0.0207(57)	0.0013(15)	0.0002(38)	0.0041(56)

a) In order to represent the correct absolute configuration, the atomic coordinates in Table 1 should be set up in the left-handed system.

these two heavy atoms, all the non-hydrogen atoms were located. The structure was initially refined by four cycles of block-diagonal-matrix least-squares to an R factor of 12%, with an assumption of isotropic temperature factors, equal weights being employed for all reflections. The function minimized was $\sum w(|F_0|-|F_c|)^2$.

In the subsequent refinement, anisotropic thermal parameters were used. The weighting scheme employed was as follows:

$$w = 0.3 \quad \text{for } F_0 < 6.1$$
$$w = 1.0 \quad \text{for } 30.6 \geq F_0 \geq 6.1$$
$$w = 30.6/F_0 \quad \text{for } F_0 > 30.6$$

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[10] The real part of the dispersion correction was applied for the cobalt atom.[11] The three cycles of the least-squares calculation improved the R factor to 9.97%. In the last cycle, the shifts in the atomic coordinates were less than $(^1/_{10})\sigma$ for heavy atoms and less than $(^1/_8)\sigma$ for light atoms. A difference synthesis of the electron density computed at this stage confirmed the crystal structure, though no peaks corresponding to any of the hydrogen atoms were yielded. The final atomic coordinates, the temperature factors, and their e.s.d.'s are given in Table 1. A complete list of the calculated and observed structure factors is preserved by the Chemical Society of Japan.[12]

In order to determine the absolute configuration of the complex cation, the oscillation photographs were taken with Cu$K\alpha$ radiation about the c axis. Some Bijvoet pairs, indicative of appreciable anomalous intensity differences, are listed in Table 2, together with the observed inequality relationships. The right-handed coordinate system for the reciprocal lattice was carefully used throughout the present work. The values of F_c^2 shown in Table 2 were calculated on the basis of the set of atomic coordinates given in Table 1. A comparison of the observed inequality relationships with the calculated ones indicates that the model used in the calculations is a mirror image of the absolute structure of the crystal.

TABLE 2. CALCULATED AND OBSERVED INTENSITIES

h	k	l	$F_c^2(hkl)$	Obsd.	h	k	$\bar{l}$	$F_c^2(hk\bar{l})$
8	3	1	149	>	8	3	$\bar{1}$	903
13	3	1	223	<	13	3	$\bar{1}$	99
12	4	1	559	<	12	4	$\bar{1}$	168
3	5	1	652	<	3	5	$\bar{1}$	219
8	6	1	936	<	8	6	$\bar{1}$	342
12	6	1	682	>	12	6	$\bar{1}$	1634
1	7	1	677	>	1	7	$\bar{1}$	1556
10	7	1	2937	<	10	7	$\bar{1}$	1317
1	8	1	1361	<	1	8	$\bar{1}$	768
6	9	1	1074	<	6	9	$\bar{1}$	474
9	6	1	1986	>	9	6	$\bar{1}$	3251
9	1	1	3248	>	9	1	$\bar{1}$	5366
9	2	1	1001	>	9	2	$\bar{1}$	1587
4	3	1	3920	>	4	3	$\bar{1}$	6553

Discussion

The crystal structure viewed along the c axis is shown in Fig. 1. The crystal is composed of $(-)_{589}$-[Co ox en$_2$]$^+$ complex cations, bromide anions, and water molecules, these being held together mainly by ionic forces. The hydrogen bonds are summarized in Table 3. One of the hydrogen atoms in the NH_2 groups involving N_1, N_2, and N_3, and both of the H atoms

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10) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

11) R. W. James, "The Optical Principles of the Diffraction of X-rays," G. Bell & Sons, London (1948), p. 608.

12) The complete data of the F_o-F_c table are kept as Document No. 7301 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number.

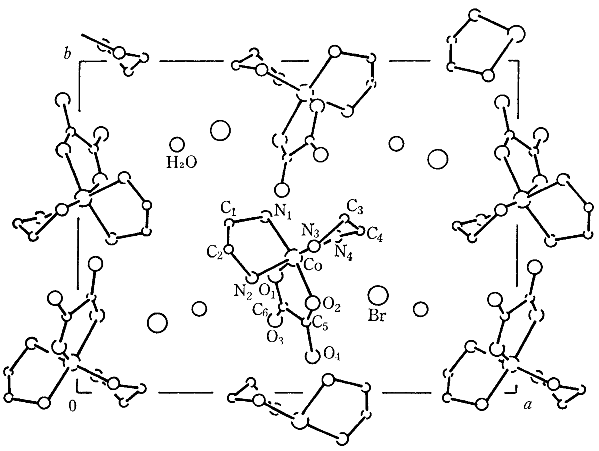


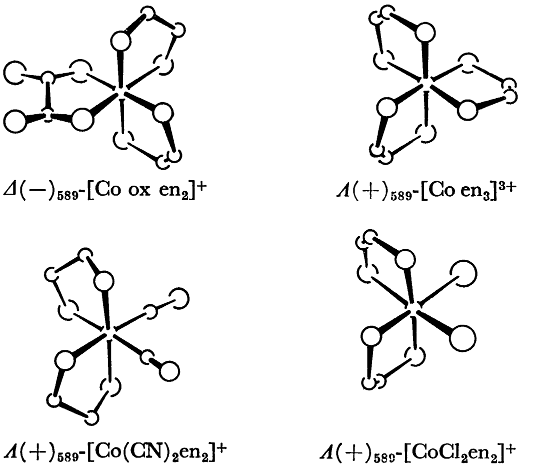
Fig. 1. The structure viewed along the *c* axis.

Table 3. Possible N-H···B hydrogen bonds

The positions of the hydrogen atoms in the NH_2 groups were calculated on the assumption that the N-H bond length is 1.03Å.

N···B		N···B	H···B	∠N-H-B
N_1	O(1−*x*, 1/2+*y*, 1/2−*z*)	2.92Å	2.01Å	146°
N_2	H_2O(1/2−*x*, 1−*y*, 1/2+*z*)	3.01	2.02	160
N_3	Br	3.41	2.47	151
N_4	Br	3.47	2.46	167
N_4	O_3(1−*x*,1/2+*y*, 1/2−*z*)	3.02	2.11	146
Br	H_2O(1−*x*, −1/2+*y*, 1/2−*z*)	3.44		

linked to N_4, participate in the hydrogen bonding, in which the oxygen atom ($O_{(H_2O)}$) or $O_{(C=O)}$) or the bromide ion takes part as the base of the hydrogen bonds. Similarly, one of the water hydrogen atoms participates in the O–H—Br^- hydrogen bond, while the other appears to remain indifferent to any hydrogen bonding.



$\Delta(-)_{589}$-[Co ox $en_2]^+$

$\Lambda(+)_{589}$-[Co $en_3]^{3+}$

$\Lambda(+)_{589}$-[Co$(CN)_2en_2]^+$

$\Lambda(+)_{589}$-[$CoCl_2en_2]^+$

Fig. 2. The absolute configurations of the complex ions.

The absolute configuration of the complex ion is depicted in Fig. 2. It is in accordance with that assigned before by several workers[3–7] and should be denoted as $\Delta(\delta\lambda)$. In the figure, the absolute configurations of $(+)_{589}$-[Co$(CN)_2en_2]^+$,[2] $(+)_{589}$-[$CoCl_2$-$en_2]^+$,[1] and $(+)_{589}$-[Co $en_3]^{3+}$ [13] are also shown as references. The oxalate ion is planar, while the ethylenediamine molecules assume the "gauche" form and are disposed in the conformation of the *ob-lel* type.

By analogy with the trisethylenediamine complex,[14] the intramolecular potential energy of the bisethylenediamine complex increases in the order of *lel-lel*<*ob-lel*<*ob-ob*.[15] However, since the potential energy difference between the least stable and the most stable conformers may be about 0.2 kcal/mol in the case of [Co ox $en_2]^+$,[16] this complex could more readily assume less stable conformations than in the case of the trisethylenediamine complex. Although the hydrogen bonds in which the hydrogen atoms of NH_2 groups participate play an important role in stabilizing the

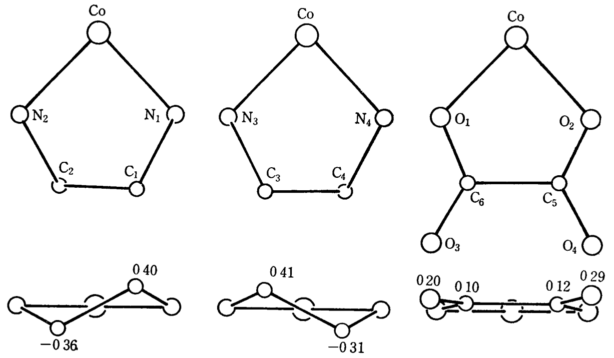


Fig. 3. The elevations and projections of the three chelate rings.

Table 4. The bond distances and angles in the complex ion

Co–N_1	1.99(2)Å	N_1–Co–N_2	86(1)°
Co–N_2	1.97(2)	N_3–Co–N_4	86(1)
Co–N_3	1.98(2)	O_1–Co–O_2	85(1)
Co–N_4	1.99(2)	Co–N_1–C_1	107(2)
Co–O_1	1.94(2)	Co–N_2–C_2	110(2)
Co–O_2	1.94(2)	Co–N_3–C_3	109(2)
N_1–C_1	1.50(3)	Co–N_4–C_4	109(2)
N_2–C_2	1.51(3)	Co–O_1–C_6	114(2)
N_3–C_3	1.51(3)	Co–O_2–C_5	112(2)
N_4–C_4	1.51(3)	N_1–C_1–C_2	107(2)
O_1–C_6	1.27(3)	N_2–C_2–C_1	104(2)
O_2–C_5	1.27(3)	N_3–C_3–C_4	106(2)
O_3–C_6	1.23(3)	N_4–C_4–C_3	107(2)
O_4–C_5	1.23(3)	O_1–C_6–C_5	113(2)
C_1–C_2	1.55(4)	O_2–C_5–C_6	115(2)
C_3–C_4	1.54(4)	O_3–C_6–C_5	120(2)
C_5–C_6	1.60(3)	O_4–C_5–C_6	119(2)
		O_1–C_6–O_3	127(2)
		O_2–C_5–O_4	126(2)

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[14] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[15] In this paper we have discussed the relative instability of the respective conformer of bisethylenediamine complex on the basis of the instability order *lel-lel-lel*<*ob-lel-lel*<*ob-ob-lel*<*ob-ob-ob*, for trisethylenediamine complex given by Corey and Bailar. However, Hawkins *et al.* have recently pointed out that this instability order should be revised to *lel-lel-lel*≃*ob-lel-lel*<*ob-ob-lel*<*ob-ob-ob* (*Inorg. Chem.*, **9**, 576 (1969)).

[16] F. P. Dwyer, T. E. McDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **85**, 661 (1963).

less stable conformers of [Cr en_3]$^{3+}$,[17] this is not likely to be the case for the bisethylenediamine complex, as has been stated elsewhere.[1,2] Thus, the specific conformation of the bisethylenediamine complex might be mainly due to the crystal packing.

The projections and elevations of the three chelate rings are illustrated in Fig. 3. Although the oxalate chelate ring is nearly planar, the (O_1, C_6, O_3) plane is slant against the (O_2, C_5, O_4) plane by 4.3°, which is considerably less than the value (17°, on average) found in K_2[Cu ox_2]·$2H_2O$.[18] The plane of the oxalate ion is bent away from the (Co, O_1, O_2) plane by 6.4°. Probably this also comes from the crystal packing. The bond length of C_5–C_6 (1.60 Å) is considerably longer than that for the usual C(sp^2)–C(sp^2) but it is comparable to that found in $K_2C_2O_4\cdot 2H_2O$ (1.573 Å).[19] In each of the two ethylenediamine chelate rings, one carbon atom is disposed above, and the other, below, the plane defined by the cobalt and two nitrogen atoms. The bond lengths and angles within the chelate rings are quite normal (Table 4).

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