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THE ISOLATION OF CALCIUM CIS(N)TRANS(O_5)-BIS(L-ASPARTATO)-COBALTATE(III)·CIS(N)TRANS(O_6)-BIS(L-ASPARTATO)-COBALTATE(III) DECAHYDRATE

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The crystals of a new type bis(L-aspartato)cobaltate(III) complex have been obtained as the calcium salt. From the absorption and circular dichroism spectra of this complex salt in solution, it has been found that the calcium salt is composed of equimolar amounts of the two cis(N) geometrical isomers.

Previously, we reported the isolation of the two geometrical isomers of calcium bis(L-aspartato)cobaltate(III).[2)] After that, Yamada, Hidaka and Douglas reported the complete separation of the three possible isomers of sodium bis(L-aspartato)cobaltate(III);[3)] the isomers were identified to be trans(N), cis(N)-trans(O_6) and cis(N)trans(O_5) isomers (O_5 and O_6 represent two oxygens of five- and six-membered chelate rings, respectively) in the order of the chromatographic elution from their absorption, IR and CD spectra. In addition, the PMR spectra also gave the same conclusion.[4)] According to those structural assignments, our two isomers in the earlier paper[2)] were two cis(N) isomers. We have now found an interesting fact that the two cis(N) isomers of the calcium salt isomerize each other in solution and single crystals composed of equimolar amounts of both isomers separate out from the resulting solution.

The preparative reaction for the bis(L-aspartato) complex and the chromatographic separation of the geometrical isomers were done similarly to those described in the previous paper;[2)] monopotassium L-aspartate (15.5 g, 0.1 mol) was let react on a solution of tricarbonatocobaltate(III) ($CoCl_2 \cdot 6H_2O$ 12 g, 0.05 mol; $KHCO_3$, 35 g). Dowex 1X8 resin in the Cl-form and an aqueous solution of $CaCl_2$ (0.05 M) were used for the chromatographic separation. Two colored bands, one red-violet and one blue-violet, were eluted in that order. The eluted solution of the first band was concentrated to a small quantity (~30 ml) under reduced pressure at ca. 40°C spending a few days. After that, a proper quantity of ethanol was added to the concentrate and the whole was allowed to stand at room temperature until needle-like crystals began to separate out. Recrystallization was carried out from a minimum amount of water by adding a small amount of

ethanol, yield about 1 g.

Found: C, 21.97; H, 4.79; N, 6.74%. Calcd for $Ca_{1/2}C_8H_{10}N_2Co\cdot 5H_2O$: C, 22.28; H, 4.68; N, 6.50%.

The absorption and CD spectra of the present complex salt in aqueous solution are shown in Fig. 1. These spectra are different from any of those for the three geometrical isomers of this complex species, but almost identical with the resultant absorption and CD spectra of the two cis(N) isomers obtained previously (the resultant curves are shown in Fig. 1). When the present complex was rechromatographed, separation into the two cis(N) species was observed. These facts indicate that a certain isomerization reaction takes place during the concentration of the eluted solution and that an 1:1 mixed complex of the two cis(N) isomers is crystallized from the solution. Recent X-ray structure analysis[5] of the present complex has shown that the asymmetric unit contains both cis(N) isomers (the paper will be published in the near future).

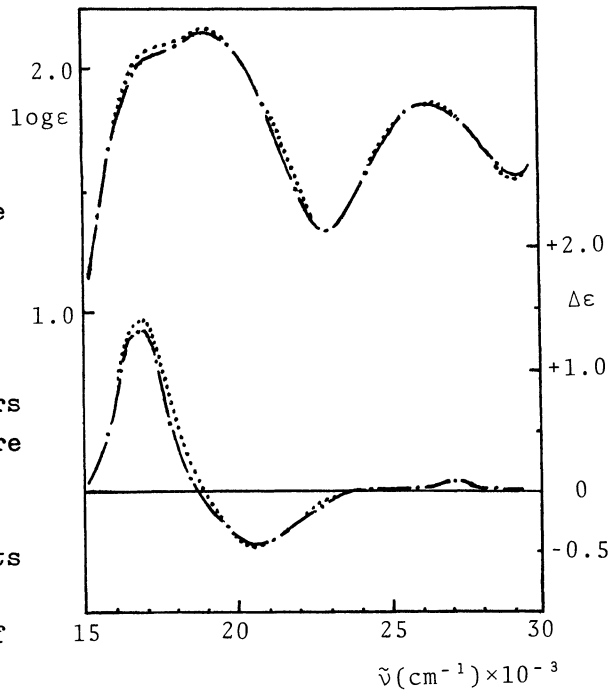

Fig.1 Absorption and CD spectra of the mixed complex (—·—) (·····: resultant curves)

The same phenomenon was observed for the complex salt isolated from the second blue-violet band. The X-ray diffraction pattern of this salt was identical with that of the complex obtained from the first band.[5] Differences in the procedures of this and previous works seemed to be in the temperatures of concentration and in the period spent for the crystallization of the complex; rather higher temperature and longer period were the conditions in the present work.

When an aqueous solution of the cis(N)trans(O_6) isomer of lithium bis(L-aspartato)cobaltate(III) prepared according to the literature[3] was allowed to stand at 40°C for 3 hours or at room temperature for 10 days, partial isomerizations of the species to another cis(N) one were observed, while isomerization to the trans(N) species was not observed.

References

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