*Contribution from the Chemical Institute, Faculty of Sciences, University of Beograd, Inorganic Chemistry Laboratory, Oxford University, England, and Institute of Chemistry, Technology, and Metallurgy, Beograd, Yugoslavia.*

# Study of the Reactions of Hexanitrocobaltates(III) with Amino Acids. VII. Geometrical Isomerism and Absolute Configuration of Dinitrobis(aminoacidato)cobaltate(III) Ions

**M. B. Ćelap, R. G. Denning, D. J. Radanović, and T. J. Janjić**

*Received May 2, 1970*

*Dinitrobis(aminoacidato)cobaltate(III) salts with L-α-aminobutyric acid, aminoisobutyric acid, L-valine, L-norvaline, L-leucine, L-norleucine, and L-isoleucine were prepared and resolved into optical isomers. We report their electronic absorption, circular dichroism and infra-red spectra, and some PMR spectra. The data confirm our earlier assumption of the geometrical isomerism and absolute configuration of analogous ions with glycine, alanine, and β-alanine. The only geometrical isomer found in our preparations is the* cis *dinitro complex with amino groups* trans. *The* $(+)_{589}$*-optical isomers are assigned the* $P(C_2)$ *absolute configuration.*

## Introduction

In earlier work[1] we have reported the preparation and properties of *cis* dinitrobis(aminoacidato)cobaltate(III) complex ions. While the *cis* disposition of the $NO_2$ groups has been unequivocally established by optical resolution of the ions, the position of the amino acid functional groups has been only tentatively determined. We have therefore prepared fourteen new optical isomers of the same type and studied their physical properties in order to check our assumptions of geometrical isomerism and absolute configuration.

## Experimental Section*

*Preparation of Optical Isomers of Dinitrobis(aminoacidato)cobaltate(III) Ions.*

1. *L-α-aminobutyrato Complexes.* To a suspension of 4.52 g (0.01 mole) potassium hexanitrocobaltate(III) in 5 ml of water a solution of 2.06 g (0.02 mole) of L-α-aminobutyric acid and 1.01 g (0.018 mole) of potassium hydroxide** in 10 ml of water was added. The mixture was heated on a steam bath with stirring for 1 hour. The brown solution was filtered hot, and the filtrate obtained was concentrated to 1/3 of its volume (some salt is precipitated at this time) and refrigerated overnight. A brown, crystalline substance was filtered off and washed with a small, amount of water ethanol and ether. 1.7 g of optically active potassium $(+)_{589}$-dinitrobis(L-α-aminobutyrato)cobaltate(III) monohydrate (*A*) was obtained. Yield of (+)-complex ion 41.2%. The potassium salt was recrystallized to constant rotation from 90% ethanol.

4 ml 10 *M* silver nitrate was added slowly to the filtrate to precipitate free nitrite ion. Silver nitrite was filtered off and the filtrate was evaporated to 5 ml. 0.6 ml 10 *M* silver nitrate was added with stirring and brown crystalline silver $(-)_{589}$-dinitrobis(L-α-aminobutyrato)cobaltate(III) monohydrate (*B*) was precipitated. This was filtered off, washed with water, ethanol and ether and dried in air. Yield 1.4 g (29% of (−)-complex ion). The product was recrystallized to constant optical rotation from hot water.

The silver analog was obtained from *A* in a similar way to that used in reference (2) for the preparation of silver dinitrobis(aminoacidato)cobaltate(III) salts. 1.03 g (0.0025 mole) of *A* yielded 1 g (86.4%) of silver $(+)_{589}$-dinitrobis(L-α-aminobutyrato)-cobaltate-(III) (*C*). It was recrystallized from hot water.

The potassium analog was obtained from *B* by ion exchange (Merck 1) in almost quantitative yield.

2. *α-aminoisobutyrato Complexes.* Silver dinitrobis(α-aminoisobutyrato)cobaltate(III) trihydrate (*D*) was obtained from the analogous potassium salt, prepared by the action of potassium α-aminoisobutyrate on potassium hexanitrocobaltate(III).[3]

2.15 g (0.005 mole) of brucine hydrochloride in 5 ml of water was added slowly with stirring to 2.58 g (0.005 mole) of *D* in 20 ml of hot water. After removing the precipitated silver chloride the filtrate was

(1) T. J. Janjić, M. B. Ćelap, and P. Spevak, *Glasnik hem. društva Beograd*, *27*, 111 (1962); M. B. Ćelap, T. J. Janjić, and D. J. Radanović, *Inorganic Syntheses*, *9*, 173 (1967); M. B. Ćelap, D. J. Radanović, and T. J. Janjić, *Inorg. Chem.*, *4*, 1494 (1965); M. B. Ćelap, D. J. Radanović, T. J. Janjić, and M. J. Malinar, *Glasnik hem. društva Beograd*, 32, 417 (1967); M. B. Ćelap, D. J. Radanović, T. I. Nikolić, and T. J. Janjić, *Inorg. Chim. Acta*, 2, 52 (1968); R. G. Denning, M. B. Ćelap, and D. J. Radanović, *Inorg. Chim. Acta*, *2*, 58 (1968); M. B. Ćelap, M. B. Dimitrijević, F. A. Coha, D. J. Radanović, T. I. Nikolić, and T. J. Janjić, to be published.

(*) The analyses and some solubilities of the obtained dinitrobis-(aminoacidato)cobaltate(III) salts are given in Table I.

(**) Excess potassium hydroxide produces some tris(aminoacidato)-cobalt(III) complexes.

(2) M. B. Ćelap, D. J. Radanović, T. I. Nikolić, and T. J. Janjić, *Inorg. Chim. Acta*, *2*, 52 (1968).

(3) M. B. Dimitrijević, « Synthesis and Investigation of the Configuration of the Dinitrobis(α-aminoisobutyrato)cobaltate(III), Dinitrodivalinatocobaltate(III), and Dinitrodinorleucinatocobaltate(III) ions », Thesis, University of Beograd, 1970.

evaporated to 10 ml by a hot air stream. The precipitated yellow crystals were dissolved by heating, and the solution filtered again. The filtrate was allowed to stand at room temperature for 6 hours. The precipitate was filtered off, washed with ethanol and ether and dried in air. Yield of L-brucine $(+)_{589}$--dinitrobis(α-aminoisobutyrato)cobaltate(III) pentahydrate 1.2 g (57%).

0.9 g (46%) of the yellow dihydrate of the other diastereoisomer crystallizes from the filtrate after standing. Both diastereoisomers were recrystallized to constant rotation from hot water.

The brown crystalline potassium and silver enantiomers were obtained from the diastereoisomers by cation exchange* in almost quantitative yield.

3. *L-norvalinato Complexes.* 2.34 g (0.02 mole) L-norvaline and 0.72 g (0.018 mole) of sodium hydroxide in 15 ml of water were added to a solution of 4.04 g (0.01 mole) sodium hexanitrocobaltate(III) in 5 ml of water, and the whole heated for 30 minutes with stirring on a steam bath. The brown solution was filtered, passed through a cation exchange column (Merck 1) in the potassium form and evaporated to dryness *in vacuo*. The brown solid was ground and extracted with 300 ml of 96% ethanol. The solution was filtered to remove the majority of potassium nitrite and the filtrate was evaporated under vacuum at room temperature to a volume of 80 ml, and then left to stand in a refrigerator for 2 hours. Yield 2 g (45.5%) of potassium $(-)_{589}$-dinitrobis(L-norvalinato)-cobaltate(III) monohydrate (*E*). The filtrate was further evaporated to 40 ml *in vacuo*, and left in a refrigerator overnight. Yield 1.8 g (41%) of $(+)_{589}$-isomer (*F*). Both isomers were recrystallized below 50°C from 96% ethanol to constant optical rotation.

The silver salts corresponding to *E* and *F* were obtained by double decomposition with silver nitrate. 1.1 g (0.0025 mole) of *E* yield 1.1 g (88.5%) of the dihydrate of the silver salt, while the same amount of *F* yields 0.9 g (68%) of the monohydrate of the corresponding silver salt. Both were recrystallized from hot water.

4. *L-valinato Complexes.* Potassium $(-)_{589}$-dinitrobis(L-valinato)cobaltate(III) dihydrate (*G*) was obtained in same way as the norvalinato complex. However the evaporation must be continued to 30 ml. The same weights of starting materials yield 1.7 g (37% of (−)-complex ion) of this isomer. It was recrystallized from 96% ethanol to constant rotation.

Silver $(+)_{589}$-dinitrobis(L-valinato)cobaltate(III) (*H*) was obtained from the filtrate of the reaction mixture, which was evaporated to dryness *in vacuo*. The solid obtained was extracted with 100 ml of absolute ethanol, and evaporated again to dryness. The solid obtained after evaporation of the extract was dissolved in 5 ml of warm water, and 0.6 ml 10 *M* silver nitrate solution was added. *H* was filtered off and washed with water, ethanol and ether. Yield 1 g (20.4% of (+)-complex ion). It was recrystallized below 80°C from water.

Silver $(-)_{589}$-dinitrobis(L-valinato)cobaltate(III) monohydrate (*I*) was obtained from *G* by double decomposition with silver nitrate. 1.14 g (0.0025 mole) of *G* gave 1.14 g (89.6%) of *I*. It was recrystallized from hot water.

Potassium $(+)_{589}$-dinitrobis(L-valinato)cobaltate(III) was obtained by ion exchange (Merck 1) almost quantitatively.

5. *L-norleucinato and L-leucinato Complexes.* Sodium $(-)_{589}$-dinitrobis(L-norleucinato)cobaltate(III) dihydrate (*J*) and the monohydrate of the corresponding L-leucinato complex (*K*) were obtained by the same method used for compound *E**, except that the ethanolic extracts were concentrated to 50 ml before standing in a refrigerator overnight. 4.04 g (0.01 mole) sodium hexanitrocobaltate(III), 2.6 g (0.02 mole) L-norleucine or L-leucine, and 0.72 g (0.018 mole) of sodium hydroxide gave 2.1 g of *J* (44.6% of (−)-complex ion) and 2.2 g of *K* (48.6% of (−)-complex ion), respectively. Both isomers were recrystallized from 90% ethanol to constant rotation.

Silver $(+)_{589}$-dinitrobis(L-norleucinato)cobaltate(III) monohydrate (*L*) and silver $(+)_{589}$-dinitrobis(L-leucinato)cobaltate(III) (*M*) were prepared from the filtrates remaining from the preparation of *J* and *K*, by the same method used for *H*, except that the extraction of dry solid was with 50 ml of absolute ethanol. Yield of *L* 1.2 g (22.3% of (+) complex ion). Yield of *M* 0.8 g (15.4% of (+)-complex ion). Both salts were recrystallized from hot water to constant rotation.

The silver salts of *J* and *K* were obtained by double decomposition with silver nitrate. 1.17 g (0.0025 mole) of *J* gave 1.2 g (89%) of silver $(-)_{589}$-dinitrobis-(L-norleucinato)-cobaltate(III) monohydrate and 1.3 g (0.0025 mole) of *K* gave 1.25 g (93%) of silver $(-)_{589}$-dinitrobis(L-leucinato)cobaltate(III) monohydrate. Both isomers were recrystallized from hot water.

The sodium salts of *L* and *M* were obtained as monohydrates by ion exchange (Merck 1) almost quantitatively.

6. *L-isoleucinato Complexes.* 8.08 g (0.02 mole) sodium hexanitrocobaltate(III) in 5 ml of water was mixed with a solution of 5.2 g (0.04 mole) L-isoleucine and 1.44 g (0.036 mole) of sodium hydroxide in 30 ml of water, and the mixture heated on a steam bath, with stirring, for 30 minutes. The brown solution was filtered, evaporated to dryness under vacuum and the solid ground was extracted with 200 ml of absolute ethanol. The extract was filtered to remove sodium nitrite, and the filtrate again evaporated to dryness under vacuum. The solid was dissolved in 15 ml of water and the solution was left in a refrigerator overnight. 4.8 g of sodium $(+)_{589}$-dinitrobis-(L-isoleucinato)cobaltate(III) dihydrate (*P*) was collected on the filter. After evaporation to one third volume and further standing in the refrigerator an additional 0.6 g of *P* was obtained. Total yield 5.4 g (57.4% of (+)-complex ion). The product was recrystallized from hot water to constant rotation.

The filtrate from the reaction mixture was evaporated to dryness *in vacuo* and extracted with 15 ml of absolute ethanol. The extract was filtered (it contains predominantly the (−)-isomer). Evaporation and

(*) Cationic exchange resin (LW-28) was kindly supplied by prof. A. Lewandowsky, Adam Mickiewicz University, Poznan, Poland.

(*) Ion-exchange is unnecessary in the present case.

**Table I.** The Analyses and Some Solubilities of the Obtained Dinitrobis(aminoacidato)cobaltate(III) Salts*

| Optical Isomer (Molecular Weight) | Analysis Calculated | | Found | | Solubility in Water (g/100 ml) |
|---|---|---|---|---|---|
| (+)K[Co(L–abu)$_2$(NO$_2$)$_2$] . H$_2$O (412.30) | Co | 14.95 | Co | 14.73 | — |
| | K | 9.91 | K | 9.84 | |
| | N | 14.21 | N | 14.65 | |
| | H | 4.09 | H | 4.32 | |
| | H$_2$O | 4.37 | H$_2$O | 4.56 | |
| (–)K[Co(L–abu)$_2$(NO$_2$)$_2$] . H$_2$O (412.30) | Co | 14.95 | Co | 14.70 | — |
| | K | 9.91 | K | 9.90 | |
| | N | 14.21 | N | 14.33 | |
| | H | 4.09 | H | 4.44 | |
| | H$_2$O | 4.37 | H$_2$O | 4.70 | |
| (+)Ag[Co(L–abu)$_2$(NO$_2$)$_2$] (463.07) | Ag | 23.29 | Ag | 23.04 | — |
| | C | 20.75 | C | 20.97 | |
| | N | 12.10 | N | 12.13 | |
| | H | 3.48 | H | 3.68 | |
| (–)Ag[Co(L– abu)$_2$(NO$_2$)$_2$] . H$_2$O (481.08) | Ag | 23.29 | Ag | 23.21 | — |
| | C | 20.75 | C | 20.77 | |
| | N | 12.10 | N | 11.90 | |
| | H | 3.48 | H | 3.72 | |
| | H$_2$O | 3.74 | H$_2$O | 4.30 | |
| (+)C$_{23}$H$_{27}$O$_4$N$_2$[Co aibu$_2$(NO$_2$)$_2$] . 5H$_2$O (840.76) | Co | 7.85 | Co | 7.86 | 3.4 (22°) |
| | C | 49.60 | C | 49.54 | |
| | N | 11.19 | N | 11.36 | |
| | H | 5.77 | H | 6.01 | |
| | 5H$_2$O | 10.72 | 5H$_2$O | 10.78 | |
| (–)C$_{23}$H$_{27}$O$_4$N$_2$[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O (786.70) | Co | 7.85 | Co | 7.71 | 3.1 (22°) |
| | C | 49.60 | C | 49.48 | |
| | N | 11.19 | N | 11.03 | |
| | H | 5.77 | H | 6.19 | |
| | 2H$_2$O | 4.58 | 2H$_2$O | 5.40 | |
| (+)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O (430.31) | Co | 14.29 | Co | 14.08 | — |
| | K | 9.40 | K | 9.49 | |
| | N | 13.59 | N | 13.76 | |
| | H | 4.40 | H | 4.57 | |
| | H$_2$O | 4.37 | H$_2$O | 4.60 | |
| (–)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O (430.31) | Co | 14.29 | Co | 14.12 | — |
| | K | 9.48 | K | 9.36 | |
| | N | 13.59 | N | 13.38 | |
| | H | 4.40 | H | 4.57 | |
| | H$_2$O | 4.37 | H$_2$O | 4.60 | |
| (+)Ag[Co aibu$_2$(NO$_2$)$_2$] . 3H$_2$O (517.12) | Ag | 23.29 | Ag | 23.16 | 2.88 (22°) |
| | C | 20.75 | C | 20.98 | |
| | N | 12.10 | N | 12.20 | |
| | H | 3.48 | H | 3.94 | |
| | 3H$_2$O | 10.45 | 3H$_2$O | 10.58 | |
| (–)Ag[Co aibu$_2$(NO$_2$)$_2$] . 3H$_2$O (517.12) | Ag | 23.29 | Ag | 23.00 | 2.88 (22°) |
| | C | 20.75 | C | 20.92 | |
| | N | 12.10 | N | 11.99 | |
| | H | 3.48 | H | 3.68 | |
| | 3H$_2$O | 10.45 | 3H$_2$O | 10.58 | |
| (–)K[Co(L–nva)$_2$(NO$_2$)$_2$] . H$_2$O (440.36) | Co | 13.95 | Co | 13.94 | — |
| | K | 9.25 | K | 9.42 | |
| | N | 13.26 | N | 13.49 | |
| | H | 4.77 | H | 5.03 | |
| | H$_2$O | 4.09 | H$_2$O | 4.00 | |
| (+)K[Co(L–nva)$_2$(NO$_2$)$_2$] . H$_2$O (440.36) | Co | 13.95 | Co | 13.94 | — |
| | K | 9.25 | K | 9.40 | |
| | N | 13.26 | N | 13.28 | |
| | H | 4.77 | H | 4.66 | |
| | H$_2$O | 4.09 | H$_2$O | 4.20 | |
| (–)Ag[Co(L–nva)$_2$(NO$_2$)$_2$] . 2H$_2$O (527.15) | Ag | 21.96 | Ag | 21.95 | 0.76 (22°) |
| | C | 24.45 | C | 24.72 | |
| | N | 11.40 | N | 11.56 | |
| | H | 4.10 | H | 4.38 | |
| | 2H$_2$O | 6.83 | 2H$_2$O | 6.59 | |

**Table I.** (Continued)

| Optical Isomer (Molecular Weight) | Analysis Calculated | | Found | | Solubility in Water (g/100 ml) |
|---|---|---|---|---|---|
| (+)Ag[Co(L—nva)$_2$(NO$_2$)$_2$] . H$_2$O (509.14) | Ag | 21.96 | Ag | 22.00 | 2.85 (22°) |
| | C | 24.45 | C | 24.96 | |
| | N | 11.40 | N | 10.94 | |
| | H | 4.10 | H | 4.61 | |
| | H$_2$O | 3.52 | H$_2$O | 3.45 | |
| (—)K[Co(L—val)$_2$(NO$_2$)$_2$]. 2H$_2$O (458.37) | Co | 13.95 | Co | 13.93 | — |
| | K | 9.25 | K | 9.41 | |
| | N | 13.26 | N | 12.79 | |
| | H | 4.77 | H | 5.09 | |
| | 2H$_2$O | 7.86 | 2H$_2$O | 8.20 | |
| (+)K[Co(L—val)$_2$(NO$_2$)$_2$] . H$_2$O (440.36) | Co | 13.95 | Co | 13.90 | — |
| | K | 9.25 | K | 9.35 | |
| | N | 13.26 | N | 12.94 | |
| | H | 4.77 | H | 4.40 | |
| | H$_2$O | 4.09 | H$_2$O | 5.05 | |
| (—)Ag[Co(L—val)$_2$(NO$_2$)$_2$] . H$_2$O (509.14) | Ag | 21.96 | Ag | 22.12 | 3.18 (23°) |
| | C | 24.45 | C | 24.13 | |
| | N | 11.40 | N | 11.57 | |
| | H | 4.10 | H | 4.37 | |
| | H$_2$O | 3.52 | H$_2$O | 4.04 | |
| (+)Ag[Co(L—val)$_2$(NO$_2$)$_2$] (491,12) | Ag | 21.96 | Ag | 22.00 | 1.88 (23°) |
| | C | 24.45 | C | 24.61 | |
| | N | 11.40 | N | 11.30 | |
| | H | 4.10 | H | 4.26 | |
| (—)Na[Co(L—nle)$_2$(NO$_2$)$_2$] . 2H$_2$O (470.32) | Co | 13.57 | Co | 13.48 | — |
| | Na | 5.29 | Na | 5.39 | |
| | N | 12.90 | N | 12.69 | |
| | H | 5.57 | H | 5.64 | |
| | 2H$_2$O | 7.66 | 2H$_2$O | 8.00 | |
| (+)Na[Co(L—nle)$_2$(NO$_2$)$_2$] . H$_2$O (452.30) | Co | 13.57 | Co | 13.49 | — |
| | Na | 5.29 | Na | 5.40 | |
| | N | 12.90 | N | 12.89 | |
| | H | 5.57 | H | 5.67 | |
| | H$_2$O | 3.98 | H$_2$O | 4.05 | |
| (—)Ag[Co(L—nle)$_2$(NO$_2$)$_2$] . H$_2$O (537.19) | Ag | 20.78 | Ag | 20.77 | 0.64 (21°) |
| | C | 27.76 | C | 28.12 | |
| | N | 10.79 | N | 10.93 | |
| | H | 4.66 | H | 4.85 | |
| | H$_2$O | 3.35 | H$_2$O | 3.60 | |
| (+)Ag[Co(L—nle)$_2$(NO$_2$)$_2$] . H$_2$O (537.19) | Ag | 20.78 | Ag | 20.78 | 1.56 (21°) |
| | C | 27.76 | C | 27.68 | |
| | N | 10.79 | N | 10.59 | |
| | H | 4.66 | H | 4.30 | |
| | H$_2$O | 3.35 | H$_2$O | 3.34 | |
| (—)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O (452.30) | Co | 13.57 | Co | 13.37 | — |
| | Na | 5.29 | Na | 5.28 | |
| | N | 12.90 | N | 13.00 | |
| | H | 5.57 | H | 5.64 | |
| | H$_2$O | 3.98 | H$_2$O | 4.22 | |
| (+)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O (452.30) | Co | 13.57 | Co | 13.45 | — |
| | Na | 5.29 | Na | 5.31 | |
| | N | 12.90 | N | 12.81 | |
| | H | 5.57 | H | 5.77 | |
| | H$_2$O | 3.98 | H$_2$O | 4.70 | |
| (—)Ag[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O (537.19) | Ag | 20.78 | Ag | 20.65 | 1.40 (22°) |
| | C | 27.76 | C | 28.12 | |
| | N | 10.79 | N | 11.15 | |
| | H | 4.66 | H | 5.10 | |
| | H$_2$O | 3.35 | H$_2$O | 3.57 | |
| (+)Ag[Co(L—leu)$_2$(NO$_2$)$_2$] (519.18) | Ag | 20.78 | Ag | 21.00 | 0.67 (22°) |
| | C | 27.76 | C | 27.58 | |
| | N | 10.79 | N | 10.91 | |
| | H | 4.66 | H | 4.48 | |

**Table I.** (Continued)

| Optical Isomer (Molecular Weight) | Analysis Calculated | | Found | | Solubility in Water (g/100 ml) |
|---|---|---|---|---|---|
| (+)Na[Co(L—ile)$_2$(NO$_2$)$_2$] . 2H$_2$O (470.32) | Co | 13.57 | Co | 13.40 | — |
| | Na | 5.29 | Na | 5.20 | |
| | N | 12.90 | N | 12.98 | |
| | H | 5.57 | H | 5.75 | |
| | 2H$_2$O | 7.66 | 2H$_2$O | 8.40 | |
| (−)Na[Co(L—ile)$_2$(NO$_2$)$_2$] (434.29) | Co | 13.57 | Co | 13.49 | — |
| | Na | 5.29 | Na | 5.18 | |
| | N | 12.90 | N | 12.70 | |
| | H | 5.57 | H | 5.86 | |
| (+)Ag[Co(L—ile)$_2$(NO$_2$)$_2$] (519.18) | Ag | 20.78 | Ag | 20.72 | 1.46 (22°) |
| | C | 27.76 | C | 27.70 | |
| | N | 10.79 | N | 10.88 | |
| | H | 4.66 | H | 4.52 | |
| (−)Ag[Co(L—ile)$_2$(NO$_2$)$_2$] (519.18) | Ag | 20.78 | Ag | 20.76 | 0.80 (22°) |
| | C | 27.76 | C | 28.08 | |
| | N | 10.79 | N | 11.20 | |
| | H | 4.66 | H | 5.20 | |

(*) The following symbols were used: Habu = α-aminobutyric acid; Haibu = α-aminoisobutyric acid; Hnva = norvaline; Hval = valine; Hnle = norleucine; Hleu = leucine; Hile = isoleucine; $C_{23}H_{26}O_4N_2$ = L—brucine. Potassium salts were dried for analysis at 105° for 2 hours. Silver salts were dried at 80° *in vacuo*. Calculated values are for anhydrous salts, except for the potassium salts of the α-aminoisobutyrate-complex which were monohydrates at 140°C.

**Table II.** The Electronic Spectra of Some Optical Isomers of the Dinitrobis(aminoacidato)cobaltate(III) Salts*

| Optical Isomers | $\lambda_1$ (mμ) | log $\varepsilon_1$ | $\lambda_2$ (mμ) | log $\varepsilon_2$ | $\lambda_3$ (mμ) | log $\varepsilon_3$ |
|---|---|---|---|---|---|---|
| (+)Ag[Co gly$_2$(NO$_2$)$_2$] | 468 | 2.29 | 334 | 3.56 | 250 | 4.42 |
| (+)Ag[Co(L—ala)$_2$(NO$_2$)$_2$] | 468 | 2.30 | 334 | 3.51 | 250 | 4.39 |
| (−)Ag[Co(L—ala)$_2$(NO$_2$)$_2$] | 468 | 2.33 | 334 | 3.52 | 250 | 4.39 |
| (+)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O | 468 | 2.34 | 334 | 3.51 | 252 | 4.41 |
| (+)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O | 468 | 2.30 | 334 | 3.50 | 252 | 4.39 |
| (−)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O | 468 | 2.29 | 334 | 3.51 | 252 | 4.41 |

(*) The Perkin-Elmer 137-UV Spectrophotometer and $3\times10^{-3}$—$3.5\times10^{-5}M$ water solutions were used.

further extraction was repeated several times following the optical rotation. Finally, the solid was dissolved in 5 ml of water and the solution filtered to remove some tris(aminoacidato)-complex. 0.5 ml 10 *M* silver nitrate solution was added. The precipitate was filtered off, washed with water, ethanol and ether, and dried in air. Yield of silver $(-)_{589}$-dinitrobis(L-isoleucinato)cobaltate(III) (*Q*) 0.4 g (3.8% of (−)-complex ion). This was recrystallized from hot water to constant rotation.

The silver salt of *P* was prepared by double decomposition with silver nitrate. 1.17 g (0.0025 mole) of *P* yield 1.2 g (93%) of silver $(+)_{589}$-dinitrobis(L-isoleucinato)cobaltate(III). It was recrystallized from hot water.

The anhydrous sodium salt of *P* was prepared by ion exchange (Merck 1) almost quantitatively.

## Discussion

*Geometrical Isomerism.* The experimental part describes the preparation of fourteen optical isomers of dinitrobis(aminoacidato)cobaltate(III) type by the action of the corresponding amino acid on hexanitrocobaltate(III) ion. These are listed in Table I. The UV and visible absorption spectra of some complexes are given in Table II. They are virtually identical to each other and to the previous complexes in this series, whose *cis* $NO_2$ configuration was determined conclusively by their resolution into optical isomers (the *cis* $NO_2$ configuration of the complexes obtained in this paper was also confirmed by their resolution). We would regard this as strong evidence for the presence of the same *cis* $NO_2$ geometrical isomer in every case. The presence of *trans* carboxylate groups would be expected to give rise to a strong tetragonal field which would cause a pronounced splitting in the visible absorption band. Such a splitting was found in the *trans*(0) bis(glycinato)ethylenediaminecobalt(III) ion by Shimura *et al.*,[4] and in the *trans*(0) bis(glycinato)-1-propylenediaminecobalt(III) ion by Kojima and Shibata.[5] The absence of splitting in the present spectra (see for example Ref. 6) excludes therefore the *trans* carboxylato geometrical isomer. Two possible geometrical isomers with nitro groups *cis* remain. These have either one amino group *trans* to carboxylate (I) or two amino groups *trans* to each other (II) (see Ref. 6).

(4) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, *39*, 1257 (1966); *40*, 1868 (1967).
(5) Y. Kojima, and M. Shibata, *Inorg. Chem.*, *9*, 238 (1970).
(6) M. B. Celap, D. J. Radanović, T. I. Nikolić, and T. J. Janjić, *Inorg. Chim. Acta*, *2*, 52 (1968).
(7) R. G. Denning, M. B. Celap, and D. J. Radanović, *Inorg. Chim. Acta*, *2*, 58 (1968).

These isomers may be distinguished by PMR. Isomer I has non-equivalent rings, and II has equivalent rings. In our previous work[7] we observed no splitting in the three complexes studied. While this suggested the presence of isomer II, it remained possible that the two resonances of isomer I were unresolved. We now observe an absence of splitting of the methyl resonances of L-leucine in both optical isomers (Table III). The methyl resonance is only split by coupling to the neighbouring proton ($J = 5$ cps, a typical value for leucine[8]). The magnitude of the differences of the chemical shifts to be expected in these isomers is shown by the methyl resonances of the isobutyric acid complex. These are split by 7 cps due to the difference in chemical shift of the environment on either side of the amino acid ring. Models show one methyl group close to a neighbouring carboxylate group and the other close to a nitro group. This result allows us to confirm that the L-alanine complexes previously studied[7] have the configuration of isomer II, since in isomer I the L-alanine methyl group appears in one chelate ring close to a carboxylate group and in the other ring close to a nitro group. Consequently we would anticipate a splitting of the L-alanine methyl resonance in isomer I of about 7 cps. We can therefore firmly assign the structure II to our series of the dinitrobis(aminoacidato)cobaltate(III) ions. This is consistent with the PMR results for the glycine, L-alanine, and L-leucine complexes.

**Table III.** Methyl Proton Chemical Shifts*

| | | |
|---|---|---|
| (+)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O | 95 | 102 |
| (+)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O | 65 | 70 |
| (—)Na[Co(L—leu)$_2$(NO$_2$)$_2$] . H$_2$O | 65 | 70 |

(*) In cps at 60 Mc, downfield from TMS (external). All resonances have the same area.

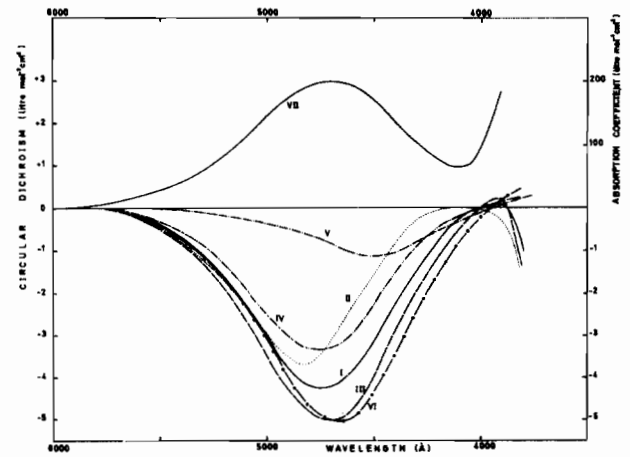


Figure 1. Circular dichroism spectra of (—)$_{589}$-dinitrobis(aminoacidato)cobaltate(III) optical isomers with the following amino acids: glycine (I); D-alanine (II); L-alanine (III); α-aminoisobutyric acid (IV); L-leucine (V); L-isoleucine (VI). Absorption spectrum of the glycine complex ion (VII).

Finally we believe that all the complexes possess the same geometrical configuration because of the similarities which exist not only in their electronic absorption spectra but also in their IR and CD spectra, which we discuss later.

*Absolute Configuration and Circular Dichroism.* In our earlier study of the circular dichroism of glycine, alanine, and β-alanine complexes,[7] the absolute configuration was tentatively assigned by a comparison of the sign of the Cotton effect with that of the dinitrobis(l-propylenediamine)cobalt(III) complex, for which X-ray data were available. The present series of amino acids, whose alkyl chains vary in length, makes possible the study of stereospecific effects in the complexes. In Figure 1 we show the circular dichroism spectra of D-alanine, glycine, L-alanine, α-aminoisobutyric acid, L-leucine, and L-isoleucine. The remaining amino acid complexes, with one exception (which will be discussed later), have spectra very similar to those of L-leucine. The complete results are collected in Table IV. All (+)$_{589}$-isomers have positive Cotton effects. We previously assigned (+)-isomers the P($C_2$) absolute configuration. We now present evidence confirming this absolute configuration, based on a stereospecific argument. The isoleucine complexes were prepared in homogeneous aqueous conditions, and subsequently evaporated at low temperature. It follows that the resulting solid should contain the two diastereoisomers in the same proportion established in the solution. The relative yields should therefore indicate stereospecificity. We find approximately 57% of the (+)$_{589}$-complex ion and 4% of the (—)$_{589}$-complex ion. Assuming equilibrium in the preparation was complete we could attribute a large steric hindrance to the (—)-isomer. Molecular models show that in the M($C_2$) absolute configuration the alkyl groups, which are particularly bulky, exibit large steric interactions, while in the P($C_2$) isomer this interaction is not possible. The location of the alkyl groups can be specified by the octants of the octahedron which they occupy. Defining the nitro group directions as +x and +y in a right handed Cartesian axis system the P($C_2$) isomer has alkyl groups in the opposite octants: (—x, y, z) and (x, —y, —z), while the M($C_2$) isomer has the groups in adjacent octants: (—x, —y, z) and (—x, —y, —z). From this we conclude that the (+)$_{589}$-isomer has the P($C_2$) absolute configuration, and shows a positive Cotton effect. Our present conclusion therefore confirms the earlier assumption.

The Figure 1 and Table IV show that all the large alkyl groups reduce the magnitude of the Cotton effect with respect to glycine complexes in both (+) and (—)-isomers. Furthermore the similarity of all the CD spectra for the compounds with these large groups suggests that the circular dichroism is independent of electronic perturbations originating at the carbon chain (*i.e.* octant contributions[9]). Of the twelve L-amino acid complexes in Table IV, six (+)-isomers have CD maxima in the range +1.66 to +2.83 litre mole$^{-1}$ cm$^{-1}$ (five in the range +2.44 to +2.83) and five (—)-isomers have CD maxima in the range —1.14 to —1.54 litre mole$^{-1}$ cm$^{-1}$. The only exception is the (—)-isoleucine complex. An

(8) R. G. Denning, and T. S. Piper, *Inorg. Chem.*, *5*, 1056 (1966).

(9) C. J. Hawkins, and E. Larsen, *Acta Chem. Scand.*, *19*, 1969 (1965)

**Table IV.** Circular Dichroism Data and Specific Rotations*

| Compound | $\varepsilon_l - \varepsilon_r$ (liter mole$^{-1}$ cm$^{-1}$) | Wavelength (Å) | $[\alpha]_D^{20°}$ |
|---|---|---|---|
| (+)K[Co(L–abu)$_2$(NO$_2$)$_2$] . H$_2$O | +2.77 | 4790 | +232 |
| (–)K[Co(L–abu)$_2$(NO$_2$)$_2$] . H$_2$O | –1.26 | 4500 | –284 |
| (+)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O | CD spectrum not recorded | | +484 |
| (–)K[Co aibu$_2$(NO$_2$)$_2$] . 2H$_2$O | –3.35 | 4750 | –484 |
| (+)K[Co(L–nva)$_2$(NO$_2$)$_2$] . H$_2$O | +2.53 | 4790 | +190 |
| (–)K[Co(L–nva)$_2$(NO$_2$)$_2$] . H$_2$O | –1.31 | 4500 | –225 |
| (+)K[Co(L–val)$_2$(NO$_2$)$_2$] . H$_2$O | +2.44 | 4790 | +165 |
| (–)K[Co(L–val)$_2$(NO$_2$)$_2$] . 2H$_2$O | –1.54 | 4500 | –279 |
| (+)Na[Co(L–leu)$_2$(NO$_2$)$_2$] . H$_2$O | +2.80 | 4790 | +310 |
| (–)Na[Co(L–leu)$_2$(NO$_2$)$_2$] . H$_2$O | –1.14 | 4500 | –205 |
| (+)Na[Co(L–nle)$_2$(NO$_2$)$_2$] . H$_2$O | +1.66 | 4820 | +210 |
| (–)Na[Co(L–nle)$_2$(NO$_2$)$_2$] . 2H$_2$O | –1.30 | 4500 | –240 |
| (+)Na[Co(L–ile)$_2$(NO$_2$)$_2$] . 2H$_2$O | +2.83 | 4790 | +183 |
| (–)Na[Co(L–ile)$_2$(NO$_2$)$_2$] . H$_2$O | –5.04 | 4650 | –600 |

(*)The circular dichroism spectra were recorded on a Roussel-Jouan Dichrograph (Model CD 185) in aqueous solutions with the concentration of 0.01 g/10 ml. The optical rotations were measured on a Perkin-Elmer Model 141 Digital polarimeter in aqueous solution (c = 0.1-0.2 g/100 ml).

**Table V.** Rotational Strengths of Some Dinitrobis(amino-acidato)cobaltate(III) Optical Isomers

| Ligand | (–)-Isomers $\Delta\varepsilon_{max}$ | (–)-Isomers λ (Å) | (+)-Isomers $\Delta\varepsilon_{max}$ | (+)-Isomers λ (Å) |
|---|---|---|---|---|
| D-ala | –3.66 | 4850 | +5.04 | 4700 |
| gly | –4.25 | 4750 | +4.25 | 4750 |
| L-ala | –5.04 | 4700 | +3.66 | 4850 |
| L-leu | –1.14 | 4500 | +2.80 | 4790 |

effect common to large substituents could be the conformation induced in the chelate ring by any large group. The substituent effects on the CD spectra are more pronounced in the (–)-isomers than in the (+)-isomers. Table V shows that while the (+)-isomers show a steady trend of decreasing circular dichroism in the order: D-alanine > glycine > L-alanine > L-leucine, the (–)-isomers have a clear discontinuity between L-alanine and L-leucine. Further increase in the size of the alkyl group has an insignificant effect. If the sole influence of the alkyl groups was due to their electronic perturbations these ligands might be expected to provide a smooth series. We therefore suggest a conformational change is occurring in the chelate ring. One side of the chelate ring is adjacent to a large nitro group while the other is adjacent to a small carboxylate oxygen atom. In the (–)-isomers the alkyl group of an L-amino acid occurs adjacent to oxygen and the α-hydrogen adjacent to a nitro group. We assume the latter interaction predominates in determining the conformation of the chelate ring when the substituent is methyl or when it is hydrogen, while the former interaction predominates in the case of the larger alkyl groups causing an inversion of ring puckering. However, in the (+)-isomer the alkyl group is adjacent to the nitro group and the conformational distortion will be in the same direction regardless of the size of the substituent. We therefore expect the electronic vicinal effects to dominate the changes in circular dichroism in this case. These effects would lead to rotational strengths changing in the order: D-alanine, glycine, L-alanine, L-leucine. This is illustrated in Table V.

In the (–)-isomers the electronic vicinal effect of L-alanine leads to a more negative CD than that of the glycine complex, but the conformational change induced by the larger substituents such as in L-leucine greatly reduces the rotational strength and changes the general shape of the CD curve. This conclusion is supported by observation that while all the (+)-complexes and the (–)-complexes with D-alanine, glycine, and L-alanine have CD spectra of broadly similar shape, the remaining (–)-isomers have quite different CD spectra occurring at shorther wavelength. Our argument predicts that the conformational puckering in the (+)-complexes is the mirror image of that in the (–)-complexes of D-alanine, glycine, and L-alanine, both being puckered away from the nitro groups, while the puckering in the other (–)-complexes is towards the nitro groups. The CD spectra reflect these effects and demonstrate the importance of the amino acid ring conformation, as opposed to electronic vicinal effects in determining the CD spectra. Both α-aminoisobutyric acid isomers necessarily have a methyl group adjacent to a nitro group. We therefore expect these to adopt the same conformation as the (+)-isomers and to show spectra of similar shape. This is confirmed by Figure 1 and Table IV.

The one exceptional CD spectrum is that of the (–)-isoleucine isomer, in which we have postulated a severe steric interaction. Unlike the effects just discussed which involve conformation within a chelate ring, inter-chelate strain might be expected to distort the coordination sphere itself leading to large effects of a different nature in the CD spectrum.

Conformations of amino acid chelate rings have been discussed by Mason *et al.*[10] for tris(aminoacidato)-cobalt(III) complexes. They conclude that the ring may adopt two conformations analogous to the *k* and *k'* conformations of ethylenediamine rings (Corey and Bailar[11]). Our results support the hypothesis of two well-defined conformations.

*Infra-red Spectra**. The assignment of these spec-

(10) E. Larsen, and S. F. Mason, *J. Chem. Soc.* (A), *1966*, 313.
(11) E. J. Corey, and J. C. Bailar, *J. Am. Chem. Soc.*, *81*, 2620 (1959).
(*) Infra-red spectra were taken on a Perkin-Elmer Model 337 Infracord spectrophotometer using potassium bromide disc technique.

tra uses evidence from deuteration and comparison with the previous work[2,12] on glycine and alanine complexes. In addition we refer to the spectra of tris(aminoacidato)cobalt(III) complexes[13-15] and nitro complexes of cobalt(III)[16,17].

From the spectra of deuterated materials we have assigned the $NH_2$ vibrations, finding an isotope factor NH/ND for the stretching vibrations of 1.35 to 1.37, and for the bending vibrations 1.17 to 1.20.

The NH stretching vibrations appear in the range 3345 to 3130 $cm^{-1}$; the intense bands at 1650 and 1618 $cm^{-1}$ are assigned to the asymmetric stretching of the coordinated carboxylate group, while those at 1390 and 1340 $cm^{-1}$ are assigned to the symmetric stretch; the asymmetric stretching vibrations of the $NO_2$ group are assigned to the bands between 1460 and 1420 $cm^{-1}$, and the symmetric stretches to those between 1330 and 1310 $cm^{-1}$; the $NO_2$ bending vibrations occur in these complexes between 840 and 815 $cm^{-1}$.

(12) M. B. Ćelap, D. J Radanović, T. J. Janjić, and M. J. Malinar, *Glasnik hem. društva Beograd*, *32*, 417 (1967).
(13) M. Mori, M. Shibata, E. Kyuno, and M. Kanaya, *Bull. Chem. Soc. Japan*, *34*, 1837 (1961).
(14) A. J. Saraceno, I. Nakagawa, S. Mizuchima, C. Curran, and J. V Quagliano, *J. Am. Chem. Soc.*, *80*, 5018 (1958).
(15) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, *83*, 4528 (1961).
(16) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, *80*, 4817 (1958).
(17) I. Nakagawa, T Shimanouchi, and K. Yamasaki, *Inorg. Chem.*, *3*, 772 (1964).

The broad similarity of all these spectra support our suggestion that all the complexes derive from the same geometric isomer.

## Conclusion

We conclude from the PMR spectra, the electronic absorption spectra, the IR spectra, and the resolution into optical isomers of the dinitrobis(aminoacidato)-cobaltate(III) ions that all the complexes of this type prepared in this and previous work have (a) same geometrical configuration and (b) this configuration can be described as *cis* nitro, *trans* amino.

The absolute configuration of the $(+)_{589}$-isomers is found, from the sign of the Cotton effect and from stereospecificity, to be $P(C_2)$.

Our analysis of the circular dichroism spectra of the complexes, as a function of the size of the amino acid alkyl substituent, leads us to postulate the presence of a conformational inversion of the chelate ring in this series.

*Acknowledgments.* We thank Mr. S. R. Niketic for the circular dichroism spectra and Professor F. Woldbye for the use of his instrument.