In contrast, a preliminary observation by Wilmarth and Tsiang[22] suggests that the related anation reaction

$$\mathrm{Co(DH)_2(SO_3)OH_2^- + NCS^- \longrightarrow Co(DH)_2(SO_3)(NCS)^{2-} + H_2O} \quad (9)$$

proceeds by the limiting SN1 mechanism

$$\mathrm{Co(DH)_2(SO_3)OH_2^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Co(DH)_2(SO_3)^- + H_2O} \quad (10)$$

$$\mathrm{Co(DH)_2(SO_3)^- + NCS^-} \xrightarrow{k_3} \mathrm{Co(DH)_2(SO_3)NCS^{2-}} \quad (11)$$

with $k_2 = 11$ sec^{-1} and $k_{-2}/k_3 = 0.85\ M$ at 25°. If the corresponding reactions of NCS^- with $Co(DH)_2(NO_2)OH_2$ and $Co(DH)_2(I)OH_2$ are assumed to proceed by analogous mechanisms, then the measured values of k_1 for these reactions, *i.e.*, 5.8×10^{-4} and $12 \times 10^{-4}\ M^{-1}$ sec^{-1}, respectively, can be equated with k_2k_3/k_{-2}. These values are about 10^4 times lower than the corresponding value (13 M^{-1} sec^{-1}) for the reaction of $Co(DH)_2(SO_3)OH_2^-$ with NCS^-. The marked *trans*-labilizing effect of SO_3^{2-} and the limiting SN1 kinetic behavior exhibited by the sulfito complex parallel the effects of SO_3^{2-} on the anation reactions of $Co(NH_3)_4(SO_3)OH_2^+$ and $Co(CN)_4(SO_3)OH_2^{3-}$.[4,5]

It is also of interest to compare the present results with a recent determination of Randall and Alberty[23] of the kinetics of the replacement of water in aquocobalamin by NCS^-. The kinetics were found to be similar to those of the anation reactions reported here, with $k_1 = 7.1 \times 10^3\ M^{-1}$ sec^{-1} (*i.e.*, about 10^7 times the corresponding value for $Co(DH)_2(NO_2)OH_2$ or $Co(DH)_2(I)OH_2$)[24] and $k_{-1} = 1.8$. The much higher substitution rates exhibited by this and other cobalamin complexes,[25] in comparison with the corresponding bis(dimethylglyoximato)cobalt(III) complexes, are of interest in the light of the striking parallels between other aspects of the chemistry of the two series of complexes, noted by Schrauzer.[7] The origin and significance of these differences in substitution lability are not clear and merit further investigation.

[22] Cited in ref 5.

[23] W. C. Randall and R. A. Alberty, *Biochemistry*, **5**, 3189 (1966).

[24] A paper which appeared subsequent to the submission of this article [W. C. Randall and R. A. Alberty, *ibid.*, **6**, 1520 (1967)] reports similarly high values of k_1 for the replacement of water in aquocobalamin by other ligands, *i.e.*, N_3^-, 1.7×10^3; NCO^-, 7.3×10^2; imidazole, 27; CN^-, 1.5×10^3, all in M^{-1} sec^{-1} at 25°.

[25] J. M. Pratt and R. G. Thorp, *J. Chem. Soc.*, 187 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCES, UNIVERSITY OF BEOGRAD,
AND INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, BEOGRAD, YUGOSLAVIA

The Synthesis and Characterization of the Geometrical Isomers of Tris(β-alaninato)cobalt(III) Complexes

BY M. B. ĆELAP, S. R. NIKETIĆ, T. J. JANJIĆ, AND V. N. NIKOLIĆ

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Two geometrical isomers (red and violet) of the tris(β-alaninato)cobalt(III) complex have been prepared. Their electronic absorption spectra show the red isomer to be facial and violet isomer to be peripheral. The infrared spectra in the region 4000–400 cm^{-1} are reported, and the partial resolution of peripheral isomer by selective adsorption on quartz has been achieved.

It is well known that the coordination compounds of trivalent cobalt with amino acids of the type $Co(am)_3$ (where am = anion of an amino acid) can exist in two geometrical isomeric forms, *i.e.*, a violet α form and a red β form, having the peripheral (1,2,6) and facial (1,2,3) configurations, respectively. These compounds have been prepared by the following methods.

(1) Dissolving cobalt(III) hydroxide in the solution of the corresponding amino acid gives a product in which the peripheral isomer predominates. In this way the complexes with glycine,[1,2] DL-alanine,[2,3] L-alanine,[4-6] D-alanine,[5] DL-valine,[7] L-leucine,[2,6,7] and DL-phenylalanine[7] were prepared.

(2) The reaction of alkali salts of amino acids with hexaamminecobalt(III) chloride favors formation of the facial isomer of the corresponding tris(aminoacido)cobalt(III) complex. The method was applied[2] to the complexes of glycine, DL-alanine, and L-leucine.

(3) Using the reaction between alkali tricarbonatocobaltates(III) and amino acids—glycine, DL-alanine, and L-leucine—in the presence of acetic acid, Mori and co-workers[2] obtained both isomers in approximately equal amounts.

(4) Finally, the tris(aminoacido)cobalt(III) complexes were prepared by direct synthesis, namely, by the oxidation of cobalt(II) acetate in the presence of an amino acid.[8] Thus the complexes with DL-alanine and DL-valine have been prepared.

The above results show that the tris(aminoacido)cobalt(III) complexes studied up to now were prepared

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

[2] M. Mori, M. Shibata, E. Kyuno, and M. Kanaya, *Bull. Chem. Soc. Japan*, **34**, 1837 (1961).

[3] H. Ley and K. Ficken, *Ber.*, **50**, 1123 (1917).

[4] I. Lifshitz, *Z. Physik. Chem.*, **114**, 485 (1925).

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

[6] R. G. Denning and T. S. Piper, *ibid.*, **5**, 1056 (1966).

[7] V. Carassiti and M. Claudi, *Ann. Chim.* (Rome), **50**, 581 (1960).

[8] P. Spacu, C. Gheorgiu, M. Brezeanu, and S. Popescu, *Analele Univ. "C. I. Parhon" Bucuresti, Ser. Stiint. Nat.*, **19**, 43 (1958).

merely with α-amino acids. The tris(aminoacido)cobalt(III) complexes with β-amino acids apparently have not been previously described. The aim of this work was to prepare and investigate the isomers of tris(β-alaninato)cobalt(III).

Experimental Section

Violet Isomer of Tris(β-alaninato)cobalt(III).—The solution of 5.35 g (0.06 mole) of β-alanine in 10 ml of water was added to a slurry of 3.62 g (0.01 mole) of $Na_3Co(CO_3)_3 \cdot 3H_2O$ (prepared as described in ref 9). The mixture was heated on a steam bath for 1 hr with continuous stirring. The solution was filtered and the filtrate was evaporated to a small volume on a steam bath. To the viscous residue, while it was still hot, a few milliliters of ice-cold water was added at once. A solid separated in the yield of 2.7 g (84%). The crude product was recrystallized from a small amount of hot water; the needlelike crystalline substance was obtained; dec pt 238°. *Anal.* Calcd for $C_9H_{18}O_6N_3Co$: Co, 18.23. Found: Co, 18.35. (Cobalt was determined electrogravimetrically with the samples dried at 105°.)

Red Isomer of Tris(β-alaninato)cobalt(III).—The method used for the preparation of red isomer was similar to that described by Mori and co-workers[2] for the corresponding complexes with glycine and DL-alanine. To the solution of 5.35 g (0.02 mole) of $Co(NH_3)_6Cl_3$ (prepared as described in ref 10) in 20 ml of water the solution of 5.35 g (0.06 mole) of β-alanine in 20 ml of 3 *N* potassium hydroxide was added. The mixture was heated on a steam bath until no more ammonia was evolved. The procedure takes about 6 hr. The dark violet solution was transferred to a porcelain dish and evaporated on a steam bath to a small volume (approximately 5–6 ml). This solution was passed down a 100-cm column, 2.5 cm in diameter, packed with 500 g of acid alumina (Merck for chromatography). The column was eluted with water. The small red unidentified band was eluted first which was followed by a somewhat larger violet band corresponding to the peripheral isomer of $Co(\beta\text{-ala})_3$. (Hala = alanine ($C_3H_7O_2N$).) The intense red band which was completely separated from the former ones was due to the facial isomer of $Co(\beta\text{-ala})_3$. Finally, there were two sharp unidentified bands which were strongly adsorbed near the top of the column. By evaporating the corresponding fractions to dryness in a vacuum desiccator over concentrated H_2SO_4, 1.5 g (23%) of the peripheral and 2.5 g (40%) of the facial isomer of $Co(\beta\text{-ala})_3$ were obtained. The facial isomer separated in the form of red crystals which decompose on heating at 175°. *Anal.* Calcd for $C_9H_{18}O_6N_3Co \cdot 3H_2O$: Co, 15.62; C, 28.60; H, 6.50; N, 11.01. Found: Co, 15.71; C, 28.70; H, 6.55; N, 10.58. (The combined water could not be removed by heating the substance over P_2O_5 for 5 hr at 140° under diminished pressure.) Both isomers are extremely soluble in water but insoluble in most organic solvents. Aqueous solutions are stable for a long period of time.

Visible Absorption Spectra of the Isomers of Tris(β-alaninato)cobalt(III).—The absorption spectra in the visible region were measured on a Perkin-Elmer Model 137-UV spectrophotometer, with 7–8 × 10^{-3} *M* aqueous solutions, using the 1-cm silica cells. The spectra are summarized in Table I and Figure 1.

Infrared Spectra.—The infrared spectra in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer Model 337 Infracord spectrophotometer, calibrated against polystyrene, using the KBr-disk technique. Table II summarizes the band assignments for the principal frequencies in $Co(\beta\text{-ala})_3$ complexes.

Partial Resolution of the Peripheral Isomer of Tris(β-alaninato)cobalt(III) into Optical Antipodes.—Partial resolution was achieved using the method described by Bailar and Peppard.[11] To a solution of 0.25 g of the peripheral isomer of $Co(\beta\text{-ala})_3$ in 50 ml of water, 5 g of powdered natural Brazil levorotatory quartz (100 mesh) was added. The suspension was shaken for 1 hr at room temperature. After the removal of the quartz particles (by filtration) the solution showed an angle of rotation of −0.06°. The measurements were carried with a Franz Schmidt & Haensch Model S polarimeter using a 10-cm cell and a red filter with the maximum transmittance at 740 mμ. The light source was a 250-w bulb.

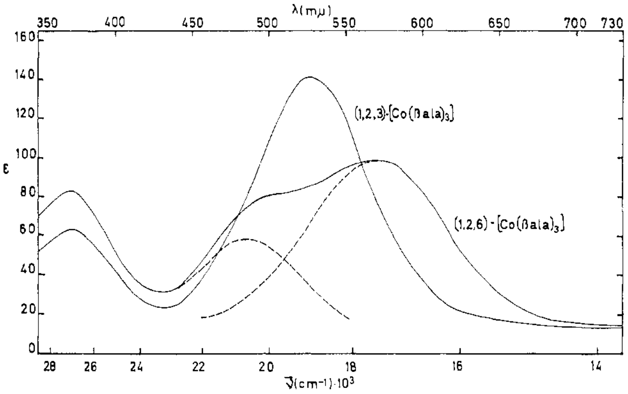

Figure 1.—Absorption spectra of $Co(\beta\text{-ala})_3$ complexes.

Separation of the Geometrical Isomers of Tris(β-alaninato)cobalt(III) by Thin Layer Chromatography.—Thin layer chromatography was used to check the purity of preparations and to follow the reactions. Glass plates 27 × 78 mm were coated with a slurry of silica gel "G" (Merck), air-dried, and activated for 1 hr at 115°. The solvent mixture used was ethanol–water in a ratio of 80:20. Running time for the chromatograms was about 30 min over 8 cm of length, at room temperature (22°). The spots were detected visually after drying the developed plates with a hair dryer. The R_f value for the peripheral isomer was 0.45, while the facial isomer remained at the start line.

Results and Discussion

Synthesis.—As one can see from the Experimental Section, the classic method for the preparation of tris(aminoacido)cobalt(III) complexes using cobalt(III) hydroxide failed in this case (see Hearn[12]). The reason is the low solubility of cobalt(III) hydroxide and the reduced stability of the six-membered ring in comparison with the five-membered rings (see Mann[13]).

The synthesis of the violet isomer of tris(β-alaninato)cobalt(III) was achieved by the indirect method, *i.e.*, the reaction of 6 moles of β-alanine with 1 mole of sodium tricarbonatocobaltate(III)

$$Na_3Co(CO_3)_3 \cdot 3H_2O + 6H_2NCH_2CH_2COOH = Co(H_2NCH_2CH_2COO)_3 + 3H_2NCH_2CH_2COONa + 6H_2O + 3CO_2$$

For the preparation of the red isomer of tris(β-alaninato)cobalt(III) the reaction between hexaamminecobalt(III) chloride and potassium β-alaninate was used

$$Co(NH_3)_6Cl_3 + 3H_2N(CH_2)_2COOK = Co(H_2NCH_2CH_2COO)_3 + 3KCl + 6NH_3$$

By this procedure a small amount of the violet isomer was also obtained.

Absorption Spectra.—In the course of the study of the geometrical isomerism in the tris(β-alaninato)-

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[9] H. F. Bauer and W. C. Drinkard, *Inorg. Syn.*, **8**, 202 (1966).

[10] J. Bjerrum and J. P. McReynolds, *ibid.*, **2**, 216 (1946).

[11] J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

[12] Hearn, Thesis, University of Illinois, 1951; J. C. Bailar, Jr., and D. H. Busch in "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., ACS Monograph No. 131, Reinhold Publishing Corp., New York, N. Y., 1956, p 39.

[13] F. C. Mann, *J. Chem. Soc.*, **129**, 2681 (1926).

cobalt(III) complexes, the electronic absorption spectra in the visible region were investigated (Figure 1). The characteristic difference between the isomers appears in the region of the first absorption band. The violet isomer reveals a distinct inflection in this region, while the red isomer has a symmetrical absorption band. These facts confirm that the configurations of the violet and red isomers are peripheral (or 1,2,6) and facial (or 1,2,3), respectively, which agrees with the assignment given by others[14-17] in the case of the tris(aminoacido)cobalt(III) species with α-amino acids. The inflection in the spectrum of the violet isomer can be attributed to the splitting of the $^1T_{1g}$ state corresponding to the rhombic crystal field in the peripheral isomer. The red isomer, which has a sharp single band at 19,011 cm^{-1}, belongs to the cubic crystal field. By the analysis of the spectrum of the violet isomer, the overlapped band was found at 20,492 cm^{-1}. The characteristic numerical values of the visible absorption bands for both of the isomers of tris(β-alaninato)cobalt(III) are given in Table I, together with the values of the corresponding compounds with α-aminopropionic acid. Comparison of these values shows that the first absorption bands in the β-alaninato complexes are shifted toward the red, while the second bands in both of the classes of tris(aminoacido)cobalt(III) complexes remain at approximately the same wavelength.

TABLE I

ELECTRONIC ABSORPTION SPECTRA OF TRIS(ALANINATO)COBALT(III) COMPLEXES

Complex[a]	$\tilde{\nu}_0$, cm^{-1}	ϵ_0	$\delta(+)$,[b] cm^{-1}	$\delta(-)$,[b] cm^{-1}
1,2,3-Co(ala)$_3$	19,230	186	1700	1300
	26,738	160	2183	1717
1,2,6-Co(ala)$_3$	18,553	100	. . .	. . .
	26,882	152	2217	1883
1,2,3-Co(β-ala)$_3$	19,011	141	1909	1559
	27,027	61	2736	2463
1,2,6-Co(β-ala)$_3$	17,554	100	. . .	1544
	20,492	64	1444	. . .
	27,027	84	2736	2463

[a] ala = DL-alaninate; β-ala = β-alaninate. [b] $\delta(+)$ and $\delta(-)$ are half-band widths toward larger and smaller wavenumbers, respectively: C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

Infrared Spectra.—The assignment of the bands in the infrared spectra of the isomeric tris(β-alaninato)cobalt(III) complexes has been made by a comparison with the reported frequency values for β-alanine[18] and other published data[19,20] and by observing the changes in spectra of deuterated complexes. The observed infrared frequencies for the peripheral isomer of Co(β-ala)$_3$ are given in Table II. The principal frequencies for the facial isomer of Co(β-ala)$_3$ are the same as for the α isomer, except that the multiplicity of the peaks is less pronounced in comparison with the α isomer. This is different from the observation of Quagliano and co-workers[20] for the corresponding glycinato complexes.

TABLE II

INFRARED FREQUENCIES (CM^{-1}) OF TRIS(β-ALANINATO)COBALT(III) COMPLEX[a]

Assignment	Frequencies
NH_2 str	3230 s, 3160 s, 3080 s
CH_2 str	2965 w, 2900 w
NH_2 bend and CO_2^- asym str	1640 vs, 1610 vs, 1570 vs
CH_2 bend	1460 m
CO_2^- sym str	1410 s, 1370 s
	1350 w
CH_2 wag	1330 m
	1310 m, 1290 s
Skeletal asym and NH_2 twist	1205 w, 1185 m, 1150 s
	1075 w, 1020 m, 980 m
Skeletal sym	910 s, 895 s
	885 m, 880 m, 710 w, 680 w
CO_2^- wag	645 w
	504 w, 425 w

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; asym, antisymmetric; sym, symmetric; str, stretch.

Resolution.—In order to obtain the additional proof for the trisbidentate configuration of the isolated complexes, an attempt was made to resolve the isomers of the Co(β-ala)$_3$ complex into optical antipodes. The partial resolution by the method of preferential adsorption on levorotatory quartz was successfully achieved so far only in the case of the peripheral isomer.

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