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CHROMATOGRAPHIC STUDY OF OPTICAL RESOLUTION I.

COMPLETE RESOLUTION OF THE NEUTRAL COMPLEX, FACIAL ISOMER OF TRIS(β-ALANINATO)COBALT(III)

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Based on the consideration of crystal structures of three diastereomeric salts composed of the tris(ethylenediamine)metal complex and the d-tartrate anion, an attempt was made to resolve tris(β-alaninato)cobalt(III) by the chromatographic technique, and a complete resolution was achieved through a Sephadex column using sodium d-tartrate 30% aqueous ethanol solution as an eluent.

Racemic metal complex ions are usually combined with suitable optically active counter ions to form diastereomeric salts, through which optical resolution is made. However, neutral complexes have no counter ions to be combined with, so that diastereomeric salts can not be obtained. Thus, preferential adsorption of one type of enantiomer on an optically active adsorbent (for example, quartz 1), starch 2), d-lactose 3), etc.) over the other type of enantiomer is the important method of optical resolution of neutral complexes. Since the interaction between a neutral complex and an adsorbent is generally very weak, resolution thus obtained is only partial. No example of complete resolution has been reported. However, if we pick up a neutral complex having a large dipole moment, a resolving agent must interact with it fairly well, so that we can reasonably expect a complete chromatographic resolution under appropriate conditions.

As a part of our structural studies of optical resolution, we have determined the crystal structures of a series of diastereomeric salts, Λ-[Co(en)$_3$]Br d-tart 5H$_2$O,4) Λ-Li[Cr(en)$_3$](d-tart)$_2$ 3H$_2$O,5) and Λ-H[Co(en)$_3$](d-tart)$_2$ 3H$_2$O.6) Although these compounds are quite different in chemical formulas, cell dimensions and space group symmetries, they have a remarkable resemblance to each other in the formation of the local block structure around the complex cation; the face-to-face close contact mode of the d-tart anion with the Λ-$[M(en)_3]^{3+}$ cation is essentially identical in these three cases. In contrast to this, the consideration using a molecular model revealed that the combination of the d-tart anion and the Δ-$[Co(en)_3]^{3+}$ cation does not form such a close contact structure. Determination of the association constants between the Λ- or Δ-$[Co(en)_3]^{3+}$ cation and the d-tart anion showed that the preferential association of the Λ-d pair over the Δ-d pair actually occurs.7) Thus, it was presumed that such a close contact structure exists also in solution. Therefore, it is not surprising to see the $[Co(en)_3]^{3+}$ complex completely resolved by chromatographic techniques.8, 9)

Since the discrimination of the Λ cation by the d-tart anion (through the face-to-face contact) is made along the three-fold axis of the $[M(en)_3]^{3+}$ complex, it is evident that only the upper half of the complex is involved in optical resolution. Therefore, it is expected that optical resolution is possible in the complex containing a triangular facet made of three NH_2 groups. The facial isomer of $[Co(\beta\text{-ala})_3]$ is expected to be such a complex. In fact, the NMR spectrum of this complex in CF_3COOH (Fig. 1) shows two broad peaks due to amino hydrogens just like that of the $[Co(en)_3]^{3+}$ complex.10) This indicates that there are two kinds of amino hydrogens (axial and equatorial) and that the upper half of fac-$[Co(\beta\text{-ala})_3]$ is quite similar to the moiety of $[Co(en)_3]^{3+}$.

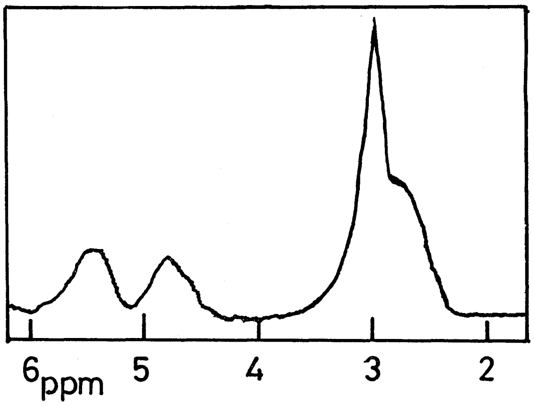

Fig. 1. NMR spectrum of fac-$[Co(\beta\text{-ala})_3]$ in CF_3COOH

Further, fac-$[Co(\beta\text{-ala})_3]$ dissolved in 1M Na_2d-tart aqueous solution shows an induced CD peak in the d-d absorption region (Fig.2). This suggests that the d-tart anion is actually discriminating the Λ from the Δ and inducing different molecular distortions in these enantiomers. (In contrast, mer-$[Co(\beta\text{-ala})_3]$ dissolved in the d-tart solution does not show such an induced CD peak. This means that the d-tart anion can not discriminate

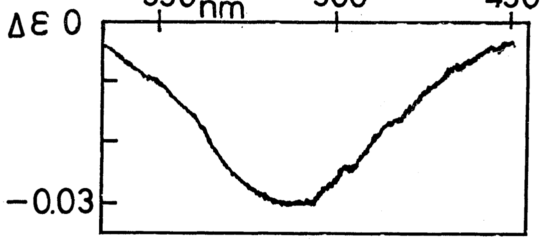

Fig. 2. Induced CD spectrum of fac-$[Co(\beta\text{-ala})_3]$ in Na_2d-tart solution

the Λ from the Δ of the meridional complex.)

Thus, we tried to resolve fac-[Co(β-ala)$_3$] through a Sephadex column. A column of 3 cm diameter was filled with a 113 cm length of the Na form of the CM Sephadex C-25 which had been treated with 30% ethanol. An automatic fraction collector was connected to the lower end of the column to collect 4 ml sample solutions. The column was charged with 70 mg of the complex in 10 ml of water and was eluted with 0.1M Na$_2$d-tart in 30% aqueous ethanol solution. The absorbance of each fraction was measured at 534 nm to draw the elution curve. As shown in Fig. 3, the curve has two completely separated peaks. The fractions corresponding to the two peak maxima showed the CD spectra of opposite sign, which proved that complete resolution was achieved(Fig. 4). With an eluent containing no d-tart anion, the complex was eluted as a single band. Thus, it was verified that the d-tart anion, not the Sephadex skeleton plays a decisive role in the present resolution.

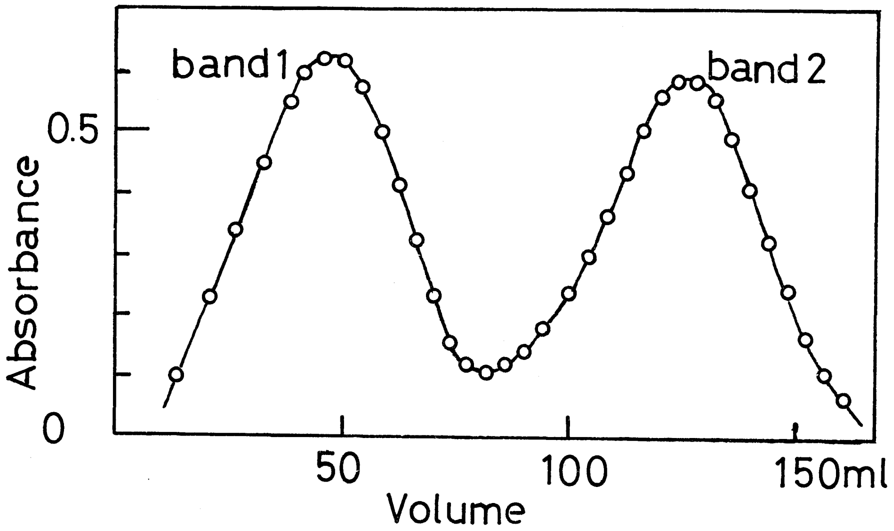

Fig. 3.
Elution curve of fac-[Co(β-ala)$_3$]
(elution rate: 4 ml/20 min.)

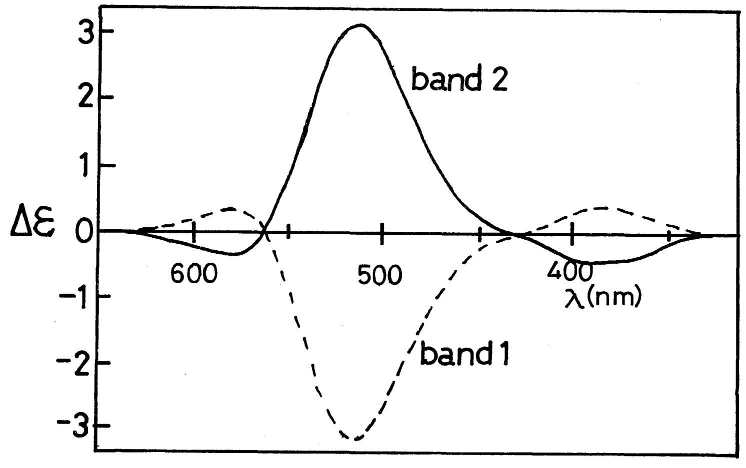

Fig. 4.
CD spectra of eluted fractions
(recorded with a JASCO J 40CS)

Preparation of the Complex The facial and meridional isomers of $[Co(\beta\text{-ala})_3]$ were prepared and separated after M. B. Celap et al.[11] The NMR and IR spectra of the facial isomer were identical with those reported in the literature. However, the following discrepancies were found.

1. Reaction time 30-40 hrs. (ours) 6 hrs. (lit.)
2. Analytical data Found: C, 32.31; H, 6.03; N, 12.45%. (ours)
   Calcd for $[Co(\beta\text{-ala})_3]\ 0.5H_2O$: C, 32.54; H, 5.76; N, 12.65%.
   The literature described $3H_2O$ for water of crystallization.
3. Absorption spectrum The values of λ_{max} and ε_{max} are
   534 nm (267) 375 nm (89) (ours)
   534 nm (141) 372 nm (61) (lit.)

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