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STRUCTURAL STUDY OF OPTICAL RESOLUTION I. THE CRYSTAL STRUCTURE OF TRIS(ETHYLENEDIAMINE)COBALT(III) BROMIDE d-TARTRATE PENTAHYDRATE

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The crystal structure of the title compound has been determined by X-ray analysis. The absolute configuration of the complex cation is found to be Λ-δδδ. In the crystal four oxygen atoms of the tartrate anion face the three axial N-H hydrogen atoms of the complex cation and the bromide anion is placed underneath the three axial N-H hydrogen atoms of the reverse side. Thus, around the complex cation the local "$[Co(en)_3]Br\cdot d$-tart" block is formed.

The tartrate anion and tris(ethylenediamine)metal complex systems have been studied extensively in connection with the optical resolution of the complex cations.[1,2] Tris(ethylenediamine)cobalt(III) bromide d-tartrate pentahydrate is a typical example of these systems. As a part of our structural studies of optical resolution we have determined its crystal structure by X-ray technique.

The compound was prepared by the method of Werner,[1] and recrystallized from aqueous solution. Well-formed orange crystals: $C_{10}H_{38}N_6O_{11}CoBr$, M.W.= 557.3, triclinic, a = 8.50(1), b = 8.27(1), c = 8.16(1) Å, α = 95.3(1), β = 101.0(1) and γ = 102.4(1)°; D_m= 1.62 g/cm^3 (by flotation), Z = 1, D_c= 1.67 g/cm^3; Space group P1. Ni-Kα radiation (λ =1.6591 Å) was employed. A total of 1736 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. The standard deviation of bond length was 0.02 Å for the Co-N bonds and 0.03 Å for the remaining bonds.

Figure 1 shows a perspective drawing of the contents of the unit cell along the a-axis. The absolute configuration of the complex cation, $(+)_{589}$-$[Co(en)_3]^{3+}$, is of Λ-δδδ form and that of the d-tartrate anion is of L form, and both configurations are in accordance with the results in the earlier studies.[3,4]

A projected sketch of all atoms in a particular "$[Co(en)_3]Br\cdot d$-tart" group in this crystal, excluding the hydrogen atoms, is shown in Figure 2. As shown in this figure, four carbon atoms in the tartrate anion(TC1-TC2-TC3-TC4) form a plane which is perpendicular to the threefold axis of the complex cation, and the four oxygen atoms(TO2,TO3,TO4 and TO5) face the three axial N-H hydrogen atoms of the lel-type ethylenediamine ligands in the complex cation. The N--O distances are as follows: N1--TO2 3.05, N2--TO4 3.06, N3--TO3 2.98, N1--TO3 3.05, N2--TO2 3.18, N3--TO4 3.23 and N3--TO5 3.21(2) Å. Thus, the face to face close contact of the complex cation with the d-tartrate anion occurs on a triangular facet of the octahedral complex.

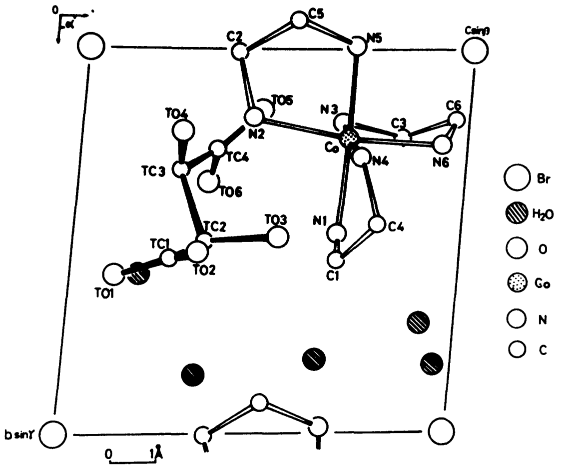

Fig.1 A perspective drawing of the contents of the unit cell viewed along the a-axis.

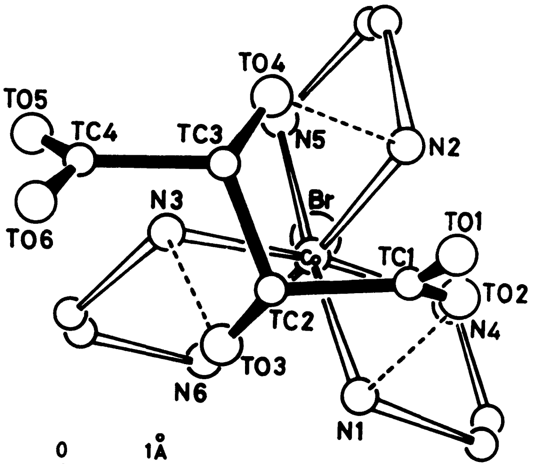

Fig.2 A sketch of the local "$[Co(en)_3]Br\cdot$d-tart" block projected down the three-fold axis of the complex cation.

Underneath the triangular facet of the reverse side the bromide anion is placed, making the N-H--Br type hydrogen bonds to the three axial N4-,N5-, and N6-H hydrogen atoms(N4--Br 3.35, N5--Br 3.25 and N6--Br 3.45(2) Å). Therefore, the complex cation is completely and firmly held between the bromide and d-tartrate anions, and the presence of the local "$[Co(en)_3]Br\cdot$d-tart" unit is strongly suggested in this diastereoisomeric salt. Furthermore, five water molecules in this crystal are extensively linked via hydrogen bonding to each other, to the bromide anions as well as to the free $-COO^-$ groups in the d-tartrate anions, resulting in three-dimensional network built up around the local block. Consequently, the local block is separated from other neighboring d-tartrate anions.

The above findings lead us to suggest that the structural features of this local block is related to the stereoselection ability of the d-tartrate anion toward the racemic-$[Co(en)_3]^{3+}$ cation. If the formation of such a local block is to play a dominant part in the optical resolution for these metal complexes, then a similar unit should be anticipated to found in other diastereoisomeric d-tartrate of $[M(en)_3]$ complex. In fact, our recent X-ray study of $Li[Cr(en)_3](d\text{-tart})_2\cdot 3H_2O$ has revealed that the local "Λ-δδδ-$[Cr(en)_3](d\text{-tart})_2$" block is existent also in this crystal.[5)]

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