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### SYNTHESIS AND GEOMETRICAL ISOMERISM OF DIGLYCINATO( $\beta$ -AMINOISOBUTYRATO)COBALT(III) COMPLEX

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# SYNTHESIS AND GEOMETRICAL ISOMERISM OF DIGLYCINATO( $\beta$ -AMINOISOBUTYRATO)COBALT(III) COMPLEX

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The synthesis of the facial and meridional isomers of diglycinato( $\beta$ -aminoisobutyrate)cobalt(III) complex,  $[\text{Co}(\beta\text{-ibu})_2\text{gly}]_2$ , is described; the isomers were prepared by the action of  $\beta$ -aminoisobutyric acid on the *cis(0)-cis(N)*-isomer of carbonatodiglycinatocobaltate(III) ion. Their geometrical configurations were determined by means of electronic absorption spectroscopy as well as by adsorption and partition chromatography.

## INTRODUCTION

A greater number of tris(aminocarboxylato)cobalt(III) complexes have been described. They contain three identical  $\alpha$ <sup>1-5</sup> and  $\beta$  aminocarboxylato ligands<sup>6,7</sup>, respectively. In addition, the corresponding complexes containing two identical and one different  $\alpha$  aminocarboxylato ligand have been also described.<sup>8</sup>

Accordingly, as far as we know, the mixed complexes of this type, containing at the same time both  $\alpha$ -aminocarboxylato and  $\beta$ -aminocarboxylato ligands, have not been described. Therefore, in this paper, we have studied the possibility for their preparation.

## EXPERIMENTAL

### *Preparation of the Facial and the Meridional Isomers of Diglycinato( $\beta$ -aminoisobutyrate)cobalt(III) Complex*

A mixture of 4.8 g (0.015 mol) of the *cis(0)-cis(N)*-isomer of potassium carbonatodiglycinatocobaltate(III)<sup>8,9</sup> and 3.1 g (0.03 mol) of  $\beta$ -aminoisobutyric acid was dissolved in 75 ml of water in a 250 ml flask. The solution was then heated on a water-bath at 40°C for eight hours. After cooling, the reaction mixture was filtered off, and the obtained filtrate was left overnight in a refrigerator. The meridional isomer of diglycinato( $\beta$ -aminoisobutyrate)cobalt(III), separated in the form of thin violet needles, was filtered off and obtained in an amount 0.8 g

(recrystallized from water heated at 80°C). The remaining filtrate was evaporated in *vacuo* to a volume of 40 ml; to this solution 15 ml of ethanol was added and the mixture obtained was left overnight in a refrigerator. An additional amount of 0.15 g of the meridional isomer which separated out was filtered off and the filtrate was again evaporated to a volume of 30 ml, which was placed on a (70 x 30 cm) column containing 200 g of neutral alumina ("Lafoma", Skopje). The elution was performed with 90% ethanol whereby the violet (meridional) isomer moved down the column more rapidly than the red (facial) one. In the course of elution fractions of 10 ml were collected; their content was examined by paper chromatography (see page 4). Fractions containing two or more compounds were chromatographed separately by repeating the above procedure. All fractions exhibiting one and the same chromatographic zone were united, concentrated and cooled for 48 hours in a refrigerator. In this way there was obtained 0.45 g (9%) of the facial isomer of diglycinato( $\beta$ -aminoisobutyrate)cobalt(III) in the form of microcrystalline precipitate, and 0.15 g of the violet meridional isomer (the total yield of this isomer amounted to 1.1 g, 24%). Anal. Calcd. for violet (meridional) isomer  $\text{CoC}_8\text{H}_{16}\text{O}_6\text{N}_3 \cdot 3/2\text{H}_2\text{O}$ : C, 28.59; H, 5.70; N, 12.50;  $\text{H}_2\text{O}$ , 8.03. Found: C, 28.47; H, 5.90; N, 12.82;  $\text{H}_2\text{O}$ , 7.84. Anal. Calcd. for red (facial) isomer  $\text{CoC}_8\text{H}_{16}\text{O}_6\text{N}_3 \cdot \text{H}_2\text{O}$ : C, 29.37; H, 5.54; N, 12.84;  $\text{H}_2\text{O}$ , 5.50. Found: C, 29.18; H, 5.80; N, 12.70;  $\text{H}_2\text{O}$ , 5.34.

C, H and N content was examined by elemental microanalysis, and water content was determined by weighing air-dried substance (previously washed with

ethanol and ether) and the substance dried at 105°C till constant weight.

### Chromatographic Investigation

Paper chromatography was carried out on Whatman No 1 paper strips (30 x 3 cm). Chromatograms were developed in a cylinder (50 x 22 cm) saturated with solvent vapour, spots being detected by dipping the developed paper strips into ammonium sulphide solution. The results obtained are given in Table I.

TABLE I  
R<sub>F</sub>-Values obtained by paper-chromatography

| Complex  | R <sub>F</sub> -Values <sup>a</sup> |      |      |
|--|-------------------------------------|------|------|
|  | I                                   | II   | III  |
| <i>cis</i> (0)- <i>cis</i> (N)-K/Co gly <sub>2</sub> CO <sub>3</sub> / | 0.20                                | 0.18 | 0.40 |
| <i>fac</i> -/Co gly <sub>3</sub> / <sup>b</sup>                        | 0.22                                | 0.20 | 0.40 |
| <i>fac</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> /                      | 0.30                                | 0.60 | 0.50 |
| <i>fac</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> / <sup>c</sup>            | 0.85                                | 0.85 | 0.90 |
| <i>mer</i> -/Co gly <sub>3</sub> / <sup>b</sup>                        | 0.25                                | 0.22 | 0.37 |
| <i>mer</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> /                      | 0.50                                | 0.60 | 0.65 |
| <i>mer</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> / <sup>c</sup>            | 0.90                                | 0.90 | 0.93 |

<sup>a</sup>Solvent-mixture: I. n-Propanol (75 ml), water (20 ml), nitric acid (d. 1.41)(5 ml). Time of developing about 7 hours. II. Dioxane (85 ml), water (10 ml), nitric acid (d. 1.41)(5 ml). Time of developing about 7 hours. III. Methanol (90 ml), water (5 ml), nitric acid (d. 1.41) (5 ml). Time of developing about 4 hours.

<sup>b</sup>Obtained by dissolution of cobalt(III) hydroxide in glycine.<sup>10</sup>

<sup>c</sup>Obtained by the action of β-aminoisobutyric acid on hexamminecobalt(III) chloride.<sup>7</sup>

Thin-layer chromatography was carried out on (20 x 13 cm) plates coated with 2 mm layer of silica gel G ("Kemika", Zagreb), according to Stahl. The preparation and development of plates was carried out in the usual way.<sup>11</sup> The solvent-mixture used was the following: isopropanol (90 ml), water (5 ml) and nitric acid (d. 1.41)(5 ml). Time of development was about 7 hours. The spots were detected by spraying the plate with ammonium sulphide solution. The results obtained are given in Table II.

### Electronic Absorption Spectra

Electronic absorption spectra were recorded on a Carl Zeiss Spectralphotometer VSU 2 with 5 x 10<sup>-3</sup> M aqueous sulphuric acid solutions (1:1). The results obtained are given in Table III and Figure 2.

TABLE II  
R<sub>F</sub>-Values obtained by thin-layer chromatography on silica gel G

| Complex  | R <sub>F</sub> -Value |
|--|-----------------------|
| <i>cis</i> (0)- <i>cis</i> (N)-K/Co gly <sub>2</sub> CO <sub>3</sub> / | 0.82                  |
| <i>fac</i> -/Co gly <sub>3</sub> /                                     | 0.00                  |
| <i>fac</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> /                      | 0.00                  |
| <i>fac</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> /                         | 0.00                  |
| <i>mer</i> -/Co gly <sub>3</sub> /                                     | 0.70                  |
| <i>mer</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> /                      | 0.75                  |
| <i>mer</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> /                         | 0.85                  |

## RESULTS AND DISCUSSION

### Synthesis

As seen from the Experimental, in this paper we succeeded to obtain the red and one violet isomer of diglycinato(β-aminoisobutyrate)cobalt(III) complex, by the action of β-aminoisobutyric acid on the *cis*(0)-*cis*(N)-isomer of potassium carbonatodiglycinatocobaltate(III).<sup>8,9</sup> In this way there was obtained a new type of tris(aminocarboxylato)-cobalt(III) complexes which contain two α-aminocarboxylato and one β-aminocarboxylato ligands in contrast to the so far described tris(aminocarboxylato)-cobalt(III) complexes which contain either three α-aminocarboxylato or three β-aminocarboxylato ligands.<sup>1-8</sup> These mixed complexes are of interest since they can be used for the study of the effect of the ring enlargement on various properties of complexes, as for example their spectra and R<sub>F</sub>-values.<sup>1,3,14</sup>

### Configuration

Theoretically diglycinato(β-aminoisobutyrate)-cobalt(III) complex might appear in the form of

TABLE III  
Absorption maxima (λ, nm), and log ε of investigated compounds

| Complex  | λ <sub>1</sub> | log ε <sub>1</sub> | λ <sub>2</sub> | log ε <sub>2</sub> |
|--|----------------|--------------------|----------------|--------------------|
| <i>fac</i> -/Co gly <sub>3</sub> / <sup>a</sup>                | 520            |                    | 372            |                    |
| <i>fac</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> / <sup>b</sup> | 526            | 2.18               | 374            | 2.20               |
| <i>fac</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> / <sup>c</sup>    | 534            |                    | 372            |                    |
| <i>mer</i> -/Co gly <sub>3</sub> / <sup>a</sup>                | 537            |                    | 372            |                    |
| <i>mer</i> -/Co(β- <i>ibu</i> )gly <sub>2</sub> / <sup>b</sup> | 560            | 1.88               | 371            | 2.04               |
| <i>mer</i> -/Co(β- <i>ibu</i> ) <sub>3</sub> / <sup>c</sup>    | 571            |                    | 372            |                    |

<sup>a</sup>Reference 12.

<sup>b</sup>This work.

<sup>c</sup>Reference 7.

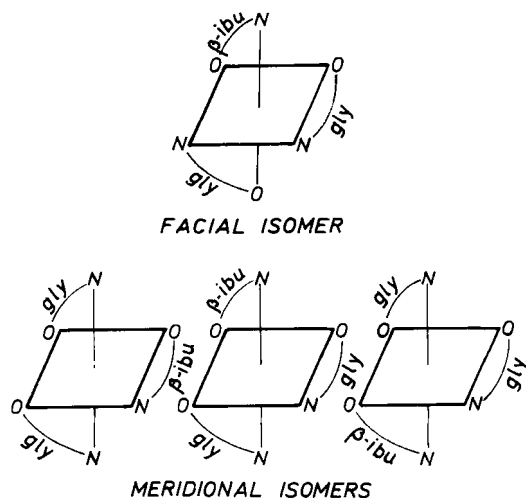


FIGURE 1

four geometrical isomers, one facial, and three meridional (Figure 1).

The facial isomer of tris(aminocarboxylato)cobalt(III) complex has a cubic symmetry of the ligand field, in contrast to the meridional one which has a rhombic ligand field. Therefore, the red isomer, which exhibits a symmetric first absorption band (due to a  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  electronic transition), was assigned the facial configuration, and the violet isomer, having a nonsymmetric first absorption band, the meridional configuration (Figure 2).

The decreased symmetry of the ligand field causes the splitting of the triply degenerated energy level which gives rise to the nonsymmetry of the first absorption band. This agrees with the results obtained by Basolo and coworkers<sup>1,2</sup> in the case of

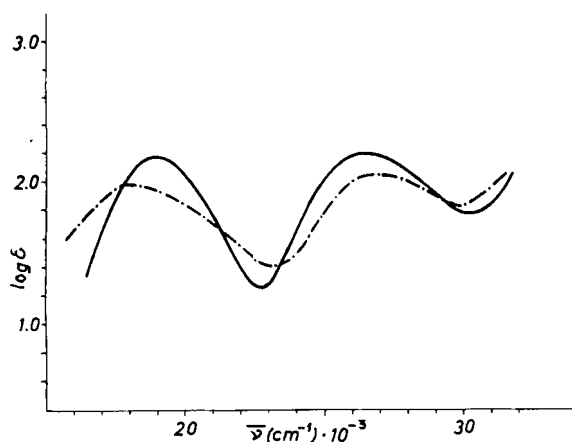


FIGURE 2

triglycinatocobalt(III), and the results published by Čelap and coworkers<sup>6</sup> for tris( $\beta$ -alaninato)cobalt(III). Moreover, as seen from Table III, the position of the first absorption maximum in the electronic spectra of mixed isomers is consistent with the relative ligand field strengths of  $\alpha$ -aminocarboxylato and  $\beta$ -aminocarboxylato ligands.<sup>1,3</sup>

The established geometrical configurations agree also with the  $R_f$ -values of the isomers obtained. As seen from Table I, the  $R_f$ -values of mixed isomers, obtained by partition paper chromatography, lie between  $R_f$ -values of the corresponding isomers of triglycinatocobalt(III) and tris( $\beta$ -aminoisobutyrate)cobalt(III).<sup>1,4</sup>

Finally, the configuration of the meridional isomer was confirmed by  $R_f$ -values obtained by thin-layer chromatography on silica gel (Table II): the  $R_f$ -value of this isomer was found to be between the  $R_f$ -values of the meridional isomers of triglycinatocobalt(III) and tris( $\beta$ -aminoisobutyrate)cobalt(III). The  $R_f$ -value of the facial isomer was found to be zero (on account of its pronounced polarity), similar to the corresponding isomers having three  $\alpha$ -aminocarboxylato or three  $\beta$ -aminocarboxylato ligands; this is also in agreement with earlier results obtained by other authors.<sup>7</sup>

However, we have not been able so far to establish on the base of data obtained which of the three theoretically possible meridional isomers represents the obtained violet complex.

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