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THE ISOLATION OF OPTICALLY ACTIVE COMPLEX OF LITHIUM CIS-DIAMMINEDICARBONATOCOBALTATE(III)

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From an aqueous solution of $Li(\pm)[Co(CO_3)_2(NH_3)_2]$ in the presence of $(-)_{589}[Co(ox)(en)_2](C_2H_3O_2)$, $Li(-)_{589}[Co(CO_3)_2(NH_3)_2]$ has been isolated with a ca. 70% yield. The CD spectrum of the complex has been measured.

The diamminedicarbonatocobaltate(III) complex, cis-$[Co(CO_3)_2(NH_3)_2]^-$, was once isolated as the potassium salt in our laboratory.[1] Since then, attempts to resolve the racemic salt by means of diastereoisomer formation were continued, but they were unsuccessful because no satisfactory resolving agent was found. However, we now succeeded in obtaining one enantiomer of lithium salt of the complex by a somewhat strange way. This paper deals with this subject.

The racemic lithium salt was first prepared; the potassium salt, $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$[2] (15 g) was dissolved in cold water (150 cm^3, ca. 10°C), and the solution was then charged on an ion-exchange column containing Dowex 50W-X8 resin in Li^+ form (100-200 mesh, 7 x 15 cm). By the injection with cold water, a blue solution effused from the column. To the effluent was added ammonium carbonate (3 g) and then the solution was evaporated to a small volume (ca. 50 cm^3) under reduced pressure at ca. 35°C. The concentrated solution was filtered and then kept in a refrigerator until crystals were deposited. The crude product thus obtained was recrystallized two times from water. The yield was about 3 g. Found: C, 10.92; H, 3.04; N, 12.66%. Calcd for $Li[Co(CO_3)_2(NH_3)_2]$: C, 10.92; H, 2.75; N, 12.73%. The solubility of this salt in water was considerably lower than that of the potassium salt.

The above racemate (5 g, 0.02 mol) was dissolved in water (50 cm^3), and the solution was then added to an aqueous solution containing $(-)_{589}[Co(ox)(en)_2]^+$ (0.01 mol in 40 cm^3 H_2O) in the form of acetate.[3] After ammonium carbonate (3 g) had been added to the mixed solution, the solution was evaporated to a small volume (ca. 30 cm^3) under reduced pressure. The concentrated solution was filtered and then kept in a refrigerator, whereupon blue powdered crystals were separated out. This first crop of crystals was collected by filtration. When the filtrate was again evaporated in the presence of ammonium carbonate, the second crop of crystals was obtained, then the $(-)_{589}[Co(ox)(en)_2]^+$ remained in the mother liquor. The combined crystals were washed with successively cold aqueous methanol (50%), ethanol and ether. The yield was about 3.5 g (ca. 70%). Found: C, 10.83; H, 3.05; N, 12.60%.

This complex exhibited levo-rotatory at 589 nm. The use of the $(+)_{589}[\mathrm{Co(ox)(en)_2}]^+$ instead of the $(-)_{589}$ complex resulted in the isolation of lithium salt of the dextro-rotatory. The use of the potassium salt or the sodium salt instead of the lithium salt gave no isolation of active complex.

The absorption and CD spectra of the $(-)_{589}$ complex are shown in Fig. 1. The CD spectrum has one peak at 17800 $\mathrm{cm^{-1}}$ ($\Delta\varepsilon = -2.32$) in the first absorption band region. In an aqueous solution the complex lost its optical activity with half-life ca. 3 min. The absolute configuration of this complex will be discussed in a subsequent paper with those of related complexes.

It was strange that an enantiomeric salt was directly separated out from a mixed solution of the racemate and an optically active complex, because this kind of system generally gave the less soluble diastereoisomer. The fact that the resolved complex showed a high $\Delta\varepsilon$ value reflects high optical purity of the complex. Moreover, the fact that the yield of the $(-)_{589}$ enantiomer exceeded far more 50% suggests that the present way is a kind of assymmetric synthesis.

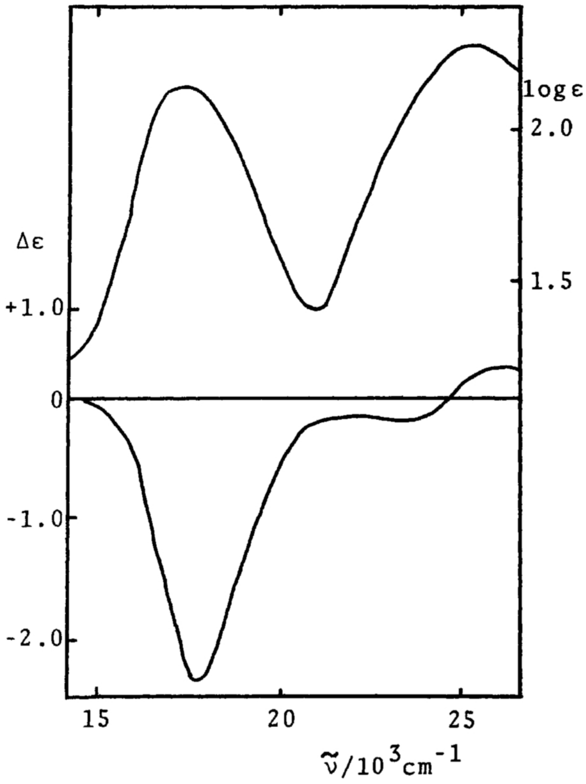

Fig.1 Absorption and CD spectra of $(-)_{589}\mathrm{Li[Co(CO_3)_2(NH_3)_2]}$

Recently, partial resolution of $[\mathrm{Co(acac)_3}]$[4] was performed by using Λ- or Δ-$[\mathrm{Co(phen)_3}]\mathrm{Cl_3}$ as an environment compound in the Pfeiffer-active system, but our way seems to be different, in mechanism, from such a Pfeiffer-active system, because no CD spectral change with the elapse of time was observed in our system consisting of the racemate and the optically active complex. In our system, different solubilities of the two enantiomers, which would be caused in the presence of the optically active complex, and rapid racemization of the more soluble enantiomer appeared to be important factors on the isolation of the less soluble enantiomer.

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