Structural Study of Optical Resolution. VI. The Crystal Structure of $(+)_{589}$-*cis*-Chloroamminebis(ethylenediamine)cobalt(III) *d*-3-Bromocamphor-9-sulfonate Monohydrate

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The crystal structure of *cis*-chloroamminebis(ethylenediamine)cobalt(III) *d*-3-bromocamphor-9-sulfonate monohydrate, $(+)_{589}$-$[CoClNH_3(en)_2](d\text{-}BCS)_2\cdot H_2O$, has been determined by three-dimensional X-ray analysis. The deep red crystals are orthorhombic, space group $P2_12_12_1$, with four formula units in the unit cell of dimensions $a=34.97(2)$, $b=14.25(1)$, and $c=7.08(1)$ Å. The calculated density of 1.64 g·cm^{-3} compares well with the observed density 1.65 g·cm^{-3}. The structure has been refined by the block -diagonal least-squares method to an *R*-factor of 0.096 for 2662 reflection data points. In the complex cation, one of the two ethylenediamine chelate rings has a "50% *ob*, 50% *lel*" type disordered character in its conformation and the other ring is in a "*lel*" type. The absolute configuration of the complex cation is denoted as $\Lambda[(50\%\lambda, 50\%\delta)\delta]$, which was determined by comparison with that of the *d*-BCS anion. There are notable differences between the two crystallographically independent *d*-BCS anions with respect to their local packing modes.

Historically, *cis*-chloro- and -bromo-amminebis(ethylenediamine)cobalt(III) cations, *cis*-$[CoXNH_3(en)_2]^{2+}$ (X=Cl$^-$ and Br$^-$), were first resolved by Werner and King;[1] their hypothesis of octahedral coordination was thereby confirmed.[1,2] In their study of optical resolution, silver *d*-3-bromocamphor-9-sulfonate, *d*-BCS·Ag, was employed as a resolving agent. Since then, optical resolutions of many metal complexes were performed using this agent.[3]

Recently, we reported the crystal structure of *cis*-dichlorobis(ethylenediamine)cobalt(III) *d*-3-bromocamphor-9-sulfonate, $(+)_{589}$-$[CoCl_2(en)_2]d$-BCS, as a part of our structural studies of optical resolution,[4-8] and found an interesting "face-to-face type" close contact of the complex cation with the bromocamphor part of the *d*-BCS anion.

It is of interest to compare the structural features of the diastereoisomer, $(+)_{589}$-$[CoClNH_3(en)_2]$ $(d\text{-}BCS)_2\cdot H_2O$, with that of the previously determined $(+)_{589}$-$[CoCl_2(en)_2]d$-BCS. Moreover, the absolute configuration of *cis*-$[CoClNH_3(en)_2]^{2+}$ cation has not been determined by the X-ray method.[9] Therefore, the X-ray crystal structure analysis of the title compound was undertaken.

Experimental

The racemic *cis*-$[CoClNH_3(en)_2]Cl$ was prepared by the published method.[10] The racemic complex was resolved by the method of Garbett and Gillard, using *d*-BCS·NH_4 as a resolving agent.[9] The deep red crystals thus obtained were recrystallized from hot aqueous solution. Well formed crystals were separated out. Found: C, 33.01; H, 5.68; N, 7.98%. Calcd for $C_{24}H_{49}O_9N_5S_2ClBr_2Co$: C, 33.13; H, 5.68; N, 8.05%.

The unit cell dimensions were determined by the least-squares refinement of the *hk*0, *h*0*l*, 0*kl*, reflection data recorded on Weissenberg photographs. The sodium chloride diffraction lines were superimposed on the films for calibration. The crystal data are as follows: orthorhombic, $a=34.97(2)$, $b=14.25(1)$. $c=7.08(1)$ Å; $D_c=1.65$ g·cm^{-3} (by flotation in chloroform-bromoform mixture); $Z=4$; and $D_c=1.64$ g·cm^{-3}. From the systematic absence for *h*00 ($h=2n+1$), 0*k*0 ($k=2n+1$), and 00*l*($l=2n+1$), the space group is $P2_12_12_1$.

A crystal 0.65 mm long with a cross-sectional area of (0.20×0.23) mm^2 was adopted for recording the *hk*0—*hk*4 intensity data with Ni *K*α radiation, using the multiple-film equi-inclination Weissenberg technique. Another crystal, 0.42 mm long with (0.27×0.31) mm^2 cross-sectional area, was used to record the intensity data of *h*0*l*. The intensities were estimated visually with a calibrated intensity scale. The range of relative intensities was 1—3322. A total of 2662 independent reflections were used for the structure determination. Lorentz, polarization, and spot-shape corrections were applied in the usual manner; corrections for absorption were not made since the linear absorption coefficient, μ(Ni *K*α), was 72.6 cm^{-1} ($\mu r=0.78$ for the former crystal).

Determination and Refinement of Crystal Structure

The structure was solved by the heavy-atom method. The positions of the two bromine atoms were easily found from the three-dimensional Patterson map. The subsequent Fourier synthesis revealed the positions of all the non-hydrogen atoms, excluding one water molecule. The position of the water molecule was found in the difference map which was synthesized at the stage of $R=0.16$ after the block-diagonal least-squares refinement of the other atoms for the 2662 observed reflections, where the *R*-value is $\Sigma||F_o|-|F_c||/\Sigma|F_o|$. The difference map showed a peak with the height of 4.0 e/Å^3 at the position $x=0.223$, $y=0.954$, and $z=0.275$. The presence of one water molecule was suggested by the elemental analysis for this compound. Thus, the peak was interpreted as due to a water molecule of crystallization.

Four cycles of further refinement with isotropic temperature factors for all the non-hydrogen atoms reduced the *R*-value to 0.14. The refinement(excluding the hydrogen atoms) was continued by applying anisotropic temperature factors for Br, Co, Cl, and S atoms and isotropic ones for O, N, and C atoms. After three cycles an *R*-value of 0.105 was obtained.

However, the value of the isotropic temperature factor of C(E2) was rather high($B=9.1$ Å^2) and the

TABLE 1. THE RATIOS(*ob* : *lel*) AND THE VALUES OF *R*-FACTORS, ISOTROPIC TEMPERATURE FACTORS, SELECTED BOND LENGTHS, AND BOND ANGLES

Ratios(*ob* : *lel*)	10 : 0	8 : 2	6 : 4	5 : 5	4 : 6	2 : 8
R-values(%)	10.49	9.81	9.64	9.63	9.64	9.83
Atoms			Temperature factors B(Å)^2			
C(E1A)(*ob*)	3.9	3.8	2.5	1.7	0.7	−1.6
C(E2A)(*ob*)	9.1	5.6	3.8	2.7	1.4	−0.9
C(E1B)(*lel*)	—	−0.2	1.5	2.5	3.2	4.2
C(E2B)(*lel*)	—	−1.0	2.2	3.6	4.6	6.5
C(E3)	2.6	2.6	2.6	2.6	2.6	2.5
C(E4)	2.7	2.8	2.8	2.8	2.8	2.8
			Distances (Å)			
N(1)-C(E1A)(*ob*)	1.52(4)	1.48(5)	1.48(5)	1.49(6)	1.50(6)	1.54(14)
N(1)-C(E1B)(*lel*)	—	1.56(13)	1.54(6)	1.53(6)	1.53(5)	1.51(5)
N(2)-C(E2A)(*ob*)	1.59(6)	1.53(5)	1.55(6)	1.56(6)	1.57(7)	1.62(14)
N(2)-C(E2B)(*lel*)	—	1.52(14)	1.50(8)	1.49(7)	1.49(6)	1.48(6)
C(E1A)-C(E2A)(*ob*)	1.32(6)	1.43(6)	1.48(7)	1.50(8)	1.52(9)	1.60(19)
C(E1B)-C(E2B)(*lel*)	—	1.51(19)	1.44(9)	1.42(8)	1.41(8)	1.37(7)
N(3)-C(E3)	1.45(4)	1.44(4)	1.44(4)	1.44(4)	1.44(4)	1.44(4)
N(4)-C(E4)	1.52(4)	1.52(4)	1.52(4)	1.52(4)	1.52(4)	1.52(4)
C(E3)-C(E4)	1.49(4)	1.45(4)	1.45(4)	1.45(4)	1.45(4)	1.45(4)
			Angles (°)			
Co-N(1)-C(E1A)(*ob*)	109(2)	109(2)	109(2)	110(2)	110(2)	110(5)
Co-N(1)-C(E1B)(*lel*)	—	110(5)	110(2)	109(2)	109(2)	109(2)
Co-N(2)-C(E2A)(*ob*)	106(2)	107(2)	107(2)	106(2)	106(3)	105(5)
Co-N(2)-C(E2B)(*lel*)	—	102(5)	104(3)	105(3)	105(3)	106(2)
Co-N(3)-C(E3)	112(2)	113(2)	113(2)	113(2)	113(2)	113(2)
Co-N(4)-C(E4)	108(2)	109(2)	109(2)	109(2)	109(2)	108(2)

resulting C(E1)–C(E2) distance, 1.32 Å, was fairly short. These results were observed also in several ethylenediamine metal complexes.[11]

Recently, Brouty *et al.* reported the crystal structure of the racemic tris(ethylenediamine)chromium(III) thiocyanate. They found the same character in its ethylenediamine ring, and tried to explain this anomaly more precisely.[12]

According to their approach, the difference map was recalculated after excluding the C(E1) and C(E2) atoms. Three peaks appeared in the map: two spherical peaks([peak I] 2.0 e/Å^3, x=0.202, y=0.770, z=0.935; [peak II] 2.2 e/Å^3, x=0.216, y=0.736, z=0.900) and one elongated peak([peak III] 3.2 e/Å^3, x=0.223, y=0.826, z=0.840). The occurrence of the "*ob-lel*" type disorder in the N(1)–C(E1)–C(E2)–N(2) ethylenediamine chelate ring[13] was thus suggested. The normal "*ob*" and "*lel*" models of the ethylenediamine ring were set up.[14] We tried to fit these models to the corresponding peaks in the difference map. The resulting positions of the four carbon atoms, C(E1A)–C(E2A) (*ob*) and C(E1B)–C(E2B) (*lel*), were included in the calculations for further refinement.

Five models with different ratios of the population of the C(E1A) and C(E2A) atoms to that of C(E1B) and C(E2B), (20% *ob*, 80% *lel*), (40, 60), (50, 50), (60, 40), and (80, 20), were refined. The starting values of the isotropic temperature factors of these four carbon atoms were set at 3.5 Å^2 (the average value of the other carbon atoms in this crystal at the stage of R=0.105). Hydrogen atom coordinates(excluded the water molecule and the methyl- and ammine- groups) were calculated(C–H 1.05, N–H 1.00 Å) assuming tetrahedral angles at carbon and nitrogen. Contributions from these forty hydrogen atoms with fixed positions and an isotropic temperature factor of B=3.5 Å^2 were also included in further least-squares iterations.

After three cycles of refinement based on the respective models, the best conventional *R*-value 0.096 was attained for the 50%-*ob*/50%-*lel* model. In the region of the corresponding four carbon atoms, a final difference map of this model showed no peak higher than 0.5 e/Å^3.

The final values of *R*-factors, isotropic temperature factors, and selected bond lengths and bond angles in the above five models are summarized in Table 1. These results suggest that the most probable ratio of conformational distribution of this ethylenediamine ring is 50%-*ob* and 50%-*lel*.

The quantity minimized was $w(|F_o|-k|F_c|)^2$ and the weighting scheme employed was w=1.0 for $F_o \geq 6.3(2.5 \times F_{min})$ and w=0.5 for $F_o < 6.3$. The atomic scattering factors for the Br^-, Co^{3+}, and Cl^- ions and for the neutral S, O, N, C, and H atoms were taken from Ref. 15. The dispersion effects were neglected.

All the computations were carried out by a HITAC-8700 computer at the Hiroshima University Computer Center. The computer programs used were FOUR-

TABLE 2. POPULATIONS(m) AND FINAL ATOMIC PARAMETERS AND TEMPERATURE FACTORS (with their e.s.d.'s)

Atom	m	x	y	z	B
Br(A)	1.0	0.0070(1)	0.4388(2)	0.7312(6)	a)
Br(B)	1.0	0.2073(1)	0.5114(2)	1.1067(6)	a)
Co	1.0	0.1647(1)	0.7793(3)	0.5904(7)	a)
Cl	1.0	0.2073(2)	0.6952(4)	0.4184(11)	a)
S(A)	1.0	0.0739(2)	0.6862(5)	0.0552(11)	a)
S(B)	1.0	0.1754(2)	0.0844(4)	0.9176(12)	a)
O(A1)	1.0	0.0860(5)	0.770(1)	0.154(3)	4.2(4)
O(A2)	1.0	0.0950(5)	0.603(1)	0.112(3)	5.0(4)
O(A3)	1.0	0.0734(5)	0.700(1)	−0.144(3)	4.2(4)
O(A4)	1.0	−0.0578(5)	0.601(1)	0.645(3)	4.8(4)
O(B1)	1.0	0.2010(5)	0.113(1)	1.066(3)	4.8(4)
O(B2)	1.0	0.1487(5)	0.010(1)	0.973(3)	3.7(4)
O(B3)	1.0	0.1984(5)	0.057(1)	0.751(3)	4.1(4)
O(B4)	1.0	0.1591(5)	0.515(1)	0.716(3)	3.6(4)
N(1)	1.0	0.2072(5)	0.862(1)	0.662(3)	2.3(3)
N(2)	1.0	0.1774(5)	0.707(1)	0.825(3)	2.8(4)
N(3)	1.0	0.1260(5)	0.856(1)	0.718(3)	2.7(4)
N(4)	1.0	0.1521(5)	0.859(1)	0.372(3)	2.8(4)
N(5)	1.0	0.1244(5)	0.684(1)	0.528(3)	2.2(3)
C(E1A)	0.5	0.2199(11)	0.839(3)	0.857(7)	1.7(8)
C(E2A)	0.5	0.2189(12)	0.735(3)	0.879(8)	2.7(9)
C(E1B)	0.5	0.2300(12)	0.817(3)	0.822(8)	2.5(9)
C(E2B)	0.5	0.2023(14)	0.771(4)	0.937(9)	3.6(10)
C(E3)	1.0	0.1042(6)	0.913(1)	0.589(4)	2.6(4)
C(E4)	1.0	0.1301(6)	0.944(2)	0.441(4)	2.8(4)
WO	1.0	0.2230(5)	0.954(1)	0.279(3)	4.2(4)
C(A1)	1.0	−0.0304(7)	0.607(2)	0.321(4)	3.1(5)
C(A2)	1.0	−0.0312(7)	0.591(2)	0.544(4)	3·2(5)
C(A3)	1.0	0.0093(6)	0.560(2)	0.611(4)	3.0(5)
C(A4)	1.0	0.0334(6)	0.560(1)	0.408(4)	2.2(4)
C(A5)	1.0	0.0193(6)	0.480(2)	0.293(4)	3.0(5)
C(A6)	1.0	−0.0255(7)	0.506(2)	0.246(5)	3.5(5)
C(A7)	1.0	0.0132(6)	0.647(2)	0.311(4)	2.8(5)
C(A8)	1.0	0.0168(7)	0.738(2)	0.420(5)	3.4(5)
C(A9)	1.0	0.0244(6)	0.665(2)	0.108(4)	3.0(5)
C(A10)	1.0	−0.0619(7)	0.661(2)	0.238(5)	3.5(5)
C(B1)	1.0	0.1364(6)	0.358(2)	0.791(4)	2.5(4)
C(B2)	1.0	0.1645(6)	0.440(2)	0.788(4)	3.0(5)
C(B3)	1.0	0.1986(7)	0.412(2)	0.915(5)	3.4(5)
C(B4)	1.0	0.1874(7)	0.319(2)	0.991(4)	3.7(6)
C(B5)	1.0	0.1502(8)	0.334(2)	1.126(5)	4.1(6)
C(B6)	1.0	0.1164(7)	0.364(2)	0.981(5)	3.9(6)
C(B7)	1.0	0.1665(6)	0.274(2)	0.813(4)	2.4(4)
C(B8)	1.0	0.1961(7)	0.264(2)	0.650(4)	3.5(5)
C(B9)	1.0	0.1459(6)	0.180(2)	0.852(4)	2.4(4)
C(B10)	1.0	0.1086(7)	0.353(2)	0.615(5)	3.9(6)

a) See Table 3.

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS($\times 10^3$) EXPRESSED IN THE FORM $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(A)	80(2)	71(2)	37(2)	3(2)	14(4)	17(2)
Br(B)	117(3)	45(1)	73(3)	−8(2)	−44(3)	−7(2)
Co	55(2)	47(2)	36(3)	−1(2)	2(2)	−2(2)
Cl	44(3)	41(3)	26(5)	6(3)	4(3)	−10(4)
S(A)	40(3)	61(4)	12(5)	−12(3)	4(3)	3(4)
S(B)	47(3)	25(3)	38(6)	1(2)	−10(4)	−4(4)

TABLE 4. BOND DISTANCES AND ANGLES(e.s.d.'s in parentheses)
The values of BCS(B) is shown in square brackets.

(a) Bond lengths (Å)			
Co-N(1)	1.96(2)	S(A)-O(A1)	1.45(2)[1.44(3)]
Co-N(2)	2.00(2)	S(A)-O(A2)	1.45(3)[1.47(2)]
Co-N(3)	1.96(2)	S(A)-O(A3)	1.42(2)[1.48(2)]
Co-N(4)	1.97(2)	S(A)-C(A9)	1.80(3)[1.78(3)]
Co-N(5)	2.00(2)	O(A4)-C(A2)	1.18(4)[1.19(4)]
Co-Cl	2.27(1)	Br(A)-C(A3)	1.93(3)[1.99(3)]
N(1)-C(E1A)	1.49(6)	C(A1)-C(A2)	1.60(4)[1.53(4)]
N(1)-C(E1B)	1.53(6)	C(A2)-C(A3)	1.56(4)[1.55(4)]
N(2)-C(E2A)	1.56(6)	C(A3)-C(A4)	1.67(4)[1.48(5)]
N(2)-C(E2B)	1.49(7)	C(A4)-C(A5)	1.49(4)[1.63(5)]
N(3)-C(E3)	1.44(4)	C(A5)-C(A6)	1.64(4)[1.62(5)]
N(4)-C(E4)	1.52(4)	C(A1)-C(A6)	1.55(4)[1.52(4)]
C(E1A)-C(E2A)	1.50(8)	C(A1)-C(A7)	1.63(4)[1.61(4)]
C(E1B)-C(E2B)	1.42(8)	C(A1)-C(A10)	1.47(4)[1.58(5)]
C(E3)-C(E4)	1.45(4)	C(A4)-C(A7)	1.58(4)[1.60(4)]
		C(A7)-C(A8)	1.52(4)[1.55(4)]
		C(A7)-C(A9)	1.51(4)[1.54(4)]
(b) Bond angles (°)			
N(1)-Co-N(2)	86(1)	N(1)-Co-Cl	88(1)
N(3)-Co-N(4)	84(1)	N(2)-Co-Cl	92(1)
N(1)-Co-N(5)	174(1)	N(3)-Co-Cl	175(1)
N(2)-Co-N(5)	90(1)	N(4)-Co-Cl	92(1)
N(3)-Co-N(5)	90(1)	N(5)-Co-Cl	89(1)
N(4)-Co-N(5)	93(1)		
Co-N(1)-C(E1A)	110(2)	N(1)-C(E1A)-C(E2A)	108(4)
Co-N(1)-C(E1B)	109(2)	N(1)-C(E1B)-C(E2B)	105(4)
Co-N(2)-C(E2A)	106(2)	N(2)-C(E2A)-C(E1A)	104(4)
Co-N(2)-C(E2B)	105(3)	N(2)-C(E2B)-C(E1B)	112(5)
Co-N(3)-C(E3)	113(2)	N(3)-C(E3)-C(E4)	107(2)
Co-N(4)-C(E4)	109(2)	N(4)-C(E4)-C(E3)	108(2)
C(A2)-C(A1)-C(A6)	102(2)[106(2)]	C(A2)-C(A1)-C(A7)	96(2)[99(2)]
C(A2)-C(A1)-C(A10)	117(3)[115(2)]	C(A6)-C(A1)-C(A7)	102(2)[105(2)]
C(A6)-C(A1)-C(A10)	116(3)[115(3)]	C(A7)-C(A1)-C(A10)	120(3)[116(2)]
O(A4)-C(A2)-C(A1)	127(3)[126(3)]	O(A4)-C(A2)-C(A3)	124(3)[127(3)]
C(A1)-C(A2)-C(A3)	109(2)[107(2)]	Br(A)-C(A3)-C(A2)	111(2)[109(2)]
Br(A)-C(A3)-C(A4)	114(2)[116(2)]	C(A2)-C(A3)-C(A4)	101(2)[104(3)]
C(A3)-C(A4)-C(A5)	108(2)[108(3)]	C(A3)-C(A4)-C(A7)	99(2)[101(2)]
C(A5)-C(A4)-C(A7)	102(2)[99(2)]	C(A4)-C(A5)-C(A6)	105(2)[104(2)]
C(A1)-C(A6)-C(A5)	104(2)[102(2)]	C(A1)-C(A7)-C(A4)	97(2)[94(2)]
C(A1)-C(A7)-C(A8)	111(2)[115(2)]	C(A1)-C(A7)-C(A9)	110(2)[111(2)]
C(A4)-C(A7)-C(A8)	114(2)[108(2)]	C(A4)-C(A7)-C(A9)	115(2)[115(2)]
C(A8)-C(A7)-C(A9)	109(2)[112(2)]	S(A)-C(A9)-C(A7)	118(2)[116(2)]
O(A1)-S(A)-C(A9)	109(1)[109(1)]	O(A2)-S(A)-C(A9)	107(1)[105(1)]
O(A3)-S(A)-C(A9)	103(1)[108(1)]	O(A1)-S(A)-O(A2)	113(1)[114(1)]
O(A1)-S(A)-O(A3)	112(1)[109(1)]	O(A2)-S(A)-O(A3)	113(1)[112(1)]

MMM(Fourier synthesis)[16] and HBLS-IV (Least-squares calculation) with slight modification.[17]

The final atomic parameters, temperature factors (with their estimated standard deviations) and populations(m) are listed in Tables 2 and 3. Complete lists of the $5F_o$ and $5F_c$ values and the final atomic parameters of the hydrogen atoms have been preserved by the Chemical Society of Japan(Document No. 7835).

Results and Discussion

Cation and Anion Geometries. Figure 1 shows the crystal structure viewed along the c-axis. The crystal is built up of discrete $(+)_{589}$-*cis*-$[CoClNH_3(en)_2]^{2+}$ cations, two kinds of *d*-BCS anions(denoted as *d*-BCS(A) and *d*-BCS(B)), and water molecules. The bond distances and bond angles are listed in Table 4.

In the complex cation, the bond distances and bond angles around the cobalt atom are in good agreement with those found in the previous studies.[4,18] There are two ethylenediamine rings in the complex cation. The conformation of one ethylenediamine ring(N(1)–C(E1)–C(E2)–N(2)) is in "50% *ob*(N(1)–C(E1A)–

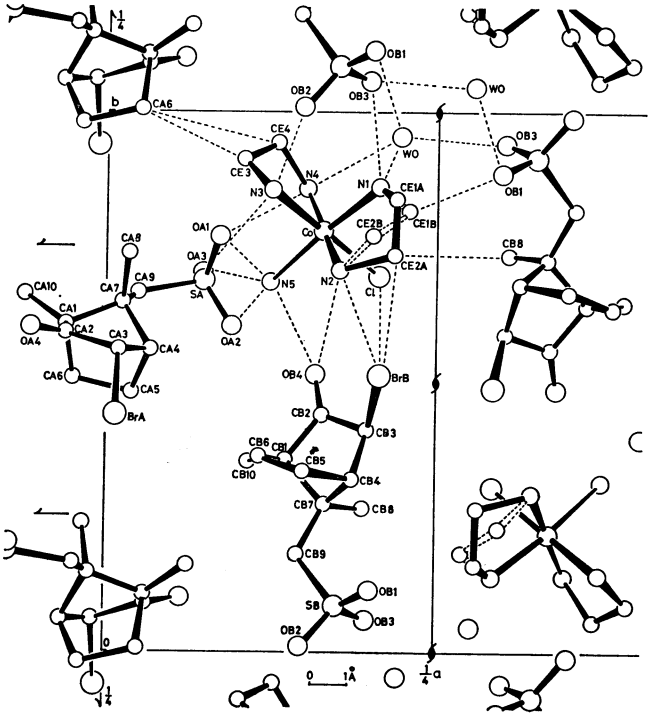

Fig. 1. A perspective drawing of the contents of the unit cell along the c-axis. Possible hydrogen bonds and short contacts are indicated by broken lines. The round brackets in the numbering scheme of the atoms are omitted.

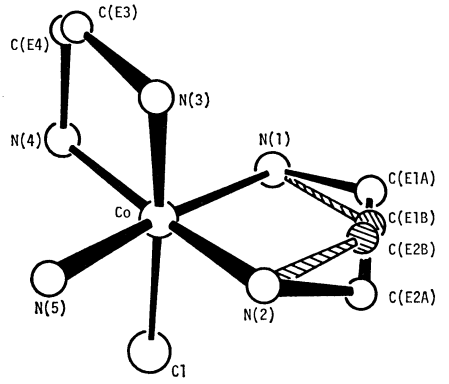

Fig. 2. The absolute configuration of the complex cation.

C(E2A)–N(2)), 50% *lel*(N(1)–C(E1B)–C(E2B)–N(2)),'' as described in the refinement part. The other ethylenediamine ring(N(3)–C(E3)–C(E4)–N(4)) is in the *lel* conformation. Thus the conformation of the two ethylenediamine rings is designated as a ''(50% *ob*, 50% *lel*), *lel*'' type.

The absolute configuration of the complex cation was assigned as *Λ* for the $(+)_{589}$-isomer, based on the *d*-BCS anion as an internal reference.[19] This configuration is in accordance with the result previously reported on the basis of spectral evidence.[9] Thus, the absolute configuration of the complex cation is denoted as *Λ*[(50% *λ*, 50% *δ*)*δ*],[13] as illustrated in Fig. 2.

Table 5. Selected intermolecular distances(≤3.53 Å)

N-H···B	N···B (Å)	H···B (Å)	∠N-H···B (°)
N(1)-H2[b]···O(B1)^{IV}	3.30	2.50	137
N(1)-H10···O(B1)^{IV}	3.30	2.63	125
N(1)-H1···O(B3)^{I}	2.87[a]	1.95	152
N(1)-H9···O(B3)^{I}	2.87[a]	1.93	156
N(1)-H2···WO	3.06[a]	2.53	113
N(1)-H10···WO	3.06[a]	2.25	138
N(2)-H3···O(B4)	2.92[a]	1.95	164
N(2)-H11···O(B4)	2.92[a]	2.27	121
N(3)-H6···O(A3)^{II}	3.05[a]	2.08	162
N(3)-H5···O(B2)^{I}	2.95[a]	1.99	159
N(4)-H7···O(A1)	3.05[a]	2.10	157
N(4)-H8···WO	2.90[a]	1.97	155
N(5)···O(A1)	3.21[a]	—	—
N(5)···O(A2)	3.32	—	—
N(5)···O(A3)^{II}	2.94[a]	—	—
N(5)···O(B4)	3.01[a]	—	—
C(E1A)-H14···O(B1)^{IV}	3.52	2.87	120
C(E1A)-H13···O(B3)^{I}	3.28	3.03	94
C(E1A)-H13···WO^{II}	3.41	2.69	126
C(E1A)-H14···WO^{II}	3.41	3.23	91
C(E1B)-H17···O(B1)^{IV}	3.18	3.05	88
C(E1B)-H18···O(B1)^{IV}	3.18	2.81	101
C(E3)-H21···O(B2)^{I}	3.43	3.01	104
C(E4)-H23···O(B2)^{III}	3.51	2.84	122
C(E4)-H24···WO	3.45	3.05	103
Br(B)···Cl^{II}	3.43	—	—
WO···O(B1)^{III}	2.83[a]	—	—
WO···O(B1)^{IV}	3.48	—	—
WO···O(B2)^{III}	3.48	—	—
WO···O(B3)^{IV}	2.76[a]	—	—
O(B2)···O(A4)^{V}	3.53	—	—
C(B9)-H39···O(A4)^{V}	3.28	2.83	106
C(B9)-H40···O(A4)^{V}	3.28	2.83	106
C(A3)-H25···O(A3)^{II}	3.47	2.48	156

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:
I (*x*, 1+*y*, *z*), II (*x*, *y*, 1+*z*)
III (*x*, 1+*y*, −1+*z*), IV (1/2−*x*, 1−*y*, −1/2+*z*)
V (−*x*, −1/2+*y*, 3/2−*z*)

a) Possible hydrogen bonds. b) H1, H2, H3, H13, and H14 belong to the *ob* conformation and H9, H10, H11, H17, and H18 to the *lel*.

The bond distances and bond angles in both *d*-BCS anions are summarized in Table 4. The structures of both *d*-BCS anions are in accordance with each other and also with the results reported in the previous studies.[4,19] The bromine atoms are in the *endo* position on C(A3) and C(B3). The sulfonate groups are attached to C(A9) and C(B9), that is in *trans*-*π* position to the keto group. Selected intermolecular bond distances are summarized in Table 5.

The Local Packing Modes of the d-*BCS Anions.* There are notable differences between the two crystallographically independent *d*-BCS anions with respect to their local packing modes in this crystal,

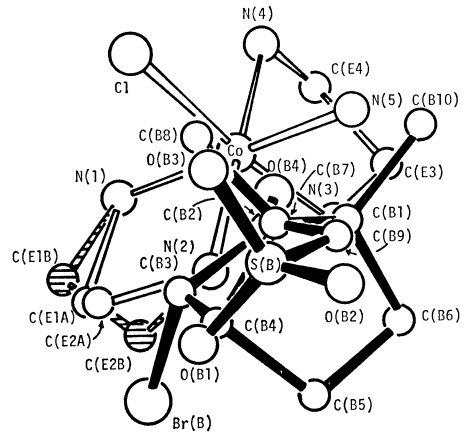

Fig. 3. A projected sketch displaying the spacial arrangement of the *d*-BCS anion and the complex cation.

In the *d*-BCS(A) anion, only the sulfonate group has short contacts with the complex cation. The distances are O(A1)···N(4) 3.05, O(A1)···N(5) 3.21, O(A2)···N(5) 3.32, O(A3)(x, y, $1+z$)···N(3) 3.05 and O(A3)(x, y, $1+z$)···N(5) 2.94 Å, suggesting the existence of the hydrogen bonds shown in Fig. 1. The bromocamphor part of the *d*-BCS(A) anion has no short contacts with the complex cation, though a few van der Waals contacts are present. These distances are C(A6)($-x$, $1/2+y$, $1/2-z$)···C(E3) 3.86 and C(A6)($-x$, $1/2+y$, $1/2-z$)···C(E4) 3.99 Å.

On the other hand, the packing mode around the *d*-BCS(B) anion bears a resemblance to that of the *d*-BCS anion in $(+)_{589}$-$[CoCl_2(en)_2]$*d*-BCS.[4] Namely, the sulfonate group tightly links the adjacent complex cations through the O···H–N hydrogen bonds and the bromocamphor part has short contacts with the complex cation. Figure 3 shows the sketch of the "$[CoClNH_3(en)_2]$*d*-BCS (B)" group projected on the "N(2), N(5), Cl" plane of the complex cation. The distances of the bromocamphor part(*d*-BCS(B)) to the complex cation are O(B4)···N(2) 2.92, O(B4)···N(5) 3.01, Br(B)···N(2) 3.59, Br(B)···C(E2A) 3.59, and Br(B)···Cl(x, y, $1+z$) 3.43 Å.

Though the bromocamphor part(*d*-BCS(B)) comes near to the "N(2), N(5), Cl" triangular facet of the octahedral complex cation, the distinct "three-to-four type" close contact found in our previous structural studies of $(+)_{589}$-$[CoCl_2(en)_2]$*d*-BCS[4] and tris(ethylenediamine)metal(III) *d*-tartrate systems[5,6,8] is not formed between the $[CoClNH_3(en)_2]^{2+}$ cation and the *d*-BCS(B) anion.

Including the "N(1), N(3), N(4)" plane of the complex cation, a hydrogen bond network is built up among the sulfonate groups of the *d*-BCS(B) anions and water molecules, as shown in Fig. 1. The hydrogen bond distances are O(B2)(x, $1+y$, z)···N(3) 2.95, O(B3)(x, $1+y$, z)···N(1) 2.87, O(B1)(x, $1+y$, $-1+z$)···WO 2.83, WO···N(1) 3.06, and WO···N(4) 2.90 Å.

Several van der Waals contacts also exist between the complex cations and the bromocamphor part of the *d*-BCS(B) anions along the b-axis, as shown in Fig. 1; C(E1B)···O(B1)($1/2-x$, $1-y$, $-1/2+z$) 3.18 and C(E2A)···C(B8)($1/2-x$, $1-y$, $1/2+z$) 3.54 Å.

The Packing of the Water of Crystallization. Hydrogen bonds in a right-handed spiral chain are formed between the sulfonate groups of the *d*-BCS(B) anions and the waters of crystallization along the twofold screw axis parallel to c($x=1/4$, $y=1$). The sequence of the chain is as follows; WO···O(B3)–S(B)–O(B1)($1/2-x$, $1-y$, $-1/2+z$)···WO($1/2-x$, $2-y$, $1/2+z$)···O(B3)–S(B)–O(B1)(x, $1+y$, z)···WO(x, y, $1+z$). The bond distances of hydrogen bonds are WO···O(B1)(x, $1+y$, $-1+z$) 2.83 and WO···O(B3) ($1/2-x$, $1-y$, $-1/2+z$) 2.76 Å.

Analogy between d-*BCS Systems and* d-*Tartrate Systems.* The ratios of the complex cation to the resolving agent-(*d*-BCS) in the crystals of $(+)_{589}$-$[CoCl_2(en)_2]$*d*-BCS and $(+)_{589}$-$[CoClNH_3(en)_2]$ $(d\text{-BCS})_2\cdot H_2O$ are 1 : 1 and 1 : 2 respectively.

It is found that the bromocamphor part of the *d*-BCS anion has a close contact with one triangular facet of the octahedral complex cation in both crystal structures. Another crystallographically independent *d*-BCS anion is present in the $(+)_{589}$-$[CoClNH_3(en)_2]$ $(d\text{-BCS})_2\cdot H_2O$, but the bromocamphor part of this anion(*d*-BCS(A)) is apart from any triangular facet of the complex cation. For a diastereomeric discrimination, the key-and-lock type association model was proposed by Fischer,[20] in which two chiral species make a compact fit. If this model is valid, the above results suggest that, though there are two *d*-BCS anions in the $(+)_{589}$-$[CoClNH_3(en)_2]$ $(d\text{-BCS})_2\cdot H_2O$, one of the *d*-BCS anions, *d*-BCS(B), plays a more important role in the diastereomeric discrimination.

Recently, three crystal structures of tris(ethylenediamine)metal(III) *d*-tartrate complexes, $(+)_{589}$-$[Co(en)_3]Br\cdot d\text{-tart}\cdot 5H_2O$, $Li\{(+)_{589}\text{-}[Cr(en)_3]\}(d\text{-tart})_2\cdot 3H_2O$, and $H\{(+)_{589}\text{-}[Co(en)_3]\}(d\text{-tart})_2\cdot 3H_2O$, have also been determined as a part of our structural studies of optical resolution.[5,6,8] The ratios of the complex cation to the resolving agent are 1 : 1, 1 : 2, and 1 : 2, respectively. Comparing the crystal structure of the 1 : 1 compound with that of the 1 : 2, we found as a common characteristic a "face-to-face type" close contact between the triangular facet of the complex cation and one *d*-tartrate anion. Moreover, though another crystallographically independent *d*-tartrate anion is present in $Li\{(+)_{589}\text{-}[Cr(en)_3]\}$ $(d\text{-tart})_2\cdot 3H_2O$ and $H\{(+)_{589}\text{-}[Co(en)_3]\}(d\text{-tart})_2\cdot 3H_2O$ crystals, one of the two –COO groups of this *d*-tartrate anion takes the place of the bromine atom in $(+)_{589}$-$[Co(en)_3]Br\cdot d\text{-tart}\cdot 5H_2O$.[5,6,8] These results again imply that one of the *d*-tartrate anions probably plays a more important role in the diastereomeric discrimination in the above 1 : 2 type salts.

It is worthy of note that only one resolving agent probably plays a more dominant role in the diastereomeric discrimination in both *d*-tartrate and *d*-BCS systems in which two crystallographically independent resolving agents are contained.

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