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Study of the Reaction of Hexanitrocobaltates(III) with Amino Acids. IV. The Reations with DL-Alanine, D-Alanine, L-Alanine, and β-Alanine[1]

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The reactions of alkali hexanitrocobaltates(III) with DL-alanine, D-alanine, L-alanine, and β-alanine have been investigated. Thereby new classes of alkali dinitrobis(aminoacido)cobaltates(III), $M[CoAm_2(NO_2)_2]$ *were obtained. It was established that the products obtained contain two nitro groups in the* cis *position.*

Introduction

In a previously published paper[2] we investigated the reactions between potassium and sodium hexanitrocobaltate(III) and glycine. In these reactions four out of six nitro groups in the complex ion were substituted by two glycine ligands yielding the corresponding dinitrodiglycinatocobaltates(III), $M^{I}[Co(H_2N\,.\,CH_2COO)_2(NO_2)_2]$. From this synthesis a new class of theoretically and biologically interesting complex compounds was obtained. In part II of this series[1] we established the *cis* configuration of dinitrodiglycinatocobaltate(III) ion. Continuing our investigation we have studied in this paper the reactions of alkali hexanitrocobaltates(III) with DL-alanine, D(—)-alanine, L(+)-alanine, and β-alanine, and the structure of the complex compounds obtained.

Experimental Section

(A) *Reactions of Potassium Hexanitrocobaltate(III) with Amino Acids.* To a suspension of 9.04 g. (20 mmoles) of potassium hexanitrocobaltate(III) in 5 ml. of water a solution of 40 mmoles of the corresponding amino acid and 2.02 g. (36 mmoles) of potassium hydroxide in 15 ml. of water was added. The mixture was heated on a water bath for 1 hour with constant stirring keeping the same volume of the solution. The hot brown solution obtained was filtered from unreacted potassium hexanitrocobaltate(III). By evaporating and cooling the filtrate the brown crystalline potassium dinitrobis(aminoacido)cobaltate(III) salt was obtained. The solid was washed with 50 percent ethanol, ethanol and ether and then recrystallized from water-ethanol mixture.

The sample used for analysis was dried at 105° for 2 hrs. Cobalt was determined by electrogravimetric analysis, and potassium gravimetrically as potassium sulfate.

The other experimental data are presented in Table I.

(B) *Reactions of Sodium Hexanitrocobaltate(III) with Amino Acids.* These reactions were carried out in an analogous way to those with the potassium salt. The other experimental data are shown in Table I.

(C) *Preparation of Silver Dinitrobis(aminoacido)cobaltates(III).* The solution of 1.87 g. (11 mmoles) of silver nitrate in 10 ml. of water was added with stirring to a solution of 10 mmoles of alkali dinitrobis(aminoacido)cobaltate(III) in 25 ml. of water. The redbrown crystalline precipitate was removed by filtration and washed with water, ethanol, and ether. The crude substance was recrystallized from hot water. The substance used for analysis was dried at 105° for 2 hrs. Silver content was determined by gravimetric analysis as silver chloride. The other experimental data are collected in Table I.

(D) *Preparation of Mercurous Dinitrobis(aminoacido)cobaltates(III).* To a solution of 10 mmoles of alkali dinitrobis(aminoacido)cobaltate(III) in 25 ml. of water a solution of 3.1 g. (5.5 mmoles) of mercurous nitrate dihydrate in 10 ml. of 1 N nitric acid was added. The crystalline orange precipitate was filtered off and washed with water, which was acidified with several drops of nitric acid, and then with ethanol and ether. The substance obtained was recrystallized from hot water and dried at 105° for two hours. The yields, analyses, and solubilities are given in the Table I.

(E) *Preparation of Hydrogen Dinitrobis(aminoacido)cobaltates(III).* The acids were obtained by passing the solution of alkali dinitrobis(aminoacido) cobaltate(III) through a Merck No.I (strong acid) cation exchange column. The solution obtained was

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(1) The reaction with DL-alanine was presented at the Symposium on the Structure and Properties of Coordination Compounds, Bratislava (Czechoslovakia, Sept. 1964, and the reactions with D-alanine, L-alanine, and β-alanine were presented at the 12th National Meeting of the Serbian Chemical Society, Belgrade (Yugoslavia), Jan 1967. For part II of this series, see M. B. Celap, D. J. Radanovis, and T. J. Janjic, *Inorg. Chem.*, *4*, 1494 (1965), and for part III see M. B. Celap, D. J. Radanovic, T. J. Janjic, and M. J. Malinar, *Glasnik Hem. Društva*, Beograd, in press.

(2) T. J. Janjic, M. B. Celap, and P. Spevak, *Glasnisk Hem. Wruštva Beograd*, *27*, 111 (1962).

Table I. The Experimental Data for Dinitrobis(aminoacido)cobaltates(III)

Compound[a]	Yield %	Analysis Calcd.	Analysis Found	Molar conduct.[b] ohm^{-1} cm^2	Solubility[c]
$K[Co\ ala_2(NO_2)_2]$	66	K 10.66 Co 16.09	K 10.66 Co 16.03	130 (25°)	---
$K[Co(d\text{-}ala)_2(NO_2)_2]\ .\ H_2O$	58	K 10.66 Co 16.09 H_2O 4.69	K 10.65 Co 16.04 H_2O 4.73	---	---
$K[Co(l\text{-}ala)_2(NO_2)_2]\ .\ H_2O$	57	K 10.66 Co 16.09 H_2O 4.69	K 10.86 Co 15.92 H_2O 4.76	---	---
$Na[Co\ ala_2(NO_2)_2]$	60	Na 6.57 Co 16.83	Na 6.53 Co 16.90	---	---
$Na[Co\beta\text{-}ala_2(NO_2)_2]$	81	Na 6.57 Co 16.83	Na 6.73 Co 16.96	155 (23°)	51 (21°)
$Ag[Co\ ala_2(NO_2)_2]\ .\ H_2O$	94	Ag 24.80 Co 13.54 H_2O 3.98	Ag 24.97 Co 13.41 H_2O 4.00	---	---
$Ag[Co\beta\text{-}ala_2(NO_2)_2]$	97	Ag 24.80 Co 13.54	Ag 24.98 Co 13.52	---	0.6 (27°)
$Hg_2[Co\ ala_2(NO_2)_2]_2\ .\ 3H_2O$	92	Hg 38.01 Co 11.16 H_2O 4.87	Hg 37.55 Co 10.92 H_2O 5.38	---	---
$Hg_2[Co\beta\text{-}ala_2(NO_2)_2]_2\ .\ H_2O$	97	Hg 38.01 Co 11.16 H_2O 1.72	Hg 37.73 Co 11.11 H_2O 1.76	---	0.3 (27°)
$H[Co\ ala_2(NO_2)_2]\ .\ 1/2H_2O$	99	Co 17.96	Co 17.73 H_2O 2.76	---	---
$H[Co\beta\text{-}ala_2(NO_2)_2]$	98		Co 17.94	---	2.1 (21°)
$H[Co\ gly_2(NO_2)_2]\ .\ 1/2H_2O$	95	Co 19.65 H_2O 2.91	Co 19.73 H_2O 2.98	---	17.5 (20°)

[a] ala = $H_3C.CH.(NH_2).COO$; d-ala = L(+)$_{589}H_3C.CH.(NH_2).COO$; l-ala = D(—)$_{589}H_3C.CH.(NH_2).COO$; β-ala = $H_2N.(CH_2)_2COO$; gly = $H_2N.CH_2.COO$. [b] 0.001 *M* solution. [c] In 100 ml. of saturated solution. The solubility has been determined only for the substances which consist of *one* racemate.

evaporated to dryness under diminished pressure at room temperature. The analyses are presented in the Table I.

(F) *Preparation of l-Brucine(+)$_{589}$-Dinitrobis(l-alaninato)cobaltate(III) dihydrate, and l-Brucine(+)$_{589}$-Dinitrobis(d-alaninato)cobaltate(III) dihydrate from Potassium Dinitrodialaninatocobaltate(III).* To a hot solution of 3.66 g. (10 mmoles) of potassium dinitrodialaninatocobaltate(III) in 15 ml. of water a hot solution of 1.08 g. (2.5 mmoles) of l-brucine dihydrate and 2.50 ml. of 1 N HNO_3 (2.5 mmoles) in 8 ml. of water was added. After 30 minutes the precipitated l-brucine(+)$_{589}$-dinitrobis(l-alaninato)cobaltate(III) dihydrate (1.8 g.) was filtered off and washed with ethanol. The orange crystalline substance was recrystallized from hot water to a constant optical rotation.

From the filtrate l-brucine(+)$_{589}$-dinitrobis(d-alaninato)cobaltate(III) dihydrate (1.3 g.) was precipitated by adding a l-brucine nitric acid solution, in an analogous way to that described above.

Anal. Calcd. for $C_{23}H_{27}O_4N_2[Co(H_3C\ .\ (NH_2)\ .\ CH\ .\ COO)_2(NO_2)_2]$: Co, 8.16. Found for l-brucine (+)$_{589}$-dinitrobis(l-alaninato)cobaltate(III): Co, 8.14. Found for l-brucine (+)$_{589}$-dinitrobis(d-alaninato)-cobaltate(III): Co, 8.16.

The dry substances used for analyses were heated at 105° for two hours. In the course of heating the first substance lost 4.78, and the second one 4.87 percent of water (calculated for $2H_2O$: 4.75).

Solubility (g. of anhydrous salt in 100 ml. of aqueous solution): l-brucine (+)$_{589}$-dinitrobis(l-alaninato)-cobaltate(III), 0.5 (20°); l-brucine(+)$_{589}$-dinitrobis-(d-alaninato)cobaltate(III), 0.6 (22°).

Optical Rotation. l-Brucine (+)$_{589}$-dinitrobis(l-alaninato)cobaltate(III), $[\alpha]_D^{20}$ +320° (0.1 g. in 100 ml. of aqueous solution); $[M]_D^{20}$ +2428°; l-brucine (+)$_{589}$-dinitrobis(d-alaninato)cobaltate(III), $[\alpha]_D^{20}$ +200° (0.1 g. in 100 ml. of aqueous solution); $[M]_D^{20}$ +1517°.

The measurements were carried out on a Franz Schmidt and Haensch, Berlin, Model S polarimeter.

(G) *Preparation of Silver (+)$_{589}$-Dinitrobis(l-alaninato)cobaltate(III) and Silver (+)$_{589}$-Dinitrobis-(d-alaninato)cobaltate(III) from Corresponding l-Brucine Salts.* A solution of 1.5 g. (2 mmoles) of the diastereoisomeric l-brucine salt in 250 ml. of water was passed through a column (70 cm. long and 1 cm. in diameter) containing strong acid cationic exchanger LW 28 in the silver form (capacity: 1.8 meq/g.). Eluent: water. The effluent was evaporated to dryness under diminished pressure at room temperature. The red brown crystalline substance was obtained. The other experimental data are given in Table II.

(H) *Preparation of Silver (—)$_{589}$-Dinitrobis(l-alaninato)cobaltate(III) and Silver (—)$_{589}$-Dinitrobis(d-alaninato)cobaltate(III) from Potassium Dinitrodialaninatocobaltate(III).* To a hot solution of 3.66 g. (10 mmoles) of potassium dinitrodialaninatocobaltate-(III) in 5 ml. of water a hot solution of 2.15 g. (5 mmoles) of l-brucine dihydrate and 5.00 ml. in 1 N

Table II. The Experimental Data for Optically Active Silver Dinitrodialaninatocobaltates(III), $Ag[Co(CH_3.(NH_2).CH.COO)_2(NO_2)_2]$, and Silver Dinitrobis(β-alaninato)cobaltates(III), $Ag[Co(H_2N.(CH_2)_2.COO)_2(NO_2)_2]$

Complex Salt	Prepared from	Analysis (Calcd. Ag, 24.80) Found	Solubility [a]	$[\alpha]_D^{20}$;[b] $[M]_D^{20}$
Silver $(+)_{589}$-Dinitrobis(l-alaninato)cobaltate(III)	DL-alanine	24.65	1.310 (23°)	+580°; +2523°
	D-alanine	24.67	---	+567°; +2466°
Silver $(-)_{589}$-Dinitrobis(l-alaninato)cobaltate(III)	DL-alanine	24.75	1.27 (23°)	−353°; −1535°
	D-alanine	24.48	---	−348°; −1514°
Silver $(+)_{589}$-Dinitrobis(d-alaninato)cobaltate(III)	DL-alanine	24.88	1.27 (23°)	+353°; +1535°
	L-alanine	24.66	---	+350°; +1522°
Silver $(-)_{589}$-Dinitrobis(d-alaninato)cobaltate(III)	DL-alanine	24.64	1.306 (23°)	−573°; −2493°
	L-alanine	25.02	---	−576°; −2506°
Silver $(-)_{589}$-Dinitrobis(β-alaninato)cobaltate(III)	β-alanine	24.68	2.38 (20°)	−225°; −979°
Silver $(+)_{589}$-Dinitrobis(β-alaninato)cobaltate(III)	β-alanine	24.46	2.39 (20°)	+222°; +996°

[a] g. in 100 ml. of saturated aqueous solution. [b] 0.1 g. in 100 ml. of aqueous solution.

HNO_3 (5 mmoles) in 8 ml. of water was added. After 2 hours the precipitate was removed by filtering. To the filtrate 0.125 ml. of 10 *M* silver nitrate solution was added, and the precipitate was filtered off. The filtrate was evaporated to half its volume, and then 0.5 ml. of 10 *M* nitrate solution was added again. The red brown crystalline mixture of diastereoisomers was filtered off (1 g.). The mixture was resolved by fraction crystallization from hot water and the separated isomers were recrystallized from hot water to a constant optical rotation. Yield 0.40 g. of silver $(-)_{589}$-dinitrobis(l-alaninato)cobaltate(III), and 0.25 g. of silver $(-)_{589}$-dinitrobis(d-alaninato)cobaltate(III). The other experimental data are shown in Table II.

(I) *Preparation of Silver $(+)_{589}$-Dinitrobis(l-alaninato)cobaltate(III) and Silver $(-)_{589}$-Dinitrobis(l-alaninato)cobaltate(III) from Potassium Dinitrobis (l-alaninato)cobaltate(III), Silver (+))$_{589}$-Dinitrobis(d-alaninato)cobaltate(III) and Silver $(-)_{589}$-Dinitrobis(d-alaninato)cobaltate(III) from Potassium Dinitrobis(d-alaninato)cobaltate(III).* Each of two pairs of diastereoisomers was obtained by a procedure analogous to that described by obtaining of inactive silver dinitrobis(aminoacido)cobaltates(III) from inactive alkali dinitrobis(aminoacido)cobaltates(III). The mixtures obtained were resolved by fractional crystallization from hot water. Two pairs of optical isomers, and their antipodes, were obtained.

Yield (3.66 g., 10 mmoles, of the corresponding optically active potassium salt was used): (i) silver $(+)_{589}$-dinitrobis(l-alaninato)cobaltate(III), 1.0 g.; silver $(-)_{589}$-dinitrobis(l-alaninato-cobaltate(III), 1.7 g.; (ii) silver $(+)_{589}$-dinitrobis(d-alaninato)cobaltate(III), 1.8 g.; silver $(-)_{589}$-dinitrobis(d-alaninato)cobaltate(III), 1.2 g.

Other experimental data are presented in Table II.

(J) *Preparation of l-Brucine $(-)_{589}$-Dinitrobis(β-alaninato)cobaltate(III) Trihydrate, Silver$(-)_{589}$-Dinitrobis(β-alaninato)cobaltate(III), and Silver$(+)_{589}$-Dinitrobis(β-alaninato)cobaltate(III).* (i) To a hot solution of 3.5 g. (10 mmoles) of sodium dinitrobis (β-alaninato)-cobaltate(III) in 7 ml. of water a solution of 2.47 g. (5 mmoles) of l-brucine nitrate dihydrate in 8 ml. of hot water was added. After cooling in a refrigerator the orange crystalline precipitate (2.8 g.) was filtered off and washed with water, ethanol, and ether. The crude product was recrystallized from hot water till constant optical rotation.

Anal. Calcd. for $C_{23}H_{27}O_4N_2[Co(H_2N.(CH_2)_2.OOO)_2(NO_2)_2]$: Co, 8.16. Found, 8.03.

The dry substance used for analysis was heated at 105° for two hours. It lost during the heating 7.60 percent of water (calculated for $3H_2O$: 7.0).

Solubility: 2.5 g. of anhydrous salt in 100 ml. of saturated aqueous solution at 20°.

Optical rotation. $[\alpha]_D^{20}$ −123° (0.2 g. in 100 ml. of aqueous solution); $[M]_D^{20}$ −955°.

(ii) The red crystalline needle-like silver $(-)_{589}$-dinitrobis(β-alaninato)cobaltate(III) was prepared by the double decomposition of l-brucine diastereoisomeric salt (1.5 g., 2 mmoles, in 20 ml. of hot water) obtained with silver nitrate (0.4 ml. 10 *M* solution). After 3 hours standing at room temperature the precipitate (0.46 g., 52 percent) was collected on a filter paper and washed with water, ethanol and ether.

Other experimental data are given in Table II.

(iii) Silver $(+)_{589}$-dinitrobis(β-alaninato)cobaltate(III) was obtained from the filtrate after the isolation of l-brucine $(-)_{589}$-dinitrobis(β-alaninato)cobaltate(III). To the above filtrate 0.5 ml. of 10 *M* silver nitrate solution was added and 1.2 g. of optically inactive salt was precipitated. After removing the precipitate by filtration, the same quantity of silver nitrate was added to the filtrate. The precipitated red crystalline substance (0.8 g.) was filtered off and washed with water, ethanol, and ether. The optically active silver salt was recrystallized from hot water till constant optical rotation. Other experimental data are shown in Table II.

(K) *Absorption Spectra.* The visible and ultraviolet absorption spectra were run in water solution using a Perkin Elmer 137-UV Spectrophotometer (Table III).

The infrared spectra were measured on a Perkin Elmer Model 337 Infracord Spectrophotometer using the potassium bromide disc technique (Table IV). The spectral analysis has been done by comparing the

Table III. The Electronic Spectra of the Optical Isomers

Complexes	ν_1,[a] 10^3 cm^{-1} (logε_1)	ν_2,[a] 10^3 cm^{-1} (logε_2)	ν_3,[b] 10^3 cm^{-1} (logε_3)
Ag(—) [Co gly$_2$(NO$_2$)$_2$]	21.36 (2.65)	29.94 (3.56)	40.00 (4.42)
Ag(—) [Co(l-ala)$_2$(NO$_2$)$_2$]	21.36 (2.60)	29.94 (3.56)	40.00 (4.47)
Ag(+)[Co(l-ala)$_2$(NO$_2$)$_2$]	21.36 (2.68)	29.94 (3.57)	40.00 (4.47)
Ag(—) [Coβ-ala$_2$(NO$_2$)$_2$]	20.92 (2.72)	29.07 (3.60)	38.76 (4.48)

[a] $C = 3.5\times10^{-4}$ *M*. [b] $C = 3.5\times10^{-5}$ *M*.

Table IV. The Infrared Spectra of the Optical Isomers[a]

Assignment	Compound[b]		
	I	II	III
NH str.	3325 (s), 3275 (s), 3150 (sh)	3344 (s), 3278 (s), 3130 (w)	3310 (m), 3240 (m), 3140 (sh)
CH str.	2980 (w), 2938 (w)	2980 (w), 2938 (w)	2970 (vw), 2900 (vw)
COO$^-$ as. str.	1660 (vs), 1635 (vs)	1610 (vs)	
NH$_2$ bend. and COO$^-$ as. str.			1610 (vs), 1570 (sh)
NH$_2$ bend.	1575 (s)	1575 (sh)	
CH$_2$ bend.			1470 (sh)
NO$_2$ as. str.	1440 (vs), 1418 (vs)	1438 (vs)	
NO$_2$ as. str. and COO$^-$ sym. str.	1382 (vs)	1390 (s)	1430 (sh), 1418 (vs) 1385 (s)
COO$^-$ sym. str.	1358 (s)	1368 (vs)	1350 (vs)
NO$_2$ sym. str. and CH bend.	1320 (vs), 1280 (vs)	1330 (vs), 1310 (vs)	
NO$_2$ sym. str. and CH$_2$ wag.			1318 (vs), 1268 (m)
Skel. as. str. (?)	1225 (w), 1198 (m)	1225 (w)	
Skel. as. str. and NH$_2$ twist.			1145 (m)
NH$_2$ twist.	1138 (vs) 1118 (s), 1105 (m)	1138 (vs) 1112 (m)	1074 (vw), 1020 (w), 982 (w)
CH$_3$ rock.	1060 (m), 1028 (vw)	1045 (m), 1030 (sh)	
Skel. sym. str.	928 (m), 862 (m)	938 (m), 868 (m)	898 (m), 885 (sh)
NO$_2$ bend.	835 (m), 828 (s)	840 (m), 832 (s)	833 (m), 825 (m)
NH$_2$ rock.	800 (w)	762 (m), 725 (w), 705 (vw)	760 (vw) 690 (vw)
	780 (w), 745 (m), 695 (w), 664 (w)		
NO$_2$ wag. and COO$^-$ rock.	608 (m), 588 (m), 572 (m)	592 (m), 578 (m)	644 (w), 615 (vw)
Co—N str. (?)	535 (vw), 435 (vw), 410 (m)	545 (w), 440 (sh), 412 (m)	505 (vw), 478 (vw), 405 (w)

[a] vs = very strong; s = medium; w = weak; vw = very weak; sh = shoulder. [b] I = Ag(—)[Co(l-ala)$_2$(NO$_2$)$_2$]; II = Ag(+)-[Co(l-ala)$_2$(NO$_2$)$_2$]; III = Ag(—)[Coβ-ala$_2$(NO$_2$)$_2$].

spectra obtained with the corresponding spectra of deuterated substances and using the published data for the spectra of similar substances.[3-8]

Results and Discussion

The reactions of alkali hexanitrocobaltates(III) with DL-alanine, D-alanine, L-alanine, and β-alanine are performed in a way analogous to the reaction between alkali hexanitrocobaltates(III) and glycine,[2] which we studied several years ago and described in the Introduction. New classes of alkali dinitrobis(aminoacido)-cobaltates(III), M[CoAm$_2$(NO$_2$)$_2$] were obtained:

$$M_3[Co(NO_2)_6]+2MAm=M[CoAm_2(NO_2)_2]+4MNO_2$$

(M = K or Na; Am = d- and l-CH$_3$.CH(NH$_2$).COO, respectively, or H$_2$N(CH$_2$)$_2$COO). Yields: 57-81 percent. Their identity was checked by determining the alkali metal and cobalt content, and the molar conductivity, (Table I). The method described could not be applied for potassium dinitrobis(β-alaninato)cobaltate-(III) which is insoluble in water. It was, therefore, impossible to separate it from unreacted insoluble potassium hexanitrocobaltate(III).

Alkali dinitrodialaninatocobaltates(III) are brown crystalline substances, while sodium bis(β-alaninato)-cobaltate(III) is red-brown. Both are easily soluble in water, slightly soluble in ethanol, and insoluble in ether. Water solutions are neutral. On heating the compounds decompose evolving gas.

The silver dinitrobis(aminoacido)cobaltates(III) were obtained in an almost quantitative yield, by the double decomposition of the alkali salts with silver nitrate. They are dark red crystalline substances, sparingly soluble in water. The yellow, crystalline mercurous salts were prepared in an analogous way. They, too, are insoluble in water. Finally, the free complex acids were obtained by ion exchange. They are brown crystalline substances easily soluble in water.

On the basis of Werner's coordination theory dinitrodialaninatocobaltate(III) complex salts, M[Co(CH$_3$.CH-(NH$_2$).COO)$_2$(NO$_2$)$_2$], could exist in 24 isomeric forms: in six of them the nitro groups would be in the *trans* position, while in the other eighteen forms they would be in the *cis* position. The *trans* forms consist of three pairs of isomers which contain DD, DL and LL amino acid ligands, respectively. Only four out of six *trans* isomers would be optically active with an enantiomorphic relationship. The *cis* forms consist of

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(3) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, *80*, 4817 (1958).

(4) M. L. Moris, and D. H. Busch, *J. Am. Chem. Soc.*, *82*, 1521 (1960).

(5) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, *83*, 4528 (1961).

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

(7) A. Leifer, and E. R. Lippincott, *J. Am. Chem. Soc.*, *79*, 5098 (1957).

(8) F. A. Cotton, "The Infra-red Spectra of Transition Metal Complexes", in J. Lewis, and R. G. Wilkins, ed., "Modern Coordination Chemistry", Interscience, p. 387 (1960).

six isomers containing D-alanine, other six contain L-alanine, and six of them contain mixed D and L ligands. All forms would be optically active.

As can be seen from the Experimental Section, we have isolated four optically active isomers from the product of the reaction between potassium hexanitrocobaltate(III) and DL-alanine consisting of two pairs of enantiomorphs (Figure 1). The composition of the isomers obtained was established by comparing them with the products of the analogous reactions using D- and L-alanine, respectively. In the first case two optically active isomers were obtained. These isomers were the optical antipodes of two other isomers obtained in the reaction with L-alanine. In this manner it was established that the same two pairs of enantiomorphs were obtained using optically active or inactive alanine, which means that the dinitrodialaninatocobaltate(I) ion contains two amino acid ligands of the same configuration. So the number of possible isomers drops from 24 to 16. These 16 isomers consist of two pairs of optical antipodes which contain nitro groups in the *trans* position, and six pairs of optical antipodes corresponding to three *cis* geometrical isomers (Figure 2).

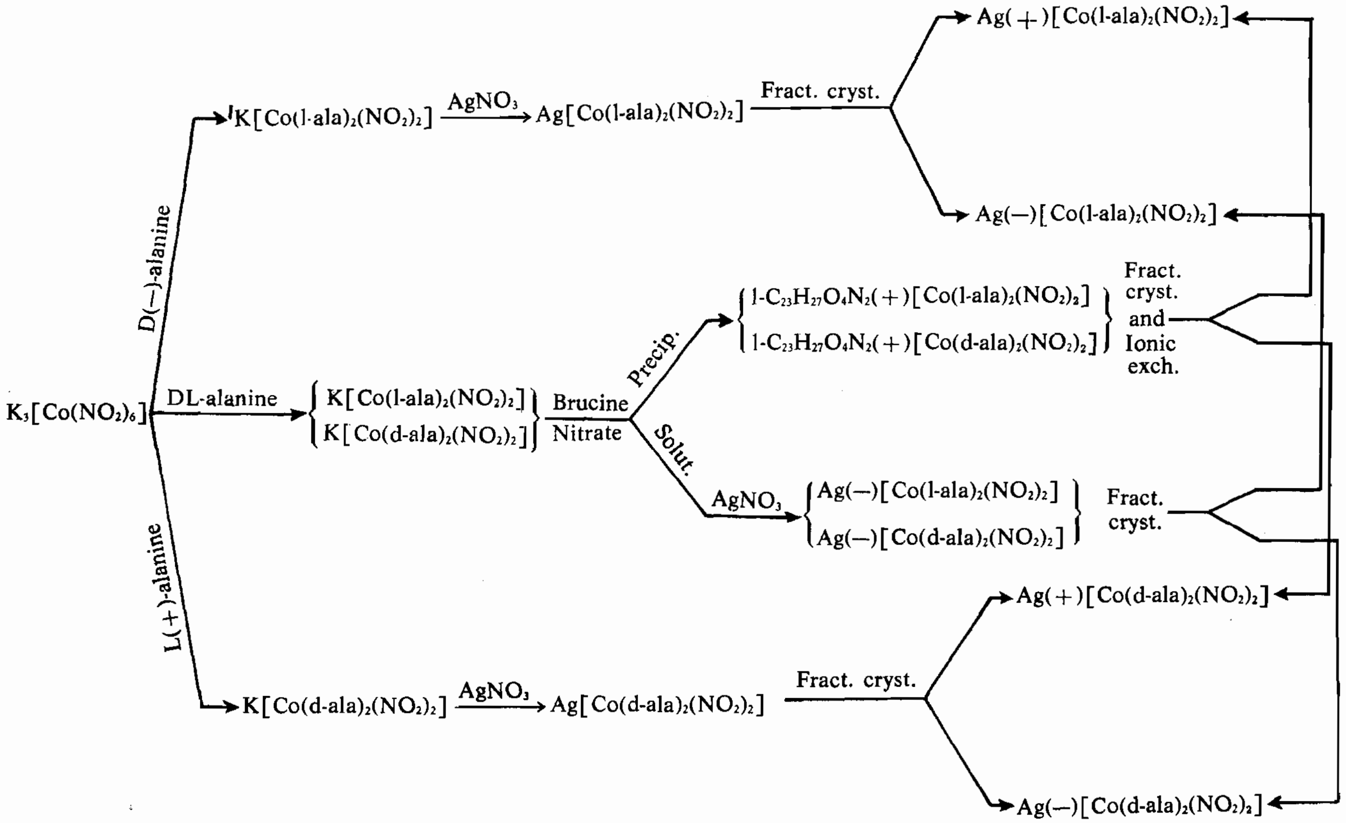

Figure 1.

As pointed out in the introduction, we established in a previous paper[1] the *cis* configuration of the very similar dinitrodiglycinatocobaltate(III) ion. Comparing its visible and ultraviolet spectra with the spectra of the optical isomers obtained (Figure 3) we found almost identical in the absorption maxima positions, intensities of the absorption bands and curve shapes. This is also supported by the position of the so called nitro specific band for *cis*-dinitro complexes.[9] Therefore, we conclude that dinitrodialaninatocobaltate(III) ion also contains two nitro groups in the *cis* position.

The dinitrobis(β-alaninato)cobaltate(III) ion could exist also in the form of several geometrical and optical isomers: two of them would contain the nitro groups in the *trans* position, while the *cis* isomers could exist in the form of three pairs of optical antipodes. Both of the *trans* isomers would be optically inactive which would distinguish them from the *cis* isomers. Since we have resolved the product obtained from the reaction between sodium hexanitrocobaltate(III) and β-alanino we conclude that dinitrobis(β-alaninato)-cobaltate(III) ion contains two nitro groups in the *cis* position. In this case it is impossible to deduce this from the visible and ultra-violet spectra, which differ

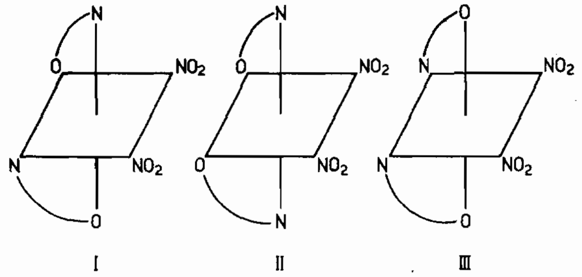

Figure 2.

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(9) Y. Shimura, *J. Am. Chem. Soc.*, *73*, 5079 (1951).

from the other spectra (Figure 3). This dissimilarity is caused by the β-amino group position in the ligand, which leads to six membered ring formation instead of the five membered ring present in the α-amino acid complexes. The same reason is responsible for shifting some of the bands in the infrared spectrum (Table IV).

We are investigating which of the three possible *cis* geometrical isomers we have obtained.

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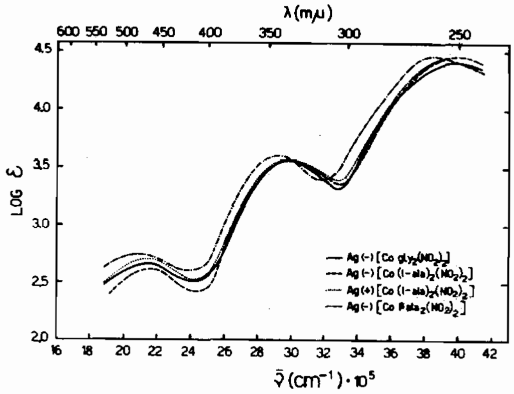

Figure 3.