Stereospecific Formation of Optically Active Chromium(III) Complexes of a Novel Binuclear Type Containing Two L-Tartrate Bridges

Sumio KAIZAKI, Jinsai HIDAKA and Yoichi SHIMURA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

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A novel mixed chromium(III) complex of L-tartrate ($C_4H_2O_6{}^{4-}$=tart) and 2, 2′-dipyridyl (=dip) was prepared as dark brown crystals by heating [$CrCl_3$(dmf)(dip)] and L-$Na_2C_4H_4O_6\cdot 2H_2O$ in a dmf-water mixture (1 : 1) at about 120°C and by adding barium chloride. Found: C, 43.51; H, 3.03; N, 7.33; Ba,[*1] 9.98%. Calcd for $C_{56}H_{42}N_8O_{24}BaCr_4$=Ba[$Cr_2$L-$tart_2H(dip)_2$]$_2$: C, 43.21; H, 2.73; N, 7.20; Ba, 8.83%. Found: H_2O, 9.24%. Calcd for Ba[Cr_2L-$tart_2$H$(dip)_2$]$_2\cdot 9H_2O$: 9.44%.

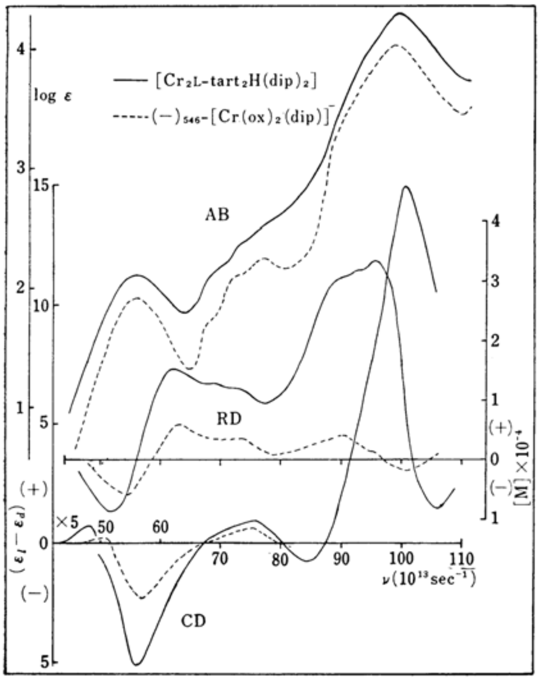

Fig. 1. Absorption (AB), CD and RD curves of the two Cr(III) complexes in water.

The absorption spectrum, the circular dichroism (CD) and the rotatory dispersion (RD) of this complex ion, in the visible region, have just twice the intensities of those of $(-)_{546}$-K[Cr$(ox)_2$(dip)]$\cdot 3H_2O$,[1,2] as is seen in Fig. 1. Regarding the intensity of CD, it is clear that the optical activity of this complex is due to a kind of configurational dissymmetry rather than vicinal effect of the coordinated L-tartrates. Construction of the molecular models shows that the most probable structure is the binuclear one same as proposed by Tapscott and Belford for the vanadyl(IV) tartrate system[3] and that the stereospecificity due to two dissymmetric L-tartrate ligands is perfect in this binuclear complex; only the [Λ—Λ] absolute configuration can be constructed, as is seen in Fig. 2. It is concluded, therefore, that $(-)_{546}$-K[Cr$(ox)_2$(dip)]$\cdot 3H_2O$ obtained from the less soluble diastereomer with $(-)_{546}$-[Co(ox)$(en)_2$]$^+$ has the Λ-configuration.

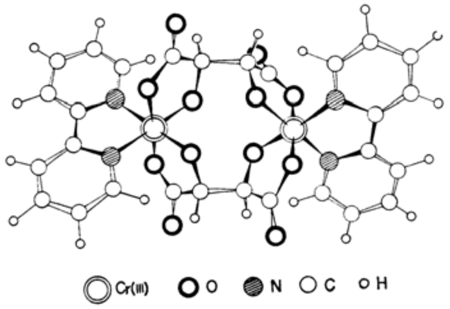

Fig. 2. Proposed structure of the binuclear complex (one proton not shown).

The similar consideration is also fit for another new binuclear complex of 1, 10-phenanthroline (=phen), NH_4[Cr_2L-$tart_2$H$(phen)_2$]$\cdot 6.5H_2O$.

Found: C, 49.26; H, 3.41; N, 8.46%. Calcd for $C_{32}H_{25}N_5O_{12}Cr_2$: C, 49.55; H, 3.26; N, 9.03%. Found: H_2O, 13.38%. Calcd for the 6.5 hydrate: H_2O, 13.09%.

[*1] The content of Ba was determined semi-quantitatively by flame spectrophotometry.

1) J. A. Broomhead, *Aust. J. Chem.*, **15**, 228 (1962).

2) Th. Bürer, *Helv. Chim. Acta*, **23**, 242 (1963).

3) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).