The Isolation of the Four Isomers of Trihydrogen Tris-(L(+)-asparato)cobaltate(III)[1]

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(Received June 25, 1966)

Two of the four possible geometrical-optical isomers of tris-(L(+)asparato)cobaltate(III), the D and L-α forms, have previously been prepared by the reaction of cobalt(III) hydroxide with L(+)-aspartic acid.[2] We have now isolated the four (D and L-α and -β) from a reaction mixture of tricarbonatocobaltate(III) with L-aspartic acid; they have been characterized by means of their absorption spectrum, optical rotatory dispersion, and circular dichroism.

An equivalent amount of L-aspartic acid (30.0 g) was added to a solution of tricarbonatocobaltate-(III) ($CoCl_2 \cdot 6H_2O$, 18.0 g scale) prepared by our previously-described procedure.[3] The mixture was then stirred in the presence of activated charcoal (1.5 g) at room temperature for 2 hr. The resulting solution was filtered, and when the filtrate was adjusted to pH about 3.3 with dilute hydrochloric acid, a red-violet material was thereby separated out. This was then treated with large volumes of hot water in order to extract an appreciably soluble isomer. A sparingly soluble, massive solid remained. This was conveniently called the β-isomer (red). The extracted isomer was reprecipitated from the solution by the addition of hydrochloric acid (the α-isomer, violet).

When the mother liquor from the reaction mixture was again adjusted to pH about 0.5, and then kept in the cold, another red isomer was obtained (β'). The filtrate was concentrated to

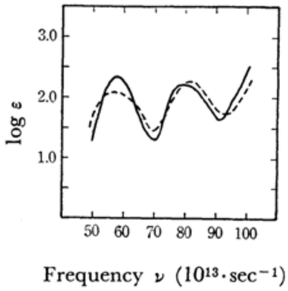

Fig. 1. Absorption spectra of α-$H_3[Co(asp)_3]$ (----) and β'-$H_3[Co(asp)_3]$ (——) in 60% perchloric acid.

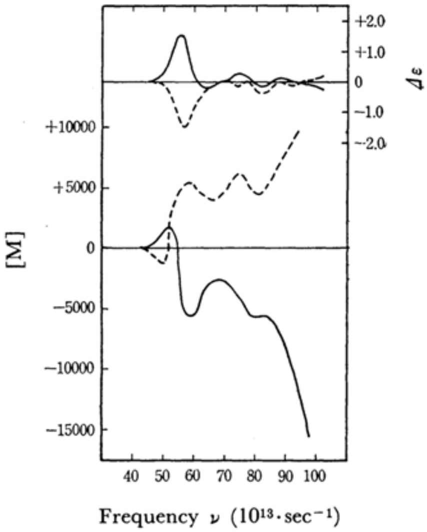

Fig. 2. The ORD and CD of β-$H_3[Co(asp)_3]$ (——) and β'-$H_3[Co(asp)_3]$ (----) in 60% perchloric acid.

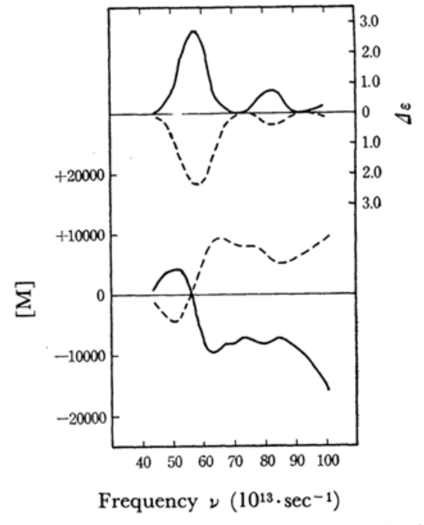

Fig. 3. The ORD and CD of α-$H_3[Co(asp)_3]$ (——) and α'-$H_3[Co(asp)_3]$ (----) in 60% perchloric acid.

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[1] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

[2] I. Lifschitz and W. Froentjes, *Rec. trav. chim.*, **60**, 225 (1941).

[3] M. Shibata, M. Mori and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

a small volume under reduced pressure. During this treatment, some deposited salts such as potassium chloride were rejected. The concentrated solution was kept in a refrigerator for several days in order to precipitate a fourth isomer (α', violet). All of these compounds were recrystallized from 60% perchloric acid or water.

Yields; about 6 (α), 5(α'), 1(β) and 12 g (β').

Found for α: C, 31.36; H, 4.13; N, 9.18%. For β: C, 31.80; H, 4.10; N, 9.15%. For β': C, 31.49; H, 4.11; N, 9.08%. Calcd for $H_3[Co(asp)_3]$: C, 31.69; H, 3.99; N, 9.23%.

Found for α': C, 29.29; H, 4.60; N, 8.11%. Calcd for $H_3[Co(asp)_3]\cdot 2H_2O$: C, 29.35; H, 4.48; N, 8.55%.

The absorption curves are given for only two isomers (α and β') in Fig. 1, since the curves are essentially the same for the corresponding isomers (α' and β). From these spectra the geometrical structures of the α and the β series may be identified as the 1. 2. 6 (mer) and 1. 2. 3 (fac) forms respectively as the 1. 2. 6 (mer) and 1. 2. 3 (fac) forms respectively.

The ORD and CD curves are given in Figs. 2—3. The absolute configuration for the β isomer, with a C_3 symmetry, can be identified as Λ or D by comparing it with the well established $\Lambda(+)$-$[Co(en)_3]^{3+}$ cation. Very recently, an X-ray study has shown that the absolute configuration of α-(+)-tris(L-alaninato)cobalt(III) is Λ.⁴⁾ By comparing our data with those on the alaninato-complex,⁵⁾ the configuration of the present α-isomer may be identified as Λ; hence, the α' isomer has the Δ(L) configuration.

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4) M. G. B. Drew, J. H. Dunlop, R. D. Gillard and D. Rogers, *Chem. Commun.*, **1966**, 42.

5) J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, **1965**, 6531.