The Isolation of the Two Isomers of Bis(L-aspartato)cobaltate(III)[1]

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There have been only a few investigations of cobalt(III) complexes containing the aspartate anion as a tridentate ligand.[2,3] We have now isolated two isomers of bis(L-aspartato)cobaltate(III) from a reaction mixture of tricarbonatocobaltate(III) with L-aspartate.

Monopotassium L-aspartate (31.0 g, 0.2 mol) was added to a solution of tricarbonatocobaltate(III) ($CoCl_2 \cdot 6H_2O$ 23.8 g scale, 0.1 mol), and the mixture was stirred at 60°C for 5 hr.[4] This solution was then acidified with acetic acid and heated on a water bath for 2 hr in order to complete the evolution of carbon dioxide. The resulting solution was treated with methanol to precipitate a red-violet material. This was dissolved in water and used for ion-exchange chromatography. Each portion of the aqueous solution was added to a column (Dowex 1×8, 100—200 mesh, Cl-form, $\phi=4$ cm, $h=30$ cm). During elution with a 0.1 M $CaCl_2$ solution, a band at the top of the column separated into two: the first eluted band (red-violet) and the second one (blue-violet). These bands were collected in fractions. Evaporation and the addition of ethanol gave the calcium salts of the desired complex. These were characterized by means of a study of their UV and CD spectra (Fig. 1). The earlier-eluted isomer is designated here as E-1, and the later-eluted one, E-2. The total yields were 5 g (for E-1) and 4 g (for E-2).

Found: C, 23.99; H, 4.76; N, 7.15% for E-1. C, 24.03; H, 4.70; N, 7.17% for E-2. Calcd for $Ca_{0.5}CoC_8H_{17}N_2O_{11.5} = Ca_{1/2}[Co(L\text{-}asp)_2] \cdot 3.5H_2O$: C, 23.77; H, 4.24; N, 6.93%.

The same isomers were also obtained by means of direct synthesis from the components and lead dioxide.

For the bis(L-aspartato)cobaltate(III) ion, three isomers are possible: (a) *trans*(N)·*cis*(O)·*cis*(O_β), (b) *cis*(N)·*trans*(O)·*cis*(O_β), and (c) bis(N)·*cis*(O)·*trans*(O_β), (O_β represents the two β-oxygen atoms). It is considered, from the order of chromatographic elution, that E-2 is either one of the two *cis*(N) isomers, while E-1 is the *trans*(N) isomer or another one of the *cis*(N) isomers. The geometry of our complex ion resembles that of the bis(L-2,3-diaminopropionato)cobalt(III) ion[5] in that they both contain two optically-active tridentate ligands. The CD curve of E-1 is similar, in appearance and magnitude, to that of the L-3[*1] isomer of the diaminopropionato complex, and the CD curve of E-2 is similar to that of L-1.[*1] The geometry of L-1 has been determined as *trans*(O)·*cis*(N_α)·*cis*(N_β); hence, it seems that E-2 has the corresponding geometry *cis*(N_α)·*trans*(O)·*cis*(O_β). On the other hand, it is impossible to relate the geometry of E-1 to that of L-3, for the latter is not known definitely.

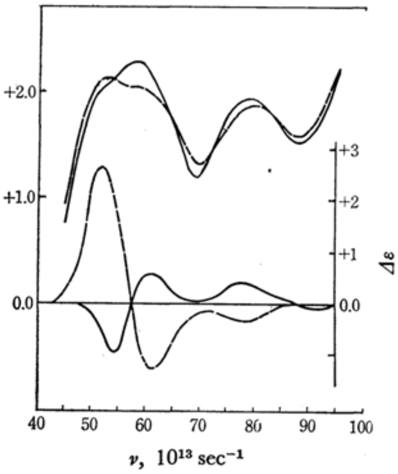

Fig. 1. UV and CD spectra of two isomers of $Ca_{1/2}$-$[Co(L\text{-}asp)_2] \cdot 3.5H_2O$.
—— the ealier-eluted isomer (E-1)
- - - the later eluted isomer (E-2)

The E-2 isomer is perhaps the first example of a complex differing in the splitting of the first band from the usual *cis*(N)–$[Co(O)_4(N)_2]$-type complexes.[6] For the *cis*(O)–$[Co(O)_2(N)_4]$-type complexes, such a splitting of the first band appears in the $[Co(L\text{-}asp)(NH_3)_3]^{+}$[2] and bis(L-2,3-diaminopropionato)cobalt(III) complexes.[5]

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[1] Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[2] J. I. Legg and D. W. Cooks, *J. Am. Chem. Soc.*, **89**, 6854 (1967).

[3] J. Hidaka, private communication.

[4] M. Shibata, H. Nishikawa and K. Hosaka, This Bulletin, **41**, 130 (1968).

[5] W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

[*1] According to the order of chromatographic elution, the isomers are designated as L-1, L-2, and L-3.[5]

[6] N. Matsuoka, J. Hidaka and Y. Shimura, This Bulletin, **40**, 1868 (1967).