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STRUCTURAL STUDY OF OPTICAL RESOLUTION III. THE CRYSTAL STRUCTURE OF CIS-DICHLOROBIS(ETHYLENEDIAMINE)COBALT(III) d-α-BROMOCAMPHOR-π-SULPHONATE

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The crystal structure of the title compound has been determined by X-ray analysis. It has been found that a face-to-face type close contact of the $(+)_{589}$-$[CoCl_2(en)_2]^+$ cation with the bromocamphor moiety of the d-BCS anion is formed in this crystal.

It is well known that d-α-bromocamphor-π-sulphonate anion, d-BCS, is one of the most efficient resolving reagent of the optical resolution process via diastereoisomer formation.[1)] For example, many cis-diacidobis(ethylenediamine)cobalt(III) complexes, cis-$[CoX_2(en)_2]^+$, were resolved by way of the fractional crystallization of the diastereoisomers with d-BCS anion.[2,3)] Among them, cis-dichlorobis(ethylenediamine)-cobalt(III) d-α-bromocamphor-π-sulphonate, cis-$[CoCl_2(en)_2]$d-BCS, studied by Bailar and Auten[2)] is considered to be a typical one. Therefore, as a part of our structural studies of optical resolution,[4,5)] we tried to determine its crystal structure by X-ray analysis.

The compound was prepared by the method of Bailar.[6)] The violet hexagonal plate crystals are monoclinic, space group $P2_1$, $C_{14}H_{30}N_4O_4SCl_2BrCo$, M.W.=560.2, a=13.76(1), b=6.80(1), c=12.08(1) Å and β=103.2(2)°, D_m=1.67 g/cm^3, Z=2, D_c=1.69 g/cm^3. Ni-Kα radiation(λ=1.6591 Å) was employed. A total of 1613 independent structure amplitudes was obtained from visual estimation. The structure was solved by Patterson and Fourier methods, and refined by anisotropic block diagonal least squares method to an R-value of 0.12. Anomalous dispersion corrections were not applied. The standard deviation of bond length was 0.01 Å for Co-Cl, 0.03 Å for Br-C, Co-N and S-O and 0.05 Å for C-N and C-C bonds.

Figure 1 shows the crystal structure viewed along the b-axis. The crystal is built up of discrete cis-$(+)_{589}$-$[CoCl_2(en)_2]^+$ cations and d-BCS anions. 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.[7,8)] The structure of the d-BCS anion is also accordant with the reported result in the previous study.[9)] The absolute configuration of the present complex cation is determined to be in Λ-δλ form from the comparison with the known absolute configuration of the d-BCS anion.[8,9)]

Figure 2 shows the sketch of the "$[CoCl_2(en)_2]$d-BCS" group projected on the "Cl(1), Cl(2),N3" plane. There is a face-to-face close contact of the bromocamphor moiety of the d-BCS anion with the "Cl(1),Cl(2),N3" triangular facet of the octahedral complex cation. The contact distances are Cl(1)--Br 4.28(1), N3--O4 3.06(4), Cl(2)--C(10) 3.99 (4) and Cl(2)--C6 3.84(4) Å. Therefore, a "three-to-four type" close contact is formed

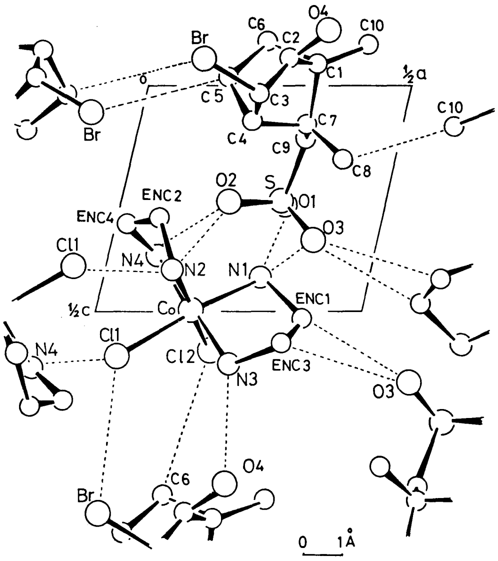

Fig.1 A drawing of the contents of the unit cell viewed down the b-axis.

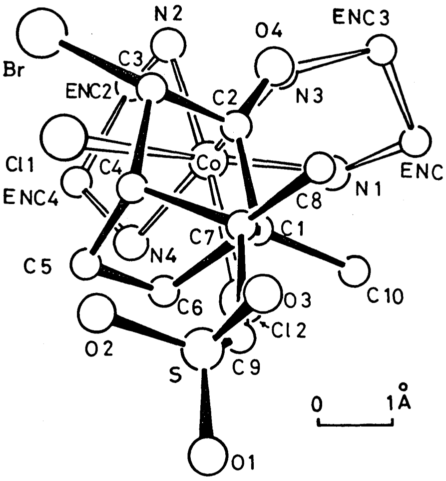

Fig.2 A projected sketch displaying the spatial arrangement of the d-BCS anion and the complex cation.

on a triangular facet of the octahedral complex cation(Cl(1),Cl(2),N3--Br,O4,C6,C(10)). It is noteworthy that this "three-to-four type" close contact in the diastereoisomeric salt was also found in our previous studies of tris(ethylenediamine)metal(III) d-tartrate systems.[4,5]

On the reverse facet of the octahedral complex cation a strong hydrogen bonding network is formed between the sulphonate groups in the d-BCS anions and the N-H hydrogens of the N1,N2,N4 atoms of the complex cation(Figure 1). The hydrogen bond distances are N1--O1 2.87(4), N2--O2 3.17(4), N1--O3(x,-1+y,Z) 3.12(4) and N4--O2(x,-1+y,z) 2.97(4) Å. Along the (0,y,1/2) screw axis the N-H--Cl type contacts are also formed between adjacent complex cations(N2--Cl(1)(-x,1/2+y,1-z) 3.42(3) and N4--Cl(1)(-x,-1/2+y,1-z) 3.25(3) Å).

Thus, in relation to the crystal packing modes, it appears that the d-BCS anion serves a double purpose. Namely, the sulphonate group tightly binds up adjacent complex cation with the O--H-N type hydrogen bonds and the bromocamphor moiety acts as a discriminative unit to the optical active complex cation forming a "three-to-four type" close contact. It is interesting that this dual character of the d-BCS anion in the crystal packing modes is also found in our recent X-ray study of $[CoClNH_3(en)_2](d\text{-}BCS)_2H_2O$ (R=11%).[10] Further structural studies are now in progress.

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