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STRUCTURAL STUDY OF OPTICAL RESOLUTION II. THE CRYSTAL STRUCTURE OF LITHIUM TRIS(ETHYLENEDIAMINE)CHROMIUM(III) d-TARTRATE TRIHYDRATE

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It has been found that, in the crystal of Li$(+)_{589}$-[Cr(en)$_3$](d-tart)$_2\cdot 3H_2O$, the complex cation Λ-$\delta\delta\delta$-$[Cr(en)_3]^{3+}$ is sandwiched between two crystallographically different d-tartrate anions. The centers of the both anions are located on the threefold axis of the octahedral complex cation and the characteristic local "[Cr(en)$_3$](d-tart)$_2$" block is formed. The structural feature of this local block bears a close resemblance to that found in $(+)_{589}$-[Co(en)$_3$]Br·d-tart·5H_2O.

As is well known, the optical resolution of tris(ethylenediamine)chromium(III) is fairly difficult in comparison with the case of analogous cobalt(III) complex.[1] Recently, however, an improved method of resolution via new diastereoisomeric salt, Li[Cr(en)$_3$](d-tart)$_2\cdot 3H_2O$, was reported by Galsbøl.[2] As a part of our structural studies of optical resolution,[3] we attempted to determine the crystal structure of this diastereoisomeric salt by X-ray analysis.

The compound was prepared by the method of Galsbøl.[2] Well-formed yellow crystals: $C_{14}H_{34}N_6O_{15}CrLi$, M.W.=585.4, monoclinic; a=9.22(1), b=16.99(1), c=7.86(1) Å and β=100.4(2)°; D_m<1.7 g/cm^3, Z=2, D_c=1.62 g/cm^3; space group $P2_1$. Ni-Kα radiation (λ=1.6591 Å) was employed. A total of 1923 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 0.12. Anomalous dispersion corrections were not applied. The standard deviation of bond length was 0.02 Å for the Cr-N bonds and 0.03-0.04 Å for the remaining bonds.

Figure 1 shows an asymmetric unit in the crystal viewed down the c-axis. The

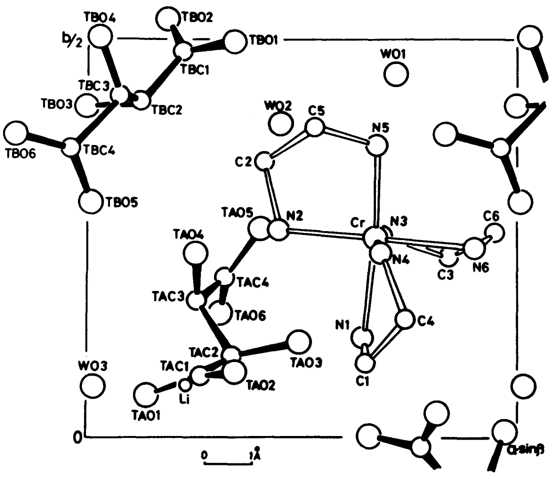

Figure 1. A drawing of an asymmetric unit viewed down the c-axis with a numbering scheme.

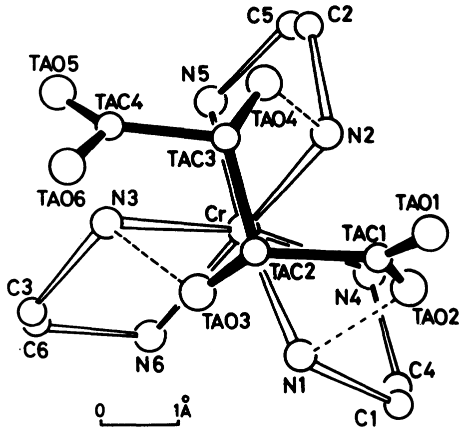

Figure 2. A projected sketch displaying the spatial arrangement of one d-tartrate anion(TA-tart) and the complex cation.

crystal is built up of Li^+ cations, $[Cr(en)_3]^{3+}$ cations, two kinds of d-tartrate anions(TA-tart and TB-tart) and three kinds of water molecules(WO1,WO2 and WO3).

In the complex cation, the bond distances and bond angles around the chromium atom are as follows: Cr-N1 2.14, -N2 2.05, -N3 2.10, -N4 2.08, -N5 2.01 and -N6 2.10 Å, and N1-Cr-N4 81.7(7), N2-Cr-N5 84.6(7) and N3-Cr-N6 83.9(8)°. These values are in good agreement with those found in the previous studies.[4] The Λ-$\delta\delta\delta$ absolute configuration of $(+)_{589}$-$[Cr(en)_3]^{3+}$ cation was confirmed by direct comparison with the known L-configuration of the d-tartrate anion.[5]

There is a distorted tetrahedral arrangement of four oxygen atoms around the lithium atom(Li--TAO2 1.94(5), --WO3 2.04(5), --TAO6'(x,y,1+z) 1.94(5) and --WO1" (1-x,-1/2+y,1-z) 2.02(5) Å).

Figure 2 illustrates the way of spatial location of TA-tart anion upon the complex cation, which is concurrently in harmony with another d-tartrate anion(TB-tart;1+x,y,z position) on the reverse side(Figure 3).

Four carbon atoms in the TA-tart anion(TAC1-TAC2-TAC3-TAC4) make a plane which is nearly perpendicular to the threefold axis of the octahedral complex cation. The four oxygen atoms of this TA-tart anion(TAO2,TAO3,TAO4 and TAO5) also lie in a plane and face the three axial N-H hydrogen atoms of the lel-type ethylenediamine ligands. The N--O distances are : N1--TAO2 2.85, N2--TAO4 3.02, N3--TAO3 2.94, N1--TAO3 2.98, N2--TAO2 3.23, N3--TAO4 3.93 and N3--TAO5 3.60(3) Å. Therefore, the

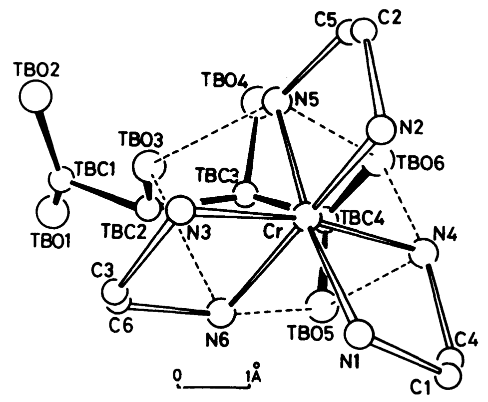

Figure 3. An association of the complex cation and another d-tartrate anion(TB-tart) on the reverse side.

face-to-face close contact of the complex cation with TA-tart anion occurs on a triangular facet of the octahedral complex. On the other hand, as depicted in Figure 3, the TB-tart anion is placed against the reverse facet of the complex cation(N4--TBO6 3.06, N5--TBO3 3.04, N6--TBO5 3.08, N4--TBO5 3.19, N5--TBO6 3.19 and N6--TBO3 3.19 Å). Three oxygen atoms(TBO5,TBO6 and TBO3), namely, one carboxylate- and one hydroxyl-group in the TB-tart anion, face the three axial N4-H, N5-H and N6-H hydrogen atoms. This mode of contact shows a distinctive contrast with that found in the TA-tart anion(Figure 2), in which case four oxygen atoms of two carboxylate- and two hydroxyl-groups make a close contact with the complex cation. Thus, to say in short, the $(+)_{589}$-Λ-$\delta\delta\delta$-$[Cr(en)_3]^{3+}$ cation is sandwiched between two crystallographically different d-tartrate anions and a characteristic local "$[Cr(en)_3](d\text{-}tart)_2$" block is formed.

It is interesting to compare this structural feature with that of $(+)_{589}$-$[Co(en)_3]Br\cdot d\text{-}tart\cdot 5H_2O$ precedently reported.[3)] Both compounds are quite different in the chemical formula, cell dimensions and space group symmetry. However, they have a remarkable resemblance to each other in the formation of the local block structure around the complex cation; the face-to-face contact mode of TA-tart anion with the complex cation is essentially identical in both of them, though, in the present case, the TB-tart anion takes place of the bromide anion of the cobalt(III) compound.

Now, it may be assumed that, if the optical resolution of $[M(en)_3]^{3+}$ cation is aptly due to the formation of such a local block, then racemic-$[Co(en)_3]^{3+}$ should be possibly resolved even by the use of some diastereoisomers other than the bromide d-tartrate pentahydrate. Based on this assumption, we prepared a new diastereoisomeric salt, $H[Co(en)_3](d\text{-}tart)_2\cdot 3H_2O$, and have determined its crystal structure by X-ray analysis(R=14%). There is a characteristic local "$[Co(en)_3](d\text{-}tart)_2$" block in this crystal too. Moreover, we have found a novel optical resolution route of $[Co(en)_3]^{3+}$ cation by way of the fractional crystallization of this salt.[6)]

Therefore, we should like to conclude that the structural feature of these local blocks plays a definitive role in the optical resolution process of tris(ethylenediamine)metal(III) complex cation by way of these d-tartrate systems.

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