

STRUCTURAL STUDY OF OPTICAL RESOLUTION IV. THE CRYSTAL
STRUCTURE OF (+)₅₈₉-OXALATOBIS(ETHYLENEDIAMINE)COBALT(III)
HYDROGEN-d-TARTRATE MONOHYDRATE

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The crystal structure of the title compound has been determined by X-ray analysis. It has been found that, in the diastereoisomer (+)₅₈₉-[Co(ox)(en)₂]H-d-tart·H₂O, the optically active complex cation is locked by the {H-d-tart}_∞ units of the right-handed spiral chain structure along the b-axis.

The hydrogen d-tartrate anion, H-d-tart⁻, is one of the most efficient resolving agent.¹⁾ Indeed, using this anion, several successful optical resolutions of monovalent complex cations have been reported.²⁾ Therefore, as a part of our structural studies of optical resolution,³⁻⁶⁾ we attempted to determine the crystal structure of the title compound by X-ray analysis.

The compound was prepared by the method of Jordan et al.²⁾ The red crystals are monoclinic, space group P2₁, C₁₀H₂₃O₁₁N₄Co, M.W.=434.2, a=8.27(1), b=14.60(1), c=7.02(1) Å, and β=104.8(2)°; D_m=1.74 g/cm³, Z=2, D_c=1.76 g/cm³. Ni-Kα radiation (λ=1.6591 Å) was employed. A total of 1029 independent structure amplitudes was obtained from visual estimation. The structure was solved by Patterson and Fourier method, and refined by anisotropic block diagonal least squares method to an R value of 0.13. The standard deviations of the bond lengths were 0.02 Å for Co-O, 0.03 Å for Co-N, and 0.05 Å for C-O, C-N and C-C bonds.

Figure 1 shows the crystal structure of the compound viewed along the c-axis. The crystal is built up of discrete (+)₅₈₉-[Co(ox)(en)₂]⁺ cations, H-d-tart anions and water molecules.

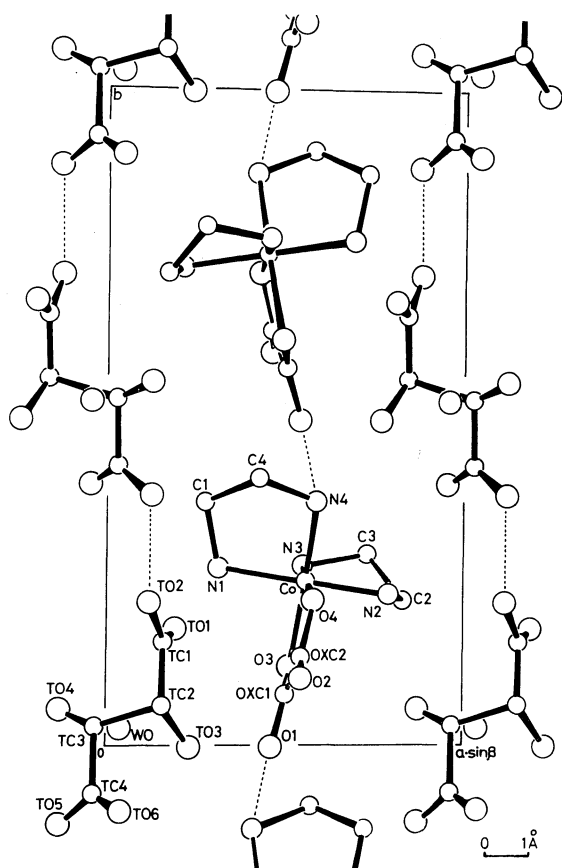


Figure 1. A perspective drawing of the contents of the unit cell viewed along the c-axis.

In the complex cation, the bond distances and bond angles around the cobalt atom are in good agreement with those found in the previous study.⁷⁾ The absolute configuration of the complex cation was determined to be of Λ - $\delta\lambda$ form from comparison with the known absolute configuration of the H-d-tart anion.⁸⁻⁹⁾ This is just the mirror image to the reported absolute configuration of $(-)_589$ -[Co(ox)(en)₂]⁺ cation.⁷⁾ Both are of the same lel-ob conformation with respect to the ethylenediamine rings.

The structure of the H-d-tart anion is in accordance with the previous study.⁹⁾ The TC1-T02 distance (1.36 Å) is much longer than any of the other C-O bond distances of the carboxyl groups (TC1-T01 1.21 Å, TC4-T05 1.29 Å and TC4-T06 1.24 Å). Therefore it seems that, in the

present H-d-tart anion, the hydrogen atom is possibly bound to T02.

The water molecules exist around the twofold screw axis at (0,y,1/2). Each complex cation is surrounded by eight H-d-tart anions in a deformed cubic environment (See Fig.1).

It is interesting to compare this structural feature with those of $(+)_589$ -[Co(en)₃]Br·d-tart·5H₂O,³⁾ Li{(+)589-[Cr(en)₃]}(d-tart)₂·3H₂O⁴⁾ and H{(+)589-[Co(en)₃]}(d-tart)₂·3H₂O.⁵⁾ Figure 2 shows the arrangement of the $(+)_589$ - Λ - $\delta\lambda$ -[Co(ox)(en)₂]⁺ cation and the H-d-tart anion projected down the quasi-threefold axis of the complex cation. The closest distance between the complex cation and the d-tart group is T02---N1 3.05 Å, and this is the only close contact in the present unit; none of characteristic "face-to-face type" close contact which are formed in the [M(en)₃]³⁺--d-tart²⁻ system³⁻⁵⁾ can be found. Thus, it is suggested that, in the optical resolution process, the discriminative role of the H-d-tart

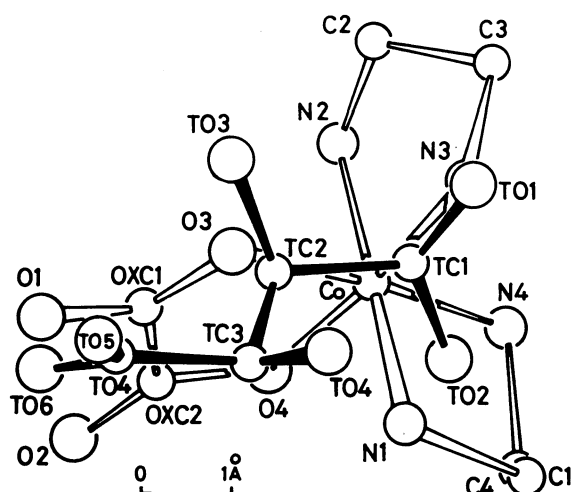


Figure 2. The arrangement of the complex cation and H-d-tart anion projected down the quasi-threefold axis of the complex cation.

anion to the monovalent complex cation is quite different from that of the d-tartrate anion in the $[M(en)_3]^{3+}$ ---d-tart $^{2-}$ system.

In the crystal, H-d-tart anions are arranged to make a specific chain structure along the b-axis, being linked to each other through the hydrogen bonding (See Fig.1). The hydrogen bond distance is $T02\cdots T05(-x, 1/2+y, 2-z)$ 2.44 Å. Along the b-axis, there is another chain of complex cations, which are joined also by the hydrogen bond ($N4\cdots O1(1-x, 1/2+y, 1-z)$ 2.89 Å). Both chains have the right-handed twofold screw symmetry (along the b-axis).

Besides, these screw chains are mutually in contact at the following short distances : $T01\cdots N1$ 2.89, $T01\cdots OXC2$ 2.92, $T03\cdots O1$ 2.98, $T03\cdots O2$ 2.90, $T04(1+x, y, z)\cdots N2$ 2.96, $T06(1-x, 1/2+y, 2-z)\cdots N2$ 2.89 and $T06(1-x, 1/2+y, 2-z)\cdots N4$ 2.98 Å. Further, along the c-axis, adjacent H-d-tart chains are linked by the water molecules with the hydrogen bonds : $W0\cdots T01$ 3.11, $W0\cdots T04$ 2.86 and $W0\cdots T06(x, y, -1+z)$ 2.77 Å.

In short, there is an extensive hydrogen bonding network in the crystal and the optically active complex cation, $(+)_{589}\text{-}\Lambda\text{-}\delta\lambda\text{-}[\text{Co}(\text{ox})(\text{en})_2]^+$, is locked by the $\{\text{H-d-tart}\}_\infty$ units of the right-handed spiral chain structure along the b-axis, suggesting that this hydrogen bonding structure should play a dominant role in the present optical resolution process.

Recently, we attempted to isolate the more-soluble diastereoisomer and succeeded in preparing good crystals of $(-)_{589}\text{-}[\text{Co}(\text{ox})(\text{en})_2]\text{H-d-tart}\cdot 2\text{H}_2\text{O}$.¹⁰⁾ Then, we have determined its crystal structure by X-ray analysis (1303 reflections, $R=13\%$). The crystals are orthorhombic, space group $P2_12_12$, $a=16.56(1)$, $b=14.14(1)$ and $c=7.39(1)$ Å; $D_m=1.72$ g/cm 3 , $Z=4$ and $D_c=1.74$ g/cm 3 . Further detailed studies are now in progress.

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