The Isolation of the Four Isomers of Tris-(L(+)-valinato)cobalt(III)[1]

By Muraji SHIBATA, Hiroaki NISHIKAWA and Yuzo NISHIDA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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Lifschitz[2] isolated α and β forms of tris-(alaninato)cobalt(III) from a reaction mixture of cobalt(III) hydroxide with dextro-alanine, and also separated the α forms into two isomers, α and α'. Recently, Douglas and Yamada[3] found a fourth isomer, β', along with the other three isomers (α, α' and β), in the cobalt(III) complexes of D- and L-alanine. At almost the same time, Dunlop and Gillard[4] reported the isolation of the four isomers of tris-(L(+)-alaninato)-cobalt(III). We have now succeeded in obtaining the analogous four isomers (α, α', β and β') of tris-(L(+)-valinato)cobalt(III).

Following the usual procedure of Ley and Winkler[5] freshly-prepared $Co(OH)_3$ (9.2 g.) was treated with L-valine (34 g.). Red forms (β and β') of the complex precipitated from the reaction mixture as a brown solid containing unreacted $Co(OH)_3$. When the precipitates were extracted with hot water and the solution was evaporated, the more soluble β' isomer crystallized. When the residue from the above was treated with SO_2-water, the β isomer remained as undissolved material. This was then recrystallized from 50% sulfuric acid.

On the other hand, a mother liquor from the reaction mixture was evaporated to dryness, and the resulting solid was treated with ethanol; unreacted L-valine was thereby left. The complex was then taken up in ethanol. The alcohol solution was concentrated under reduced pressure

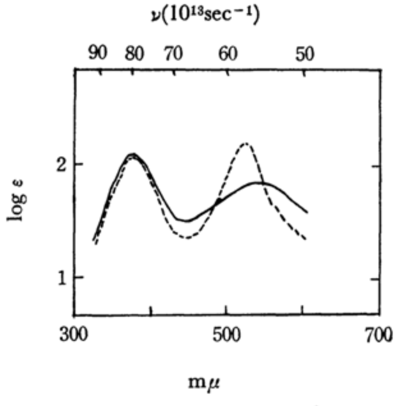

Fig. 1. Absorption spectra of —— α-[Co(L-val)$_3$], ---- β-[Co(L-val)$_3$].

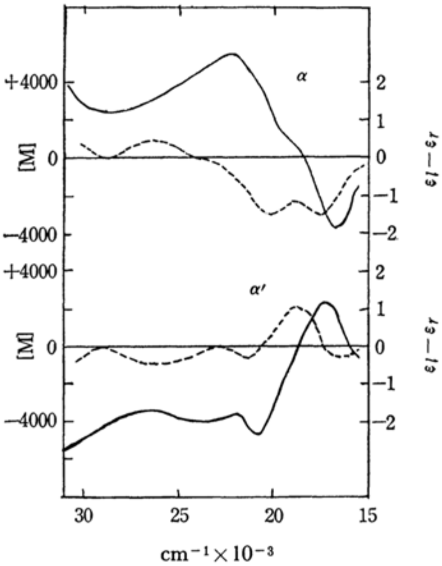

Fig. 2. Rotatory dispersion (——), and circular dichroism (----) of α- and α'-[Co(L-val)$_3$].

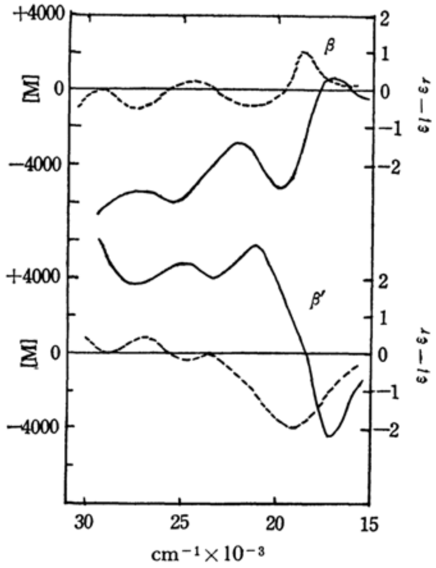

Fig. 3. Rotatory dispersion (——) and circular dichroism (----) of β- and β'-[Co(L-val)$_3$].

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[2] J. Lifschitz, *Z. physik Chem.*, **114**, 403 (1925).

[3] B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

[4] J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, **1965**, 6531.

[5] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

and then left to stand overnight to precipitate some of the β' isomer. After the β' had been removed, the solution was added to an alumina column previously washed with ethanol. When ethanol was passed through the column, violet forms (α and α') of the complex were eluted out, while a trace amount of the β' remained at the top of the column. The eluted solution was concentrated to a small volume, and then acetone was added to make an ethanol-acetone (1 : 2) solution. The mixed solvent solution was then again chromatographed by using ethanol-acetone (1 : 2) as the eluent. Two violet bands separated completely, and the α and α' were obtained from the first and the second fractions respectively, by evaporation.

Yield: α and α', about 10%; β and β', about 5%.

Found: C, 44.5; H, 7.5; N, 9.4. Calcd. for α-$[\mathrm{Co}(\text{L-val})_3]\cdot 1/2\mathrm{H_2O}$: C, 44.5; H, 7.8; N, 10.3%. Found: C, 43.5; H, 7.7; N, 9.4. Calcd. for α'-$[\mathrm{Co}(\text{L-val})_3]\cdot\mathrm{H_2O}$: C, 43.6; H, 7.7; N, 10.2%. Found: C, 39.3; H, 7.5; N, 9.21. Calcd. for β-$[\mathrm{Co}(\text{L-val})_3]\cdot 3\mathrm{H_2O}$: C, 40.0; H, 8.0; N, 9.40%. Found: C, 43.2; H, 7.3; N, 10.0. Calcd. for β'-$[\mathrm{Co}(\text{L-val})_3]\cdot\mathrm{H_2O}$: C, 43.6; H, 7.7; N, 10.2%.

The absorption curves are given for only two isomers (α and β) in Fig. 1, since the curves are essentially the same for the others (α' and β'). From these spectra, the α and α' are identified as the 1, 2, 6 (mer) isomer, and the β and β', as the 1, 2, 3 (fac) isomer. The optical rotatory dispersion and circular dichroism curves are given in Figs. 2—3. For the β and β' isomers belonging to the point group C_3, the configurations can be tentatively identified as Λ(D) for the β and Δ (L) for the β' by comparing the C. D. and O. R. D. curves of the present isomers with those of the Λ(D)-tris-(ethylenediamine)cobalt(III) ion.