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THE CRYSTAL STRUCTURE OF μ-L-TARTRATO-DICOBALT(III) COMPLEX, Δ-cis(O,O),trans(O,O)-$[(en)_2Co(tart)(3-)Co(tart)(1-)(en)_2]Na(ClO_4)_3 \cdot 5H_2O$

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The title compound was prepared by the reaction of L-tartaric acid with $[CoCO_3(en)_2]Br$. It contains a dimer cation in which two cobalt atoms are bridged through a tridentate tartrate anion. The configuration about one cobalt atom is Δ-cis, and about another is trans(O,O).

The reaction of $[CoCO_3(en)_2]^+$ with tartaric acid gives a mixture of several cobalt(III) complexes.[1∿5)] Haines et al. isolated $[Co(tart)(2-)(en)_2]Cl$ and $[Co(tart)(3-)(en)_2] \cdot H_2O$ by using TLC technique from the mixture. Gillard et al. reported the isolation of a dimer species whose suggested formula was Δ-, Δ-$[(en)_2Co(L\text{-}tart)(4-)Co(en)_2](ClO_4)_2 \cdot 5H_2O$, Sephadex G-10 being used for the isolation. The complete separations, however, have not been performed, as were noted in the above papers, nor detailed structures of the isolated complexes have been fully elucidated.

By means of SP-Sephadex column chromatography, the present authors have separated much more species; anionic, neutral, and cationic. Among them, one of the cationic species was isolated as a perchlorate, which was used for the X-ray analysis. Found: Co, 10.8; C, 18.0; H, 4.3; N, 10.1; Cl, 10.7; Na, 2.4 %. Calcd for $C_{16}H_{50}N_8O_{29}Cl_3Co_2Na$: Co, 11.1; C, 18.0; H, 4.7; N, 10.5; Cl, 10.0; Na, 2.2 %.

The red crystals are orthorhombic, space group $P2_12_12_1$, with $C_{16}H_{50}N_8O_{29}Cl_3$-$Co_2Na$, M.W. = 1065.8, a = 15.17(1), b = 18.31(3), c = 14.56(2) Å, V = 4043(8) $Å^3$, Z = 4, D_x = 1.75 g cm^{-3}, D_m = 1.71 g cm^{-3}.

Though the preliminary Weissenberg photographs showed the reflections only in the low angular range, which suggested the presence of some disorder in the crystal, X-ray structure analysis was attempted. The X-ray diffraction data were collected on a Rigaku four-circle automated diffractometer. The intensity data for the structure determination were taken with graphite-monochromatized MoKα radiation. The size of the crystal was 0.3 × 0.3 × 0.1 mm.

The intensities were measured within the first octant up to 2θ = 40° by the ω and 2θ-ω scan techniques. Among about 2000 possible reflections in the crystal, 795 independent reflections with $|Fo| \geq 3\sigma(F)$ were obtained. The usual Lorentz and polarization corrections were applied.

The structure was solved by the heavy-atom method, and was refined by the block-diagonal least-squares method. All the atoms of perchlorate ions, the cobalt atoms, and the sodium atoms were included in the refinement with anisotropic temperature

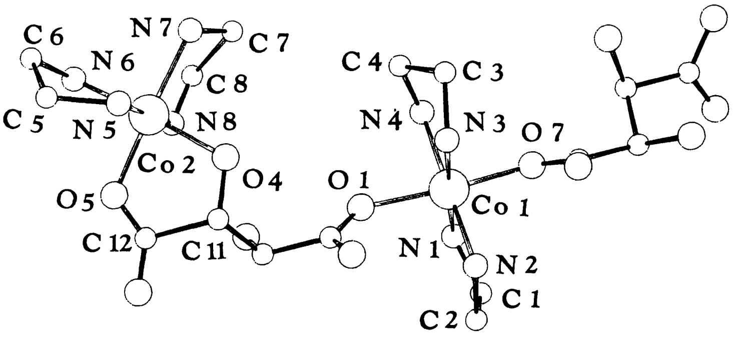

Fig. 1
The Structure of the Dimer Cation

Table 1. Bond Distances(Å) and Bond Angles(°)
Esd's are in parentheses

Co1-O1	1.92(3)	O1-Co1-O7	170.8(14)	O4-Co2-O5	84.1(14)
Co1-O7	1.89(3)	O1-Co1-N1	88.8(16)	O4-Co2-N5	97.1(15)
Co1-N1	2.01(4)	O1-Co1-N2	95.4(17)	O4-Co2-N6	173.6(15)
Co1-N2	1.97(5)	O1-Co1-N3	93.3(15)	O4-Co2-N7	94.3(16)
Co1-N3	1.91(4)	O1-Co1-N4	84.2(15)	O4-Co2-N8	87.9(15)
Co1-N4	1.97(4)	O7-Co1-N1	86.4(15)	O5-Co2-N5	89.3(16)
		O7-Co1-N2	92.4(16)	O5-Co2-N6	92.1(15)
		O7-Co1-N3	91.1(14)	O5-Co2-N7	175.2(17)
		O7-Co1-N4	88.4(15)	O5-Co2-N8	90.9(16)
Co2-O4	1.92(3)	N1-Co1-N2	88.5(18)	N5-Co2-N6	88.0(16)
Co2-O5	1.89(3)	N1-Co1-N3	176.4(17)	N5-Co2-N7	95.4(18)
Co2-N5	1.96(4)	N1-Co1-N4	94.7(17)	N5-Co2-N8	175.0(17)
Co2-N6	1.91(4)	N2-Co1-N3	94.2(17)	N6-Co2-N7	89.1(18)
Co2-N7	2.00(5)	N2-Co1-N4	176.8(18)	N6-Co2-N8	87.0(16)
Co2-N8	2.03(4)	N3-Co1-N4	82.7(16)	N7-Co2-N8	84.5(18)

factors. The equivalent temperature factors of the oxygen atoms of the perchlorate anions were condsiderably large (9.4 - 26.9). Consequently, the disorder is mainly due to the perchlorate ions. The final R was 8.2 %. The absolute configuration of the complex was determined on the basis of the configuration of the L-tartrate ligand.

Figure 1 shows the molecular structure of the complex cation, and Table 1 shows the bond lengths and the bond angles of the complex cation. The complex cation has a dimer structure in which a trinegative tartrate anion bridges two cobalt atoms. The structure about one cobalt to which the bridging tartrate ion bonds as a bidentate ligand has a cis-form. Another has a trans-form where the bridging tartrate ion and a mononegative tartrate ion bond to the cobalt as unidentates.

Table 2 shows the least-squares planes for the cis-moiety, where the cobalt-tartrate ring, plane 1, is nearly flat, while the two cobalt-ethylenediamine rings, plane 2 and 3, are of envelope.

The conformations of the ethylenediamine ligands are (λ,λ) and (δ,λ) for the trans-, and the cis-moieties, respectively, on the basis of the torsion angles of

Table 2. Least-squares Planes for the cis-moiety

Plane No.	Atoms defining the plane	Distance from the plane[a]	Other atoms	Distance from the plane[a]
1	Co2	-0.00(1)		
	O4	0.01(4)		
	O5	-0.00(4)		
	C11	-0.04(7)		
	C12	0.03(6)		
2	Co2	-0.00(1)	C5	0.55(8)
	N5	0.01(6)		
	N6	0.01(5)		
	C6	-0.03(9)		
3	Co2	0.00(1)	C7	-0.55(8)
	N7	-0.03(7)		
	N8	-0.04(5)		
	C8	0.07(7)		

[a] Distance from the calculated plane in Å.

the ethylenediamines listed in Table 3. Generally, the conformation of ethylenediamine of trans-bis(ethylenediamine)cobalt(III) is (δ,λ), the exceptions reported are for $[CoCl(NO)(en)_2]ClO_4(\lambda,\lambda)$ 6,7) and $[(NO_2)(en)_2CoO_2Co(en)_2(NO_2)](NO_3)_2 \cdot 4H_2O$-($\delta,\delta$)-($\lambda,\lambda$) 8). The trans moiety of the dimer complex described in this paper belongs to such conformation.

Table 3. Torsion Angles in the Ethylenediamines(°)

N1-C1-C2-N2	-36(7)	N5-C5-C6-N6	44(6)
N3-C3-C4-N4	-49(5)	N7-C7-C8-N8	-50(6)

The CD spectra of the complex have shown a negative band ($\Delta\varepsilon_{max}$ = -2.3 at 520 nm) in the region of d-d transition. Since the cis moiety of the complex has a Δ conformation, when the vicinal effect due to the tartrato ligand is small compared with the configurational effect, the empirical rule for the sign of CD spectra of bis(ethylenediamine)cobalt(III) complexes holds in the cis, trans-dimer complex as well.

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