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STRUCTURAL STUDY OF OPTICAL RESOLUTION V. THE CRYSTAL STRUCTURE OF HYDROGEN TRIS(ETHYLENEDIAMINE)COBALT(III) d-TARTRATE TRIHYDRATE

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A new diastereoisomeric salt, H$(+)_{589}$-$[Co(en)_3](d\text{-}tart)_2\cdot 3H_2O$, has been prepared, and complete resolution of racemic $[Co(en)_3]^{3+}$ cation has been effected by use of this salt. The X-ray structure analysis revealed that this salt has a local "$[Co(en)_3](d\text{-}tart)_2$" block similar to that previously found in Li$(+)_{589}$-$[Cr(en)_3](d\text{-}tart)_2\cdot 3H_2O$ crystal.

In the studies of optical resolution mechanisms of tris(ethylenediamine)metal-(III) complexes, we have already determined the crystal structures of several diastereoisomeric salts which include the d-tartrate anion as a resolving agent.[1,2) It is noteworthy that the characteristic "$[M(en)_3]$d-tart" local block structure is present in these crystals and moreover the "face-to-face" close contact of the complex cation with the d-tartrate anion is formed within this local block. These structural features suggest that the racemic $[Co(en)_3]^{3+}$ cation could be resolved rather via the simple tartrate than via the well-known bromide-d-tartrate.3) Therefore, we tried to prepare the title compound and actually found a new optical resolution route for the $[Co(en)_3]^{3+}$ cation by way of the fractional crystallization of the compound. And then, we have determined the crystal structure of this diastereoisomeric salt by X-ray techniques.

Preparation of H$(+)_{589}$-$[Co(en)_3](d\text{-}tart)_2\cdot 3H_2O$: The racemic $[Co(en)_3](OH)_3$ was obtained by passing an aqueous solution of $[Co(en)_3]Br_3\cdot 3H_2O$ through a Dowex 1x8 anion-exchange resin in OH^- form. To the resulting solution (pH=13.5, and the concentration of this solution was determined spectrophotometrically), a concentrated solution of d-tartaric acid was added in a molar ratio of 1:2. The mixture (pH=4.0) was allowed to stand at room temperature until the yellow-plate crystals separated after several days. Complete resolution was proved by both CD spectral data and X-ray diffraction data. Rapid cooling and incomplete pH adjusting

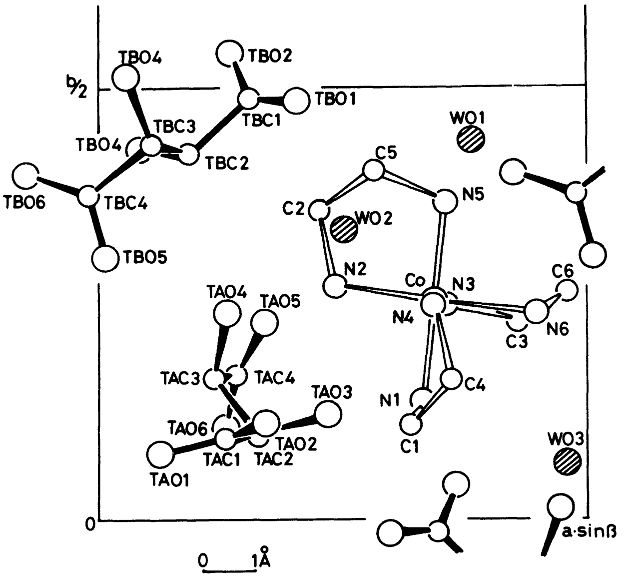

Figure 1. A drawing of an asymmetric unit viewed along the c-axis with a numbering scheme.

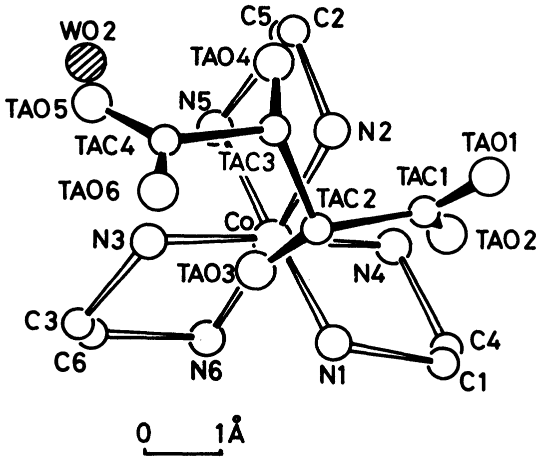

Figure 2. The arrangement of the complex cation and one d-tartrate anion (TA-tart) projected down the threefold axis of the complex cation.

occasionally gave yellow powder. Even in such a case, optical resolution was achieved by recrystallization from aqueous solution. Found: C,28.43; H,6.58; N,14.31 %. Calcd. for $C_{14}H_{39}N_6O_{15}Co$: C,28.48; H,6.46; N,14.23%. The CD spectrum was measured after d-tartrate anion was removed by mixing with $AgNO_3$, and was found to be identical with that reported in the literature.$^{4)}$

X-ray structure analysis: Well-formed yellow crystals are monoclinic, space group $P2_1$, M.W.=590.4, a=9.46(2), b=16.89(2), c=7.68(1) Å, and β=99.4(2)°; D_m=1.63 g/cm^3 (by flotation), Z=2, D_c=1.62 g/cm^3. Ni-Kα radiation (λ=1.6591 Å) was employed. A total of 1419 independent structure amplitudes was obtained from visual estimation. The structure was solved by Patterson and Fourier methods, and refined by isotropic block diagonal least squares method to an R-value of 0.13. Anomalous dispersion corrections were not made. The standard deviation of bond length was 0.02 Å for the Co-N bonds and 0.03-0.05 Å for the remaining bonds.

Figure 1 shows an asymmetric unit in the crystal viewed along the c-axis. The crystal is built up of $\Lambda(\delta\delta\delta)$-$[Co(en)_3]^{3+}$ cations, two kinds of d-tartrate anions (TA-tart and TB-tart), and three kinds of water molecules (WO1, WO2, and WO3).

Figure 2 shows how the TA-tart anion approaches the complex cation along its threefold axis. Three oxygen atoms of the TA-tart anion are close to the three axial N-H hydrogen atoms of the lel-type ethylenediamine ligands: N1--TAO2 3.03, N2--TAO4

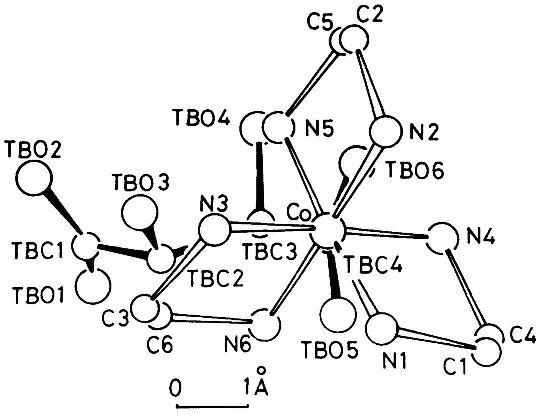

Figure 3. Association of the complex cation with another d-tartrate anion (TB-tart) on the reverse side.

3.38, N3--TAO3 3.16, N1--TAO3 3.14, and N2--TAO2 2.99 Å. Thus, there is the face-to-face close contact of the complex cation with the TA-tart anion on a triangular facet of the octahedral complex, as is expected. On the other hand, as can be shown in Figure 3, the TB-tart anion is placed against the reverse side facet of the complex cation (N4--TBO6 3.09, N5--TBO6 2.98, N4--TBO5 3.29, N6--TBO5 2.96, N6--TBO3 3.63, and N5--TBO3 3.65 Å). This mode of contact between the cation and the anion in the local "$[Co(en)_3](d\text{-}tart)_2$" block structure is similar to that found in $Li(+)_{589}\text{-}[Cr(en)_3](d\text{-}tart)_2\cdot 3H_2O$ crystal.

However, slight but significant differences can be seen between the crystal structure of $H(+)_{589}\text{-}[Co(en)_3](d\text{-}tart)_2\cdot 3H_2O$ and that of $Li(+)_{589}\text{-}[Cr(en)_3](d\text{-}tart)_2\cdot 3H_2O$. In the latter, the plane made of the four carbon atoms in the TA-tart anion is nearly perpendicular to the C_3 axis of the octahedral $\Lambda(\delta\delta\delta)\text{-}[Cr(en)_3]^{3+}$ cation, and the four oxygen atoms in the TA-tart anion are close to the three N-H hydrogen atoms in the ethylenediamine ligands,2) whereas in the present crystal, the plane made of the four carbon atoms in the TA-tart anion (TAC1-TAC2-TAC3-TAC4) is not perpendicular to the C_3 axis of the $\Lambda(\delta\delta\delta)\text{-}[Co(en)_3]^{3+}$ cation. The dihedral angle between the TACi-TAC2-TAC3-TAC4 plane and the N1--N2--N3 plane is 22.1°. Moreover, N3 is not in short contact with TAO5 in the present crystal (N3--TAO5 >4.0 Å; 3.60 Å for the Cr(III) complex). Instead, one of the water molecules (WO2) is close to N3 and TAO5 (WO2--N3 2.88 and WO2--TAO5 2.91 Å). The position of the H^+ ion could not be determined exactly; it is not clear as yet whether the H^+ ion exists in the H_3O^+ form or the d-tartH^- form. However, all C-O distances in the carboxylate groups of the d-tartrate anion are normal within the limit of our experimental errors (1.12-1.31 Å). In addition to this, the short O---H---O contact between d-tartrate anions is not found (O---H---O >2.6 Å), which is in contrast to the short O---H---O contact between the d-tartH^- anions shown in the crystal structures of $(+)_{589}\text{-}[Co(ox)(en)_2]\cdot d\text{-}tartH\cdot H_2O$ (O---O 2.44 Å)5) and $(-)_{589}\text{-}[Co(ox)(en)_2]d\text{-}tartH\cdot 2H_2O$ (O---O 2.43 Å).6) Therefore, the H^+ ion is most likely to exist in the H_3O^+ form.

In this work, we established a new optical resolution route for the $[Co(en)_3]^{3+}$ cation, and this result supports our previous assumption that the local block structure which includes the mode of the face-to-face close contact plays an important role in the optical resolution process of $[M(en)_3]^{3+}$ complex cations by way of d-tartrate diastereoisomers.

In order to elucidate optical resolution mechanisms of tris(ethylenediamine)-metal(III) tartrate systems, we recently attempted to prepare racemic tris(ethylenediamine)cobalt(III) racemic tartrate, $\{d,l\text{-}[Co(en)_3]\}_2(d,l\text{-}tart)_3 \cdot nH_2O$ (n=10-12), and determined the crystal structure of this compound by X-ray techniques.7) The crystals are monoclinic, space group $P2_1/n$, a=22.15(2), b=17.75(2), c=12.04(2) Å, and β=93.4°; D_m=1.53 g/cm^3, Z=4, and D_c=1.55 g/cm^3 (for n=10). Further detailed studies are now in progress.

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