

## Synthesis and Configuration of New Isomers of the Bis(aminocarboxylato)carbonatocobaltate(III) Ion\*

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In the reaction between potassium tricarbonatocobaltate(III) and the corresponding amino acid (glycine or  $\beta$ -alanine) two new geometrical isomers of the bis(aminocarboxylato)carbonatocobaltate(III) ion have been obtained. In case of glycine, in addition to the previously described<sup>1-3</sup> *cis*(N), *cis*(O)-isomer, the corresponding *cis*(N), *trans*(O)-isomer was also obtained, whereas in the reaction with  $\beta$ -alanine the *trans*(N), *cis*(O)-isomer was prepared. The configuration of the *trans*(N)-isomer was established using its electronic spectrum, whereas the configuration of the other two isomers was determined by means of PMR spectroscopy. In addition, the *cis*, *cis*-isomer was resolved into enantiomers by means of  $\Lambda - (+)_{589}$ -*cis*(NO<sub>2</sub>), *trans*(N)-isomer of the bis(S-arginine)dinitrocobalt(III) ion. The absolute configuration of the  $\Delta - (-)_{589}$ -*cis*(N), *cis*(O)-isomer was assumed by comparing its CD spectrum with that of the  $\Lambda - (+)_{589}$ -*cis*(N), *cis*(O)-isomer of the carbonato-bis-(S-valinato)cobaltate(III) ion.<sup>2,3</sup>

### INTRODUCTION

By the action of glycine, S-alanine and S-valine, respectively, on potassium tricarbonatocobaltate(III) Shibata *et al.*<sup>1</sup> prepared one out of the three theoretically possible isomers of the bis(aminocarboxylato)carbonatocobaltate(III) complex (Figure 1). The authors established, by means of electronic spectroscopy, that the isolated compounds do not represent the *trans*(N)-isomers, but did not find out which *cis*-isomer is in question. Somewhat later, using the same reaction, Gillard *et al.*<sup>2</sup> prepared and determined the geometrical configuration of the *cis*(N), *cis*(O)-isomer of the afore-mentioned complex with S-alanine, S-valine, S-leucine and S-phenylalanine, respectively. The absolute configuration of the  $\Lambda - (+)_{589}$ -*cis*(N), *cis*(O)-isomer of the carbonatobis(S-valinato)cobaltate(III) diastereomer was established by means of the CD spectra and confirmed later by X-ray structural analysis.<sup>3</sup>

\* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

## EXPERIMENTAL

*Synthesis of Potassium Bis(aminocarboxylato)carbonatocobaltate(III) Complexes*1. *Preparation of cis(N), cis(O)- and cis(N), trans(O)-Isomers of Potassium Carbonatodiglycinatocobaltate(III) Hydrate*

To a solution of 23.8 g (0.10 mol) of cobalt(II) chloride hexahydrate in 50 cm<sup>3</sup> of water was added 16 cm<sup>3</sup> of 30% hydrogen peroxide. The solution obtained was added dropwise to a suspension of 65.0 g (0.65 mol) of potassium bicarbonate in 60 cm<sup>3</sup> of water, placed in a 250 cm<sup>3</sup> Erlenmeyer, with stirring and cooling with ice, over two hours. To the latter solution containing potassium tricarbonatocobaltate(III) was added 15.0 g (0.20 mol) of glycine and the reaction mixture was heated in a water-bath at 60 °C for 90 minutes. The solution thus obtained was cooled to room temperature, neutralized with acetic acid (1:1) to pH 7.2, and filtered off; 50 cm<sup>3</sup> of 96% ethanol was added to the filtrate which was then left to stand overnight in a refrigerator. The separated white crystals were filtered and 50 cm<sup>3</sup> of ethanol was again added to the filtrate; upon cooling and rubbing the vessel walls with a glass rod, there crystallized out over two hours about 20 g (65%) of dark-violet *cis(N), cis(O)*-isomer of potassium carbonatodiglycinatocobaltate(III) monohydrate. The substance was recrystallized from a water : 96% ethanol (1:1) mixture at 60 °C. The purity of the substance was checked by paper chromatography (Table I). The substance for analysis was dried at 105 °C for two hours whereby it lost 5.7% of its mass, which corresponds to one water molecule (5.50%).

*Anal.* KCoC<sub>5</sub>H<sub>8</sub>O<sub>7</sub>N<sub>2</sub> (306.16) calc'd: Co 19.25; K 12.77; H 2.63; N 9.15%  
found: Co 19.29; K 12.82; H 2.97; N 9.27%.

The filtrate remaining after the separation of the *cis(N), cis(O)*-isomer was concentrated *in vacuo* at 60 °C to a volume of about 60 cm<sup>3</sup>, to which 120 cm<sup>3</sup> of 96% ethanol is added. Upon cooling with icy water and rubbing the vessel walls with a glass rod, the substance was caused to crystallize and the solution was left overnight in a refrigerator. The separated needle-like blue crystals of potassium *cis(N), trans(O)*-carbonatodiglycinatocobaltate(III) trihydrate, which are hygroscopic, were filtered off *in vacuo* on a Büchner funnel, washed with 96% ethanol and ether, and dried in a desiccator over conc. H<sub>2</sub>SO<sub>4</sub>. The yield of the crude product amounted to 3.6 g (10%). The substance was recrystallized from 80% ethanol at 50 °C. The purity of the substance was checked by paper chromatography using three different solvent mixtures (Table I). Chromatographic investigations showed that in addition to the zone corresponding to the isolated substance there is a weak zone (approximately in a 95:5 ratio) corresponding to the *cis(N), cis(O)*-isomer. The substance for analysis was dried at 105 °C for two hours, whereby it lost 14.3% of its mass, which corresponds to three water molecules (15.0%).

*Anal.* KCoC<sub>5</sub>H<sub>8</sub>O<sub>7</sub>N<sub>2</sub> (306.16) calc'd: Co 19.25; K 12.77; H 2.63; N 9.15%  
found: Co 19.38; K 12.74; H 2.89; N 9.18%.

2. *Preparation of the trans(N), cis(O)-Isomer of Potassium Bis(β-alaninato)carbonatocobaltate(III) Monohydrate*

To a solution of potassium tricarbonatocobaltate(III), prepared in the same way as it is described above 17.8 g (0.20 mol) of β-alanine was added and the reaction mixture was heated on a water-bath at 60 °C for three hours. It was cooled to room temperature, neutralized with acetic acid (1:1) to pH 7.2, and 100 cm<sup>3</sup> of 96% ethanol was added. The solution thus obtained was left to stand overnight in a refrigerator. The separated white crystals were filtered off and 200 cm<sup>3</sup> of 96% ethanol was added to the filtrate. Alternative filtration and concentration of the filtrate yielded 8 g (24%) of the blue crystalline *trans(N), cis(O)*-isomer of potassium bis(β-alaninato)carbonatocobaltate(III) monohydrate, which was recrystallized from 50% ethanol at 60 °C. The purity of the substance was checked by paper chromatography using three different solvent-mixtures (Table I).

The substance for analysis was dried at 105 °C for two hours whereby it lost 5.4% of its mass, which corresponds to one water molecule (5.12%).

Anal.  $\text{KCoC}_7\text{H}_{12}\text{O}_7\text{N}_2$  (334.145) calc'd: Co 17.64; K 11.70; H 3.62; N 8.38%  
found: Co 17.56; K 11.59; H 3.78; N 8.39%.

### Resolution of the cis-cis-Isomer of the Carbonatodiglycinatocobaltate(III) Ion

To a warm (40 °C) solution of 2.39 g (4.0 mmol) of  $\Lambda - (+)_{589}\text{-cis}(\text{NO}_2)\text{-trans}(\text{N})\text{-[Co}(\text{NO}_2)_2(\text{S-argH})_2\text{]Cl} \cdot 3\text{H}_2\text{O}^4$  in 20 cm<sup>3</sup> of water was added a solution of 1.29 g (4.0 mmol) of *cis, cis*-K[Cogly<sub>2</sub>CO<sub>3</sub>] · H<sub>2</sub>O in 20 cm<sup>3</sup> of water. The solution obtained was left to stand overnight at room temperature. Ca. 1.3 g of the less soluble  $(-)_589 - [\Lambda - (+)_{589}\text{-cis}(\text{NO}_2), \text{-trans}(\text{N})\text{-Co}(\text{NO}_2)_2(\text{S-argH})_2]$  [( $-$ )<sub>589</sub>-*cis, cis*-Cogly<sub>2</sub>CO<sub>3</sub>] · 7H<sub>2</sub>O diastereomer (I) separated in the form of small pink needles, which were separated by filtration on a Büchner funnel, washed successively with several drops of cold 48% ethanol, then 96% ethanol and finally with ether. The substance was recrystallized (usually twice) from warm (40 °C) water up to a constant optical rotation  $[\alpha]_{\text{D}}^{20} = -80^\circ$ , ( $c = 0.02$  g/100 cm<sup>3</sup> water), yielding ca. 0.7 g of pure I.

The filtrate obtained after the separation of the less soluble diastereomer I was left to stand in a refrigerator for about 2 hours, whereby there crystallized out ca. 0.5 g of a mixture of both diastereomers which were separated by filtration. The filtrate obtained after the separation of the afore-mentioned diastereomeric mixture was concentrated on a rotatory vacuum evaporator (40 °C) to half its volume and left to stand overnight in a refrigerator; there crystallized out ca. 1.2 g of  $(+)_{589} - [\Lambda - (+)_{589}\text{-cis}(\text{NO}_2), \text{trans}(\text{N})\text{-Co}(\text{NO}_2)_2(\text{S-argH})_2]$  [( $+$ )<sub>589</sub>-*cis-cis*-Cogly<sub>2</sub>-CO<sub>3</sub>] · 7H<sub>2</sub>O diastereomer (II), in the form of small pink crystals. The substance was recrystallized (usually twice) from warm (40 °C) water up to constant optical rotation  $[\alpha]_{\text{D}}^{20} = +310^\circ$  ( $c = 0.2$  g/100 cm<sup>3</sup> water), yielding ca. 0.6 g of pure II. For analysis the diastereomers I and II were dried at 105 °C for 2 hours, whereby diastereomer I lost 13.86% of its mass, while the diastereomer II loses 13.98% and both values correspond to a loss of seven water molecules (14.12%).

Anal.  $\text{Co}_2\text{C}_{17}\text{H}_{36}\text{N}_{12}\text{O}_{15}$  (766.451) calc'd: C 26.64; H 4.73; N 21.93%.

Found for:

Diastereomer I C 26.51; H 4.34; N 21.87%  
Diastereomer II C 26.72; H 4.29; N 21.72%.

A solution of 0.4 g (0.5 mmol) of diastereomer I, or II, in 10 cm<sup>3</sup> of water was passed through a cationic Dowex 50W X4 (200—400 mesh) column (10 cm long,  $\Phi$  2 cm), in potassium form. Upon elution with water the eluates obtained were evaporated to dryness on a rotatory vacuum evaporator at 40 °C to obtain the corresponding dark violet enantiomer monohydrates (in almost quantitative yield).

The enantiomers obtained are hygroscopic and therefore they were kept in a desiccator above conc. sulphuric acid. Optical rotation:  $[\alpha]_{\text{D}}^{21} = -480^\circ$  and  $370^\circ$ , respectively ( $c = 0.015$  g/100 cm<sup>3</sup> of aqueous solution). When dried at 105 °C for two hours, both substance lost between 5.6 and 5.8% of their mass, which corresponds to one water molecule (5.52%).

Anal.  $\text{KCoC}_5\text{H}_8\text{O}_7\text{N}_2$  (306.160) calc'd. for anhydrous salt:

Co 19.25; K 12.77; H 2.63; N 9.15%.

Found for  $(+)_{589}$ -enantiomer:

Co 19.05; K 12.65; H 3.02; N 9.27%

Found for  $(-)_589$ -enantiomer:

Co 19.09; K 12.60; H 2.84; N 8.99%.

### Electronic Spectra

Electronic absorption spectra in the visible and ultraviolet regions were recorded on a Varian Super Scan 3 Spectrometer with  $5 \times 10^{-3}$  mol/dm<sup>3</sup> aqueous solutions. A cell of 0.5 cm path length was used. Absorption maxima and log  $\epsilon$  values are given in Table I.

\* argH = arginine

TABLE I

Absorption Maxima (nm), log  $\epsilon$  and  $R_f$  Values Obtained by Paper-Chromatography of the Bis(aminocarboxylato)carbonatocobaltate(III) ion\*

Complex	$\lambda_1$	log $\epsilon_1$	$\lambda_2$	log $\epsilon_2$	$R_f$ values**		
					A	B	C
<i>cis</i> (N), <i>cis</i> (O) — K[CoCO <sub>3</sub> gly <sub>2</sub> ]	553	2.20	392	2.20	0.17	0.44	0.14
<i>cis</i> (N), <i>trans</i> (O) — K[CoCO <sub>3</sub> gly <sub>2</sub> ]	553	2.06	392	2.18	0.24	0.48	0.17
<i>trans</i> (N), <i>cis</i> (O) — [KCoCO <sub>3</sub> ( $\beta$ -ala) <sub>2</sub> ]	553	2.01	382	2.10	0.30	0.54	0.20
	610 (sh)***	1.93					

\* glyH = glycine,  $\beta$ -alaH =  $\beta$ -alanine.

\*\* Solvent mixtures: A Isopropanol (75 cm<sup>3</sup>) + HNO<sub>3</sub> ( $\rho$  = 1.42 g/cm<sup>3</sup>) (5 cm<sup>3</sup>) + H<sub>2</sub>O (20 cm<sup>3</sup>)

B Acetone (75 cm<sup>3</sup>) + HNO<sub>3</sub> ( $\rho$  = 1.42 g/cm<sup>3</sup>) (5 cm<sup>3</sup>) + H<sub>2</sub>O (20 cm<sup>3</sup>)

C Acetone (75 cm<sup>3</sup>) + H<sub>2</sub>O (25 cm<sup>3</sup>) + KJ (1g).

\*\*\* sh = shoulder.

### Optical Rotation

The optical rotation was measured on a Perkin Elmer 141 MC Polarimeter. The measurements were carried out in a 10 cm path length cell with aqueous solutions.

### Chromatographic Investigation

Chromatography was carried out in a 50 cm high cylinder ( $\Phi$  22 cm), by the ascending method, on Whatman No 1 paper strips (30  $\times$  3 cm). The solvent mixture was put into the cylinder one hour before chromatographic separation. The solvent travelled about 22 cm. The detection of the separated components was performed by dipping the developed paper strips into ammonium sulphide solution. All experiments were carried out at room temperature, and the results obtained are listed in Table I.

### Circular Dichroism Spectra

Circular dichroism spectra were recorded on a Jobin Yvon Dichrographe III with an aqueous solution of 5.5 mg/10 cm<sup>3</sup> concentration.

## RESULTS AND DISCUSSION

### Synthesis

As seen from the Experimental, in the reaction between potassium tricarbonatocobaltate(III) and glycine we succeeded in synthesizing, in addition to the already described<sup>2</sup> *cis*(N), *cis*(O)-isomer, the previously unidentified *cis*(N), *trans*(O)-isomer of potassium carbonatodiglycinatocobaltate(III). In contrast to this, in the reaction with  $\beta$ -alanine we have prepared the last of the three theoretically possible geometrical isomers of the bis(aminocarboxylato)carbonatocobaltate(III) ion to be identified, *i. e.* the *trans*(N), *cis*(O)-isomer of potassium bis( $\beta$ -alaninato)carbonatocobaltate(III). In addition, the *cis*(N), *cis*(O)-isomer of potassium carbonatodiglycinatocobaltate(III) was resolved into optical isomers by means of the  $\Lambda$  — (+)<sub>589</sub>-diastereomer of the bis(S-arginine)dinitrocobalt(III) complex, which had been prepared in one of our earlier papers.<sup>4</sup>



Due to the presence of a reactive carbonato ligand in the compounds obtained, it may be assumed that they will be used as starting substances for the synthesis of related complexes.

*Determination of the Geometrical and Absolute Configuration of the Isolated Isomers of the Bis(aminocarboxylato)carbonatocobaltate(III) Ion*

If we consider the positions of ligators around the central metal ion in the isomers of the bis(aminocarboxylato)carbonatocobaltate(III) ion (Figure 1),

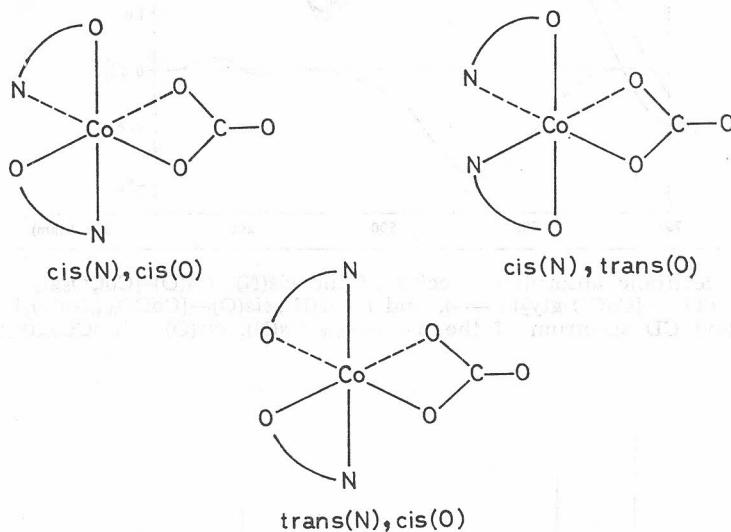


Figure 1. Geometrical isomers of the bis(aminocarboxylato)-carbonatocobaltate(III) ion.

we see that in the case of one isomer four oxygen atoms lie in one plane, while two nitrogen atoms lie on a perpendicular Z-axis, leading to a tetragonal distortion which causes the splitting of the first absorption band arising from the  ${}^1T_{1g} \leftarrow {}^1A_{1g}$  electronic transition. In contrast to this, in case of other two isomers no essential difference in their electronic spectra is expected. Therefore, the isomer of the bis( $\beta$ -alaninato)carbonatocobaltate(III) ion, whose first electronic absorption band displays an inflexion (Figure 2), was assigned *trans(N), cis(O)*-configuration. Configurations of the remaining two isomers were established by means of PMR spectroscopy.

Due to  $C_2$  molecular symmetry (Figure 1), the *cis(N), trans(O)*-isomer contains two equivalent chelate ligands; hence, in the case of the carbonatodiglycinatocobaltate(III) ion this isomer is expected to give only one methylene signal in its PMR spectrum. However, in the case of the *cis(N), cis(O)*-isomer of the complex with the same amino acid, due to  $C_1$  molecular symmetry, chelate ligands have a different chemical environment and therefore two methylene signals are expected in the PMR spectrum. On this basis, *cis(N), trans(O)*-configuration was assigned to the isomer of the carbonatodiglycinatocobaltate(III) ion, which gives only one PMR signal (Figure 3), whereas *cis(N),*

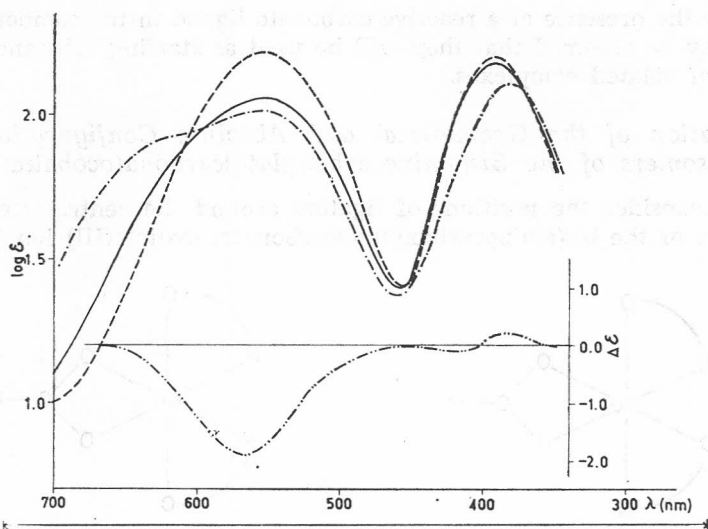


Figure 2. Electronic absorption spectra of the *cis*(N), *cis*(O)-[CoCO<sub>3</sub>gly<sub>2</sub>]<sup>-</sup> (---), *cis*(N), *trans*(O)-[CoCO<sub>3</sub>gly<sub>2</sub>]<sup>-</sup> (—), and *trans*(N), *cis*(O)-[CoCO<sub>3</sub>(β-ala)<sub>2</sub>]<sup>-</sup> (-·-·-), ions, and CD spectrum of the Δ-(→)<sub>589</sub>-*cis*(N), *cis*(O)-[CoCO<sub>3</sub>gly<sub>2</sub>]<sup>-</sup> ion.

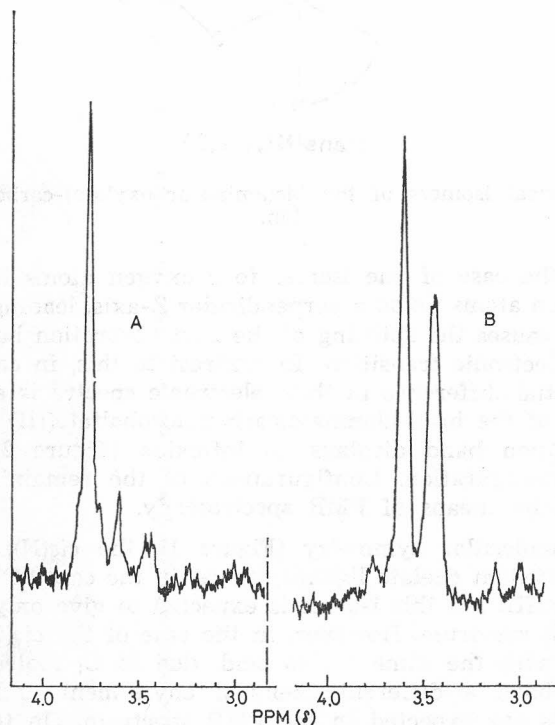


Figure 3. PMR Spectra of the *cis*(N), *trans*(O) (A) and *cis*(N), *cis*(O) (B) geometrical isomers of the carbonatodiglycinatocobaltate(III) ion.

*cis*(O)-configuration was assigned to the isomer exhibiting two PMR signals. In this way we established that in the reaction of the tricarbonatocobaltate(III) ion with glycine, *cis*(N), *trans*(O)- and *cis*(N), *cis*(O)-isomers of carbonatodiglycinatocobaltate(III) ion were obtained, whereas in the reaction with  $\beta$ -alanine, the *trans*(N)-isomer of bis( $\beta$ -alaninato)carbonatocobaltate(III) ion was isolated (Table I).

Moreover, from Figure 3(A) it is seen that in addition to the signal corresponding to the *cis*(N), *trans*(O)-isomer there are signals (at 3.4 and 3.6 ppm) which correspond to the *cis*(N), *cis*(O)-isomer of potassium carbonatodiglycinatocobaltate(III). Since we failed to obtain a sample showing only one signal corresponding to the *cis*(N), *trans*(O)-isomer, we assume that the latter isomer is partially isomerized into the *cis*(N), *cis*(O)-isomer, which renders impossible the isolation of the pure isomer.

The absolute configuration of the  $(-)$ <sub>859</sub>-*cis*(N)-*cis*(O)-isomer was determined by comparing its CD spectrum (Figure 2) with that of the  $\Lambda$   $(+)$ <sub>589</sub>-*cis*(N), *cis*(O)-isomer of potassium carbonato-bis(S-valinato)cobaltate(III) dihydrate, the configuration of which was determined by X-ray structural analysis.<sup>3</sup> Since the obtained  $(-)$ <sub>589</sub>-*cis*(N), *cis*(O)-isomer of carbonatodiglycinatocobaltate(III) ion exhibits a negative Cotton effect in the region of the first absorption band on the side of lower energy, in contrast to the  $\Lambda$   $(+)$ <sub>589</sub>-*cis*(N), *cis*(O)-isomer of bis(S-valinato)carbonatocobaltate(III) ion which shows a positive Cotton effect, it was assigned the  $\Delta$ -absolute configuration.

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#### SAŽETAK

#### Sinteza i konfiguracija novih izomera bis(amino-karboksilato)-karbonato-kobaltat(III) jona

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Reakcijom kalijum-trikarbonato-kobaltata(III) i odgovarajuće amino-kiseline (glicina ili  $\beta$ -alanina) dobivena su dva nova geometrijska izomera bis(amino-karboksilato)-karbonato-kobaltat(III)jona. U slučaju reakcije sa glicinom dobiven je, pored ranije opisanog *cis*(N)-*cis*(O)-izomera, još i *cis*(N)-*trans*(O)-izomer, a u slučaju  $\beta$ -alanina dobiven je *trans*(N)-*cis*(O)-izomer. Konfiguracija *trans*-izomera utvrđena je elektronskim spektrom, a konfiguracije preostala dva izomera pomoću PMR-spektara. Pored toga, *cis-cis*-izomer razložen je u enantiomere pomoću  $\Lambda$   $(+)$ <sub>589</sub>-*cis*(NO<sub>2</sub>)-*trans*(N)-izomera bis(S-arginin)-dinitro-kobalt(III)-jona. Apsolutna konfiguracija  $\Delta$   $(-)$ <sub>589</sub>-*cis*(N)-*cis*(O)-izomera pretpostavljena je porednjem njegova CD-spektra sa spektrom  $\Lambda$   $(+)$ <sub>589</sub>-*cis*(N)-*cis*(O)-izomera karbonato-bis(S-valinato)-kobaltat(III)-jona.