The Partial Resolution of Racemic α-Alanine through the Cobalt(III) Complex of L-Aspartic Acid[*]

By Muraji SHIBATA, Yoshiho FUJITA,
Miho NAITO and Kuniko HORI

(Received February 9, 1963)

Studies of the resolution of racemic organic acids and amine have been reported by Bailar and his co-workers[1-3]. As far as alanine is concerned, the percentages of resolutions attained through the L-tartratocopper(II) complex and copper(II) L-glutamate were 3.8 and 3.3 respectively[3]. Attempting to resolve the same racemic mixture by using a cobalt(III) complex of L-aspartic acid, we have succeeded in effecting a much higher resolution.

The reaction path which we adopted for the resolution was as follows:

$$[Co(CO_3)_3]^{-3} \xrightarrow{2\,asp} [Co(asp)_2]^{-} \xrightarrow{6\,ala} [Co(ala)_3]$$

where "asp" stands for an aspartate ion, and "ala" for an alaninate ion. The starting material, a green solution of potassium tricarbonatocobaltate(III), was prepared by our method[4]. An exactly equivalent amount of L-aspartic acid was introduced into the green solution, and the mixture was stirred in the presence of active charcoal at temperatures not exceeding 15°C. The color of the solution gradually changed to violet with the formation of the asparato-complex. A hundred per cent excess of racemic alanine was added to the above solution, and the resulting mixture was adjusted to pH 9.5~10 with potassium hydroxide and warmed to 30~40°C. When the stirring was continued, *cis-cis-tris*-alaninatocobalt(III), $[Co(ala)_3]\cdot H_2O$ separated out. This was filtered and washed thoroughly with hot water and then with ethanol and ether.

The dried *tris*-alaninatocobalt(III) was suspended in hot dilute aqueous ammonia, and hydrogen sulfide was passed into the suspension. After the removal of the cobalt sulfide by filtration with charcoal, the filtrate was concentrated to a small volume on a water-bath. The solution was once more treated with charcoal for purification, and then acetone was added to precipitate the alanine. A 5% solution of this alanine in 1N hydrochloric acid was prepared, and its optical rotation was measured. The percentage of resolution was calculated by dividing the measured specific rotation with the specific rotation of pure L-alanine, $[\alpha]_D = +14.47°$[5].

In the course of the above experiments, we have discovered the very interesting fact that the co-existence of the cellulose powder

TABLE I. PARTIAL RESOLUTION OF ALANINE

Exp. No.	$CoCl_2\cdot 6H_2O$ used	Asp used	Ala used	pH	Active charcoal	Cellu-lose	$[Co(ala)_3]\cdot H_2O$	Ala reco-vered	Mea-sured	Resolu-tion
	g.	g.			g.	g.	g.	g.	deg.	%
1	6	6.7	13.6	9.5	0.4	none	3.3	2.3	−1.99	13.8
2	6	6.7	13.6	10.8	1	3	5.6	4.1	−4.6	31.8
3	6	6.7	13.6	9.9	2	3	5.6	4.3	−4.9	33.9
4	6	6.7	13.6	9.4	2	6	5.2	4.1	−5.1	35.2

Asp, Asparitc acid; Ala, Alanine

---

[*] Presented at the Symposium on Coordination Compounds, Tokyo, November 1962.

[1] J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott, *J. Am. Chem. Soc.*, **74**, 3131 (1952).

[2] A. D. Gott and J. C. Bailar, Jr., ibid., **74**, 4820 (1952).

[3] D. Sarma and J. C. Bailar, Jr., ibid., **78**, 895 (1956).

[4] M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, **29**, 883 (1956).

[5] S. Akabori and S. Mizushima, "Proteine Chemistry", ("Tanpakushitsu-Kagaku"), 1, Kyoritsu Shuppan K. K., Tokyo (1952), p. 527.

intended for chromatography in the reaction system of $[Co(asp)_2]^-$ and racemic alaninate ion effectively increases the resolution of alanine. Some of the data for these experiments are given in Table I. In the absence of the cellulose powder, the resolution was about 13%, while in its presence a resolution over 30% was achieved. In the reaction system used here, the D-form of alanine was preferentially coordinated.

We are continuing our investigations in our attempt to find the conditions giving the highest yield of the alaninatocomplex and to discover some material more effective than the cellulose for a higher resolution.

Department of Chemistry
Faculty of Science
Kanazawa University
Sengoku-machi, Kanazawa