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Conformational Isomers of β-Triethylenetetraamine-Amino Acid Complexes of Cobalt(III)[1]

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The preparation and characterization are described for the β_1 and β_2-(RR and SS)- and the β_2-(RS and SR)-isomers for the glycine, (S and R)-alanine, and S-methionine complexes, and the β_1- and β_2-(RR and SS) isomers for the S-proline complexes of the type β-[Co(trien)aa]$I_2 \cdot H_2O$. The isomers differ in the orientation of the amino acid anion (aa) relative to the triethylenetetraamine (trien) ligand (β_1 or β_2) and the chelate ring conformations, which are designated by the absolute configurations of the coordinated secondary amine groups (R or S). The absolute configurations were assigned from the stereoselectivity of proline and spectral results. The circular dichroism (CD) spectra were used to relate configurations and conformations of the complexes, to examine the various contributions to the CD peak intensities and the additivity of these contributions.

Introduction

Sargeson and Searle[2] isolated *trans*-, α-, and β-isomers of triethylenetetraamine (trien) disubstituted complexes of cobalt(III) (Figure 1). Liu and Douglas[3] studied the circular dichroism (CD) of amino acid complexes of the type $[Co(en)_2aa]^{2+}$. They observed that the contributions to the optical activity from the spiral arrangement of the chelate rings (Δ for right and Λ for left)[4] and from the presence of an optically active ligand were additive. Bryant *et al*[5] prepared corresponding trien complexes of the type $[Co(trien)aa]^{2+}$ and we sought to characterize these compounds from their CD spectra. While these studies were in progress, Sargeson *et al.*[6] reported the detection of conformational isomers of β–$[Co(trien)(H_2O)_2]^{3+}$ in solution and Marzilli and Buckingham[7] isolated β_1- and β_2-isomers of $[Co(trien)gly]^{2+}$ and one isomer, β_2, of $[Co(trien)sar]^{2+}$ (gly = glycinate ion, sar = sarcosinate ion). They considered the possible conformational isomers of trien (Figure 2) and concluded that only the more stable conformation of trien was formed.

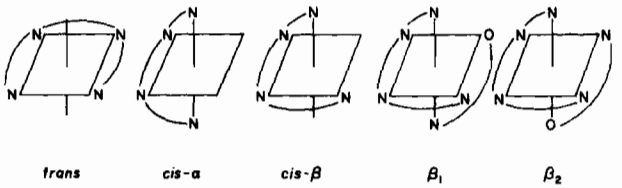

Figure 1. Isomers of Some Complexes of Triethylenetetraamine.

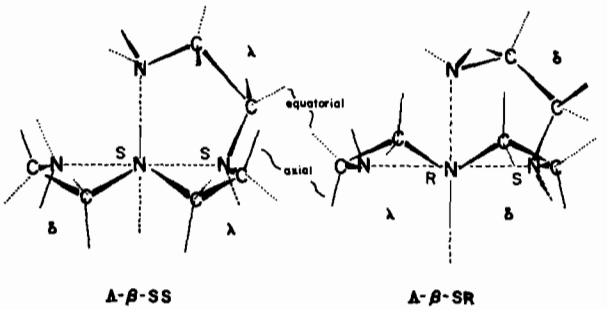

Figure 2. Conformational Isomers of β-Triethylenetetraamine Complexes.

Lin's results[8] indicated that he had four conformational isomers (RR, SS, RS and SR) in the case of β_2–$[Co(trien)(S)\text{–}ala]I_2 \cdot H_2O$ and two isomers (RR

(1) This work was supported by a research grant (GM 10829) from the Division of General Medical Studies, U. S. Public Health Service.
(2) A. M. Saregson and G. H. Searle, *Inorg. Chem.*, 6, 787 (1967).
(3) C. T. Liu and B. E. Douglas, *ibid.*, 3, 1356 (1964).
(4) I.U.P.A.C. Information Bulletin, No. 33, 68 (1968).
(3) C. T. Liu and B. E. Douglas, *ibid.*, 3, 1356 (1964).
1373 (1967).
(6) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, 6, 1032 (1967).
(7) L. G. Marzilli and D. A. Buckingham, *ibid.*, 6, 1042 (1967).
(8) C. Y. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Letters*, 4, 15 (1968).

and SS) for the corresponding S-proline complex. The assignments of absolute configurations and conformations of the proline complexes were confirmed by X-ray crystal structures.[9] Detailed studies of the β_1- and β_2-isomers of amino acid complexes of this type are now reported.

Experimental Section

Chemical Reagents and Starting Materials. Optically active amino acids were purchased from Nutritional Biochemical Corporation, Cleveland, Ohio. The reported specific rotations at the Na_D line were: (S)-alanine, +14.25° in 6 N HCl; (R)-alanine, −14.3° in 6 N HCl; (S)-methionine, +23.5 in 5 N HCl; (S)-proline, −51.8° in 0.5 N HCl, (S) and (R) refer to the absolute configuration of the amino acids.[10] *Cis*–α–(±)–[Co(trien)Cl_2]Cl [11] and *cis*–β–(±)–[Co(trien)Cl_2]Cl[12] were prepared as described in the references. The (+) or (−) indicates the sign of optical rotation at the Na_D line. For the compounds reported the sign of optical rotation at the Na_D line is the same as that of the dominant CD peak.

Preparation and Resolution of Compounds. β_2-Glycinato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. Preparative Method 1. The compound was prepared by the method of Bryant *et al.*[5] with slight modification. One and one-half grams of glycine was dissolved in a warm solution (*ca.* 50°) of 0.8 g of NaOH in 30 ml of water. To this solution 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl was quickly added and the resulting solution was heated on a water bath (*ca.* 60°) with constant stirring for 20 min., while the color of the solution changed from violet to orange-red. The solution was stored in a cold room (*ca.* 5°) over night. The impurities were removed by filtration. To the filtrate an excess of solid NaI (*ca.* 6 g) was added, with stirring, and the solution crystallized slowly in the cold room for about one week. The orange-red crystals were filtered, the filtrate was concentrated by evaporation with an air stream, and then crystallized in the cold room to yield more of the iodide salt of the complex. The total product was washed with excess ethanol (95%) to dissolve the excess NaI and air dried. The yield of the crude product was 6.6 g (60%).

Samples for study were recrystallized several times by dissolving the crude product in a minimum amount of hot water. The solution was filtered and recrystallized in the cold room. The pure complex crystallized as aggregates of rod shaped crystals.

Resolution. The racemic glycinato complex was resolved into its optical isomers using silver antimonyl–(+)–tartrate as resolving agent. Two molar equivalents of silver antimonyl–(+)–tartrate (2 moles of resolving agent per mole of complex) were added to a solution of the complex as the iodide salt. Silver iodide was removed by filtration after stirring the mixture on the water bath for 20 min. The filtrate freed from AgI was evaporated to dryness with an air stream. The dried sample was dissolved in dimethyl sulfoxide (DMSO). Absolute ethanol was added drop by drop, with stirring, until the first turbidity appeared, then the solution was cleared by adding a few drops of DMSO. The solution was cooled in the cold room over night. The first precipitate was the nearly pure (+)–isomer. The filtrate was treated several times by the same technique, the final filtrate contained the nearly pure (−)–isomer was collected from the final filtrate by precipitation with excess absolute ethanol. The two diastereoisomers were recrystallized from hot water several times until the CD curves were unchanged on further recrystallization. $\Delta\varepsilon$ for the dominant CD peak: (+)–isomer, +2.2 and (−)–isomer, −2.2.

The diastereoisomers were converted to the iodide salts by dissolving in water and treating with equivalent amounts of $AgNO_3$ to precipitate the resolving agent as silver antimonyl–(+)–tartarte, which was removed by filtration. After the addition of excess NaI, the solution was concentrated with an air stream at room temperature. It was recrystallized two or three times from warm water and then dried *in vacuo* at 55° over night. $\Delta\varepsilon$ for the dominant CD peak: (+)–isomer, +2.13 and (−)–isomer, −2.13.

β_2-Glycinato-(RS and SR)-triethylenetetraaminecobalt(III) Iodide. Preparative Method 2. Six and three-tenths grams (0.02 moles) of *cis*–α–[Co(trien)Cl_2]Cl was dissolved in 30 ml of water, NaOH (1.6 g, 0.04 moles) was added, and the resulting solution was heated on a water bath with constant stirring for 20 min. While heating, the color of the solution changed from violet to red. The solution was cooled in an ice bath, then filtered to remove the insoluble residue. The filtrate was heated on the water bath (*ca.* 60°) and 1.5 g (0.02 moles) of glycine was added with constant stirring for 20 min. The color of the solution changed from red to orange-red. The solution was cooled in the ice bath, filtered to remove impurities, and an excess of NaI was added with stirring. The iodide salt of the desired complex crystallized slowly in the cold room for about one week. The orange-red crystals were collected on a sintered-glass filter and washed with an excess of ethanol (95%) to dissolve excess NaI, and air dried. The crude product was 6.0 g (54.5%).

Resolution. The complex was converted to the antimonyl–(+)–tartrate salt as before. The dried residue was partly dissolved in a few ml of DMSO. The insoluble part was the nearly pure (+)–diastereoisomer and the filtrate contained the nearly pure (−)–diastereoisomer. The filtrate was precipitated by adding an excess of ethanol (95%). The two diastereoisomers were recrystallized from warm water until the CD peak intensities were constant. The diastereoisomers were converted to the iodide salts as described previously. $\Delta\varepsilon$ for the dominant CD peak: (+)–isomer, +1.92 and (−)–isomer −1.92.

(9) D. A. Buckingham, L. G. Marzilli, I. E. Marxwell, A. M. Sargeson, and H. C. Freeman, *J. Chem. Soc.* (D), 583 (1969).
(10) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Intern. Ed.*, 5, 385 (1966).
(11) F. Basolo, *J. Am. Chem. Soc.*, 70, 2634 (1948).

β_1-Glycinato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. Preparative Method 3. The preparation of the β_1-complex was similar to method 2, except that a two-fold excess of glycine was added. Small, deepred crystals were obtained. Yield 6.2 g (55%).

Resolution. This complex was resolved as described previously using silver antimonyl–(+)–tartrate as the resolving agent. The filtrate freed from AgI was diluted with water. Ethanol was added slowly until the first turbidity remained after complete mixing, then just enough water was added to clear the solution. On cooling in the cold room for two to three weeks, the complex crystallized as granules containing small rod-shaped crystals. After crystallization seemed to be complete, the crystals were collected and recrystallized many times using the same technique until the $\Delta\varepsilon$ value became constant. For the dominant CD peak $\Delta\varepsilon = +2.30$ for the less soluble (+)–diastereoisomer . The more soluble diastereoisomer was obtained from the mother liquor by further addition of ethanol (same procedure of addition as that for the less soluble diastereoisomer) followed by repeated recrystallization to give $\Delta\varepsilon = -2.30$. The diastereoisomers were converted to the iodide salts as described for the β_2-(RR and SS)-complex.

β_2-S(orR)-Alaninato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. This compound was prepared by method 1. One and eight-tenths grams of S(or R)-alanine, 0.8 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 30 ml of water were used. Orange-red, small, rod-shaped crystals were obtained. Yield: 7.5 g (66.3%).

The resolution was accomplished as described for the β_2-(RR and SS)-glycine complex using AgSbO–(+)–$C_4H_4O_8$ in DMSO. The $\Delta\varepsilon$ value for the iodide obtained from the less soluble diastereoisomer was +2.38 for the (+)–isomer of the S-alanine complex (or $\Delta\varepsilon = -2.38$ for the (–)–isomer of the R-alanine complex). The $\Delta\varepsilon$ for the other isomer from the more soluble diastereoisomer (in DMSO) was –2.37 for the (–)–isomer of the S-alanine complex (or, +2.36 for the (+)–isomer of the R-alanine complex).

β_2-S(or R)-Alaninato-(RS and SR)-triethylenetetraaminecobalt(III) Iodide. This compound was prepared by method 2 and resolved by a method similar to that described for the β_2-(RS and SR)-glycine complex. One and eight-tenths grams of S(or R)-alanine, 1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 30 ml of water were used. The yield was 7.6 g of the crude product (67%). After recrystallization from hot water the complex was obtained as small orange-red crystals. The $\Delta\varepsilon$ value for the iodide obtained red crystals. The $\Delta\varepsilon$ value for the iodide obtained from the less soluble diastereoisomer was +1.83 for the (+)–isomer of the S-alanine complex (or –1.83 for the (–)–isomer of the R-alanine complex). The $\Delta\varepsilon$ for the other isomer from the more soluble diastereoisomer (in DMSO) was –2.04 for the (–)–isomer of the S-alanine complex (or +2.04 for the (+)–isomer of the R-alanine complex).

Preparative Method 4. The second method of preparation was similar to method 1 except *cis*–β–[Co(trien)Cl_2]Cl was used instead of *cis*–α–[Co(trien)-Cl_2]Cl. One and eight-tenths grams of S-alanine was dissolved in a warm solution (*ca.* 50°) of 0.8 g of NaOH in 30 ml of water, then 6.3 g of *cis*–β–[Co(trien)Cl_2]Cl was quickly added and the resulting solution was heated on a water bath (*ca.* 60°), with constant stirring, for 20 *min.* while the color of the solution changed from red to orange-red. The complex was obtained as the iodide salt as before. The small orange-red crystals were identical to those from the previous methods. Yield: 55%.

β_1-S-Alaninato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. The preparation (method 3) and resolution were carried out as described for the β_1-(RR and SS)-glycine complex. Three and six-tenths grams of S-alanine, 1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 30 ml of water were used. Round, deep-red crystals were obtained, yield: 6.2 g (55%). $\Delta\varepsilon$ for the iodides: from the less soluble diastereoisomer, +2.02; from the more soluble diastereoisomer, –2.07.

β_2-S-Methioninato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. This compound was prepared (method 1) and resolved as described for the β_2-(RR and SS)-glycine complex. Three grams of S-methionine, 0.8 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 35 ml of water were used. The first isolated product was found to contain more of the (–)isomer than the (+)–isomer. On repeated recrystallization from warm H_2O, the (–)–isomer was obtained pure as rod-shaped crystals. Fractional precipitation of the filtrate by adding ethanol (95%) gave the (+)–isomer in a pure form as granual crystals. The total yield of the crude product was 7.5 g (60%). The yield ratio for the (–) and (+)–isomers was about 10: 1. The same $\Delta\varepsilon$ values were obtained for the iodide salts obtained by repeated recrystallization and from the resolution using silver antimonyl–(+)–tartrate: –2.30 and +2.38, for the two isomers. The second method for obtaining these two diastereoisomers is the same as that for the preparation of β_1-S-methioninato-(RR and SS)-triethylenetetraaminecobalt(III) iodide.

β_2-S-Methioninato-(RS and SR)-triethylenetetraaminecobalt(III) Iodide. The preparation (method 2) and resolution were similar to those described for the β_2-(RS and SR)-glycine and S-alanine complexes. Three grams of S-methionine, 1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 35 ml of water were used. Orange-red fibrous crystals were obtained. Yield: 5.6 g (45%). The $\Delta\varepsilon$ for the iodide obtained from the less soluble diastereoisomer was +1.90 and –2.03 for the other isomer. The second method for obtaining this compound was similar to method 4 for the β_2-(RS and SR)-S-alanine complex. Yield: 45%.

β_1-S-Methioninato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. This compound was prepared (method 3) and resolved as described for the β_1-(RR and SS)-glycine complex. Six grams of S-methionine,

1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 35 ml of water were used. Red needle crystals were obtained for β_1–(±)–[Co(trien)(S–meth)]I_2. Yield: 7.5 g of the crude product (60%). To the filtrate was added more solid NaI (2-3 g) accompanied by scratching the sides of the beaker, followed by cooling in the refrigerator over night. Orange-red granual crystals of the β_2–(+)–SS–isomer were obtained. Yield: 1.5 g.

The filtrate from the second crop of crystals (β_2–(+)–SS–isomer) was concentrated with an air stream, then more (*ca.* 1 g) of solid NaI was added to it. This solution was stirred and cooled in the refrigerator over night. Fine fibrous crystals were obtained for the β_2–(–)–RR–isomer. Yield: 1.2 g of the crude product. The filtrate from the second crop of crystals was expected to contain the β_1–(±), β_2–(+)–SS, and β_2–(–)–RR isomers. Further crystallization of this filtrate in the refrigerator for a long period gave a mixture of all three isomers; they could be distinguished by observing the crystal forms.

The β_1–(±), β_2–(+)–SS, and β_2–(–)–RR isomers were washed with an excess of ethanol (95%) to remove excess NaI, and recrystallized several times from hot water.

Resolution. The β_1-methionine complex resolved as described for the β_1-glycine complex using silver antimonyl–(+)–tartrate, but greater care was required. The less soluble diastereoisomer ((+)–isomer) separated as a gelatinous type of precipitate. Careful crystallization of the filtrate, by adding ethanol (95%), and cooling gave the pure (–)–isomer. If an oily layer separated instead of crystals, the pure (–)–isomer could not be obtained; the oily layer had to be worked up again. The diastereoisomers were converted to the iodide salt as described previously. The Δε for the iodide obtained from the less soluble diastereoisomer was +1.95 and –2.05 for the other isomer.

β_2-S-Prolinato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. Specific method for preparing Δ–(–)–β_2–RR–[Co(trien)(S–prol)]I_2. This compound was prepared by method 1 and resolved by a method similar to that described for the β_2-(RR and SS)-glycine complex. Two and three-tenths grams of S-proline, 0.8 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl, and 30 ml of water were used. The solution was heated and stirred constantly on a water bath (*ca.* 60°) for 20 min to obtain the desired complex. The first product, which separated as aggregates of square crystals, was found to be the (–)–isomer. Yield: 6.1 g for the crude product (51.7%). The Δε for the dominant CD peak for the iodide salt obtained by reported crystallization and as resolved using silver antimonyl–(+)–tartrate was –1.43.

Method for preparing Λ–(+)–β_2–SS– and Δ–(–)–β_2–RR–[Co(trien)(S–prol)]I_2. The preparation of the complex was similar to method 2, 2.3 g of S-proline, 1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl, and 30 ml of water were used. Yield: 6.3 g of the crude product. The first product isolated was a mixture of nearly equal amounts of the (+)– and (–)–isomers. The (+)–isomer of this product dissolved in the absolute methanol while the (–)–isomer did not. The (–)–isomer crystallized as aggregates of orange-red, square plates, while the crystals of the (+)–isomer were light, thin sheets. The Δε for the iodide salt of the more soluble diastereoisomer obtained by repeated crystallization and as resolved using silver antimonyl–(+)–tartrate was +2.4. The Δε for the other isomer from the less soluble diastereoisomer was identical to that obtained earlier, –1.34.

β_1-S-Prolinato-(RR and SS)-triethylenetetraaminecobalt(III) Iodide. This compound was prepared by method 3 and resolved by a method similar to that described for the β_1–(RR and SS)–glycine complex. Four and six-tenths grams of S-proline, 1.6 g of NaOH, 6.3 g of *cis*–α–[Co(trien)Cl_2]Cl and 30 ml of water were used. An excess of solid NaI was added with stirring after the proline had reacted. The solution was cooled in the refrigerator over night to give 1.2 g of orange-red β_2–(–)–RR–[Co(trien)(S–prol)]I_2. More solid NaI was added to the filtrate. This solution was concentrated by an air stream until solid appeared on the surface and then it was allowed to crystallize in the refrigerator to give 1.2 g of β_2–(+)–SS–[Co(trien)(S–prol)]I_2. An excess of solid NaI was added to the filtrate, the walls of the beaker were scratched, and the solution was cooled in the refrigerator over night. The yield of 4.4 g of β_1–(RR and SS)–[Co(trien)(S–prol)]I_2 was isolated as small, red crystals.

The two optical isomers of β_1–(RR and SS)–[Co(trien)(S–prol)]I_2 were separated by fraction crystallization. Two grams of β_1(RR and SS)–proline complex was dissolved in warm water and cooled in the refrigerator until small red crystals were found. The yield of 150 mg (pure product) was isolated for β_1–(–)–RR[Co(trien)(S–prol)]I_2. The filtrate was evaporated by an air stream to dryness and then washed with an excess of methanol and ethanol to dissolve the excess of NaI. Yield: 800 mg of pure β_1–(+)–SS–[Co(trien)(S–prol)]I_2. Both isomers were recrystallized several times from warm water until the CD curves were unchanged on further recrystallization. Δε for the dominant CD peaks: +1.8 and –1.90.

Physical Measurements. Infrared Spectra. The infrared spectra were recorded with a Beckman-8 Spectrophotometer equipped with sodium chloride optics. Spectra were obtained for sample mulls using Nujol as the mulling agent.

Proton Magnetic Resonance Spectra. The Pmr spectra were obtained using a Varian Associates Model A-60 spectrometer, and using sodium trimethyl silylpropane sulfonate (TPS Na) as an internal standard.

Electronic Spectra. Absorption spectra were obtained using a Cary Model 14-Spectrophotometer. A tungsten lamp was used in the visible region and a hydrogen lamp was used in the ultraviolet region. The cell length was 1 cm. Measurements were made for 0.002 to 0.008 M solutions in a 1 cm cell at room temp. CD curves were obtained with a Roussel-Jouan Dichrograph using a Sylvania Sun Gun lamp in the region 600-300 mμ. Measurements were made for

Table I. Summary of Methods Used for Preparing the β_1– and two β_2–$[Co(trien)(aa)]^{2+}$ Ions

cis–α–$[Co(trien)Cl_2]Cl$ + Na–aa(+OH^-) ⟶	β_2–(Λ–(+)–SS and Δ–(–)–RR)* β_2–(Δ–(–)–RR)**	
cis–α–$[Co(trien)Cl_2]Cl$ + $2OH^-$ ⟶	*cis*–β–$[Co(trien)(OH)_2]^+$ —(+aaH)⟶	β_2–(Λ–(+)–SR and Δ–(–)–RS* β_2–(Λ–(+)–SS and Δ–(–)–RR)**
cis–α–$[Co(trien)Cl_2]Cl$ + $2OH^-$ ⟶	*cis*–β–$[Co(trien)(OH)_2]^+$ —(+2aaH)⟶	β_1 and β_2–(Λ–(+)–SS and Δ–(–)–RR)
cis–β–$[Co(trien)Cl_2]Cl$ + Na–aa(+OH^-) ⟶	β_2–(Λ–(+)–SR and Δ–(–)–RS)* β_2–(Λ–(+)–SS and Δ–(–)–RR)**	

Na–aa = sodium salt of α–amino acid; aaH = α–amino acid; * for glycine, R– and S–alanine and S–methionine; ** for S–proline.

Table II. Analytical Data for Complexes Prepared

Complexes	Calculated %				Found %			
	C	H	N	I	C	H	N	I
$[Co(C_6H_{16}N_4)(C_2H_4NO_2)]I_2 \cdot H_2O$	17.4	4.35	12.7	46.1				
β_1–(±)–(RR and SS)–$[Co(trien)(gly)]I_2 \cdot H_2O$					17.11	4.47	12.48	45.88
β_2–(±)–(RR and SS)–$[Co(trien)(gly)]I_2 \cdot H_2O$					17.34	4.44	12.15	43.05
β_2–(±)–(RS and SR)–$[Co(trien)(gly)]I_2 \cdot H_2O$					17.71	4.43	12.34	43.06
$[Co(C_6H_{16}N_4)(C_3H_6NO_2)]I_2 \cdot H_2O$	19.2	4.6	12.4	45.0				
β_1–(±)–(RR and SS)–$[Co(trien)(S–ala)]I_2 \cdot H_2O$					19.27	4.49	12.43	44.65
β_2–(±)–(RR and SS)–$[Co(trien)(S–ala)]I_2 \cdot H_2O$					19.08	4.70	11.51	41.19
β_2–(±)–(RS and SR)–$[Co(trien)(S–ala)]I_2 \cdot H_2O$					18.91	4.70	11.44	42.38
$[Co(C_6H_{16}N_4)(C_5H_{10}NO_2S)]I_2 \cdot H_2O$	21.2	4.8	11.2	40.6				
β_1–(±)–(RR and SS)–$[Co(trien)(S–meth)]I_2 \cdot H_2O$					20.91	4.88	10.97	40.97
β_2–(–)–RR–$[Co(trien)(S–meth)]I_2 \cdot H_2O$					21.24	4.97	11.03	40.48
β_2–(±)–(RS and SR)–$[Co(trien)(S–meth)]I_2 \cdot H_2O$					21.15	4.77	10.90	40.58
$[Co(C_6H_{16}N_4)(C_5H_9NO_2)]I_2 \cdot H_2O$	22.4	4.7	11.8	43.0				
β_1–(+)–SS–$[Co(trien)(S–prol)]I_2 \cdot H_2O$					22.19	4.84	11.77	43.08
β_2–(+)–SS–$[Co(trien)(S–prol)]I_2 \cdot H_2O$					22.22	4.90	11.84	42.83
β_2–(–)–RR–$[Co(trien)(S–prol)]I_2 \cdot H_2O$					22.55	4.80	11.90	42.53

0.002-0.008 M solutions in a 2 cm cell in an air conditioned room.

Optical rotations were measured in aqueous solution in a 10 cm tube at the sodium D-line at room temp. using a Rudolph polarimeter.

Analyses. Elemental analyses were performed by Alfred Bernhardt, Elbach, West Germany. Samples for spectral study and analysis were dried *in vacuo* (10 torr) at 55° over night.

Results and Discussion

Synthesis of Complexes. The preparative procedures in this study differed from those of Marzilli and Buckingham.[7] Four procedures were used for the $[Co(trien)(aa)]^{2+}$ type complex ions. One of them was similar to the method of Bryant *et al.*[5] and our products were identical to theirs. The starting materials, reaction conditions and major products formed using glycine, R- and S-alanine, S-methionine and S-proline are given in Table I. The elemental analyses are given in Table II.

Method 1. The complexes assigned to the Λ–(+)–β_2–SS or Δ–(–)–β_2–RR conformations were prepared by the reaction of *cis*–α–$[Co(trien)Cl_2]Cl$ with the sodium salt of the amino acid. No dissymmetric synthesis was found for glycine and R- and S-alanine complexes. They were resolved into their optical isomers using silver antimonyl–(+)–tartrate as the resolving agent. The first product isolated for [Co(trien)(S–meth)]I_2 was found to contain a greater proportion of the (–)–isomer. The (–)–isomer could be obtained optically pure by repeated recrystallization of this product. Only the (–)–isomer was obtained by this procedure for S-proline. Some samples of amino acid complexes furnished by Bryant's group, and prepared by a similar method, showed the same results as reported here.

Method 2. The complexes assigned to Λ–(+)–β_2–SR or Δ–(–)–β_2–RS conformations were prepared by converting *cis*–α–$[Co(trien)Cl_2]Cl$ to *cis*–β–$[Co(trien)(OH)_2]^+$ in solution, followed by the addition of an equivalent number of moles of the amino acid. The unresolved complexes for glycine, alanine and methionine were found to be 50:50 mixtures of optical isomers. They were resolved by a procedure similar to that above. Two isomers were isolated for the proline complex by this method. The (–)–isomer was identical to that from the first method.

Method 3. The complexes assigned to the Λ–(+)–β_1–SS or Δ–(–)–β_1–RR conformations were prepared using the same *cis*–β–$[Co(trien)(OH)_2]^+$ solution as prepared in the second method, but using two molar equivalents of the amino acid. Four isomers, Λ–(+)–β_1–SS, Δ–(–)–β_1–RR, Λ–(+)–β_2–SS and Δ–(–)–β_2–RR were isolated for all four of the amino acids. The β_1-isomers were formed in greater proportions than the β_2-isomers. No stereoselectivity was obtained in the preparation of the β_1-isomers for glycine, alanine and methionine; they were resolved into their optical isomers using silver antimonyl–(+)–

tartrate. The two (internal) diastereoisomers of the β_1-proline were separated by fractional crystallization from the unresolved product in aqueous solution.

Method 4. The complexes prepared by method 1 might have been expected to have the α-configuration. According to the study of the base hydrolysis of the $[Co(trien)Cl_2]^+$ ion by Bailar *et al.*,[12] α-$[Co(trien)Cl_2]^+$ ion reacting with an equimolar amount of OH^- forms α-$[Co(trien)Cl(OH)]^+$ with retention of configuration. However, the complexes prepared by method 4 (*cis*-β-$[Co(trien)Cl_2]Cl$ reacting with the sodium salt of the amino acid) were Λ-(+)-β_2-SR and Δ-(−)-β_2-RS for S-alanine and S-methionine, and Λ-(+)-β_2-SS and Δ-(−)-β_2-RR for S-proline. Several reactions are known which bring about α to β conversions, but none causes the reverse conversion. Since the products from method 4, starting with a β-isomer, were identical to those by the other methods, it can be concluded that all of the isomers isolated have the β-configuration of trien. Attempts to prepare complexes with the α-configuration were unsuccessful.

Characteristics of Stereoisomers. The preceeding isomers were distinguished and identified on the basis of the infrared, pmr, visible, and CD spectra, and the stereoselectivity of proline complexes.

Infrared Spectra. The CH_2 or NH_2 twisting vibrational modes (990-1100 cm^{-1}) were proposed to be useful for identifying the α- and β-isomers of $[Co(trien)Cl_2]^+$ by Buckingham and Jones.[13] Marzilli and Buckingham[7] used this region to distinguish and identify β_1- and β_2-isomers of glycine complexes and the β_2-isomer of the sarcosine complex. In the present study, this region was also used to distinguish and identify β_1- and β_2-$[Co(trien)(aa)]^{2+}$ complexes.

The infrared spectra for all of the amino acid complexes show at least four strong bands in the 990-1100 cm^{-1} region.[14] The spectra for the β_1-glycine complexes are significantly different in this region, but are identical to those reported.[7] The spectra for the glycine complexes with the β_2-RR (or SS) and β_2-RS (or SR) configurations are identical and the spectra of corresponding isomers of the alanine complex are also identical, although slightly different from the spectra of the glycine complexes. The spectra for β_1-RR (or SS) complexes with glycine, alanine and methionine show only small dissimilarities. There are also small dissimilarities between the spectra for the β_2-isomers of glycine and alanine. The ir spectra for the two diastereoisomers, β_2-(+)-SS and β_2-(−)-RR, of methionine complexes are slightly different. The spectra are also slightly more complicated than those of the glycine and alanine complexes.

For each series of isomers of the S-proline complexes, the infrared spectra in comparison to those of the other amino acid complexes are very different and more complex. The ir spectrum of (−)-$[Co\,en_2(S\text{-prol})]I_2$[14] is much more simple than those of the S-proline complexes reported here; there is only one very strong band at 1040 cm^{-1} in this region for the former complex.

Proton Magnetic Resonance Spectra. The protons attached to the asymmetric secondary N-atoms of the two « coplanar » ethylenediamine chelate rings for the two conformations [RR (or SS) and RS (or SR)] of the β-trien complexes (Figure 2) have different environments. They are expected to have different chemical shifts, but the broad peak in this region makes the pmr spectra inconclusive in distinguishing the two conformational isomers. The pmr spectra do show differences between the geometrical isomers (*i.e.*, β_1 and β_2) for each series of amino acid complexes.[14] The pmr spectra for β_1- and β_2-glycine complexes in this study are identical to those reported for these complexes by Marzilli and Buckingham.[7] The pmr spectra of the alanine complexes for both β_1- and β_2-isomers show one sharp doublet at δ = 1.6 ppm[15] due to the CH_3 group coupled with the H on the same C-atom. One strong sharp band was found at δ = 2.1 ppm for both β_1- and β_2-methionine complexes. A broad band with small splitting at δ = 1.7-2.4 ppm was found for both β_1- and β_2-proline complexes. This band was assigned to the three-membered aliphatic chain in the proline ring.

Electronic Absorption Spectra and Circular Dichroism. The *d-d* absorption spectra for $[Co(trien)(aa)]^{2+}$ ions are expected to belong to the general type $[CoN_5O]$ (*i.e.*, the effective field symmetry of complexes is C_{4v}). Under C_{4v} symmetry, the average ligand field strengths for β_1- and β_2- complexes are predicted to be different,[7] therefore, the electronic spectra for both series of complexes might be expected to differ. However, the average ligand field strength of RR (or SS) and RS (or SR) conformers for each series of complexes are predicted to be the

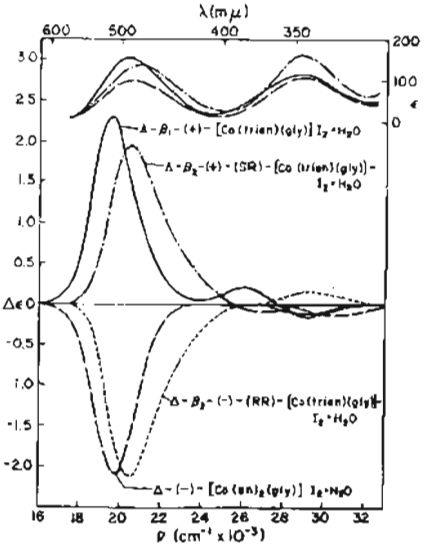

Figure 3. Circular Dichroism and Electronic Absorption Spectra for β-$[Co(trien)(gly)]I_2$ and (−)-$[Co\,en_2(gly)]I_2$

(12) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *ibid.*, *87*, 4458 (1965).
(13) D. A. Buckingham and D. Jones, *Inorg. Chem.*, *4*, 1387 (1965).
(14) B. E. Douglas and C. Y. Lin, unpublished work.
(15) D. A. Buckingham, L. J. Durham, and A. M. Sargeson, *Australian J. Chem.*, *20*, 257 (1967).

same, therefore, their electronic absorption spectra are presumed to be similar. The absorption spectra for all complexes show two broad bands in the visible region (Figure 3-8). They correspond to the $^1A_{1g} \rightarrow {}^1T_{1g}$ (first ligand field band, or band I) and the $^1A_{1g} \rightarrow {}^1T_{2g}$ (second ligand field band or band II) transitions using O_h symmetry. The spectra of both the β_2–RR (or SS)– and β_2–RS (or SR)–isomers are essentially identical (Figures 3 and 4). However, the β_1 and β_2-isomers differ significantly in band intensities and band positions. The intensity ratio for band I and band II for β_1-isomers is greater than 1 (*i.e.*, $\varepsilon_I/\varepsilon_{II} > 1$) and for β_2-isomers it is less than 1.

The absorption spectra for β_1-isomers of the glycinato, alaninato, and methioninato complexes are very similar, as are the corresponding complexes of

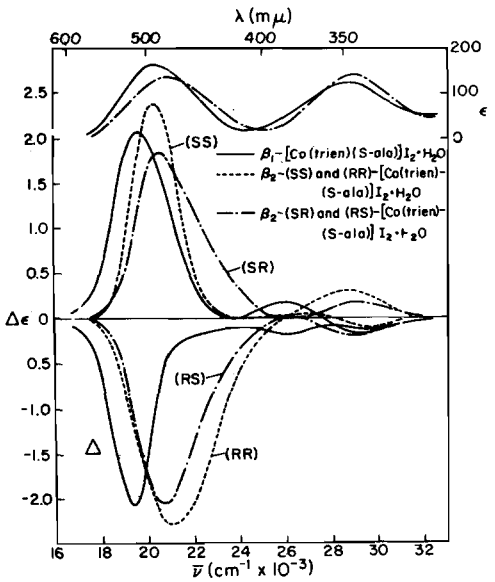

Figure 4. Circular Dichroism and Electronic Absorption Spectra for β_1– and β_2–[Co(trien)(S–ala)]$I_2 \cdot H_2O$ Complexes.

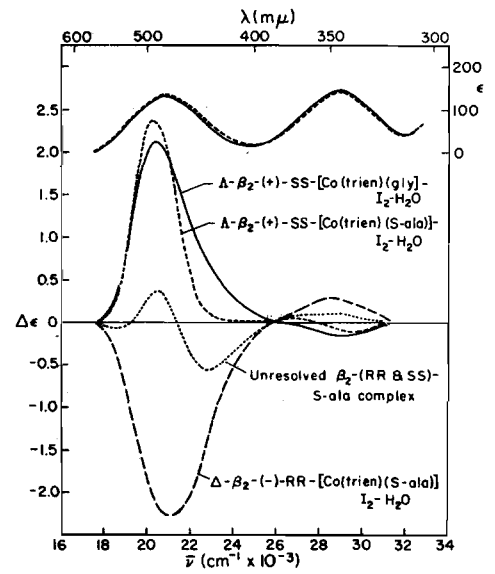

Figure 5. Circular Dichroism and Electronic Absorption Spectra for β_2–(RR and SS)–[Co(trien)(S–ala)]$I_2 \cdot H_2O$ Complexes.

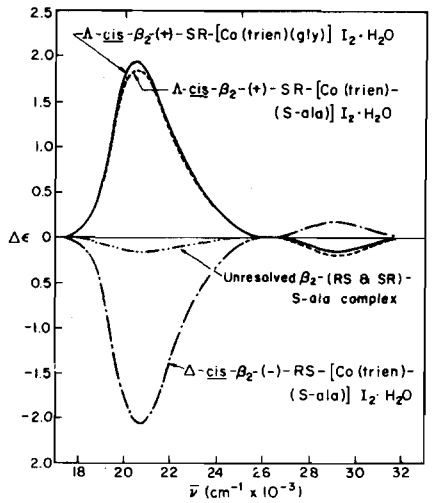

Figure 6. Circular Dichroism for β_2–(RS and SR)–[Co(trien)(S–ala)]$I_2 \cdot H_2O$ Complexes.

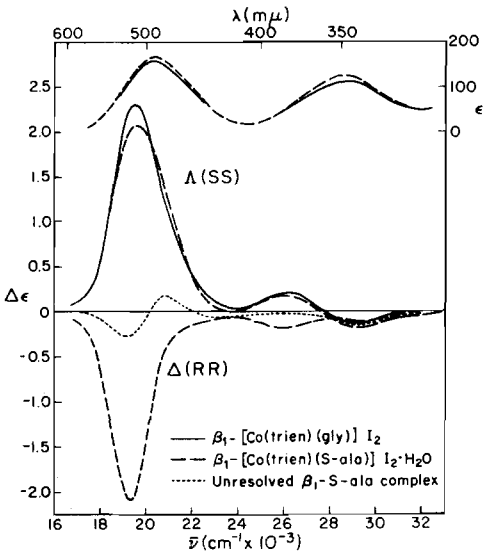

Figure 7. Circular Dichroism and Electronic Absorption Spectra for β_1–(RR and SS)–[Co(trien)(S–ala)]$I_2 \cdot H_2O$ Complexes.

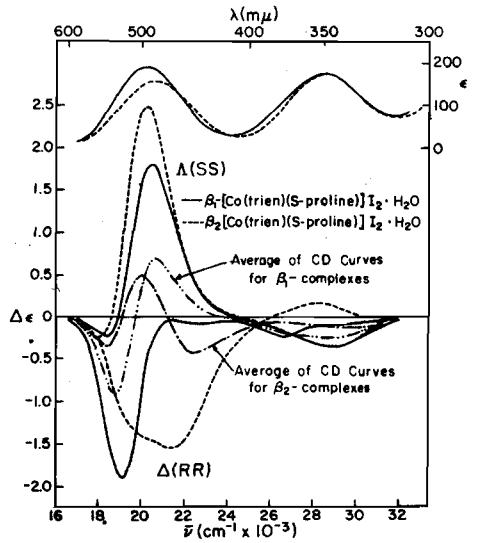

Figure 8. Circular Dichroism and Electronic Absorption Spectra for β_1– and β_2–(RR and SS)–[Co(trien)(S–prol)]$I_2 \cdot H_2O$

the β_2-series. The positions of band I and II for β_2-complexes of glycine, alanine and methionine are 478 and 346 mμ (λ_{max} values), respectively, and for β_1-complexes, 490 and 346 mμ. Both bands are shifted about 5 mμ to longer wavelengths for both β_1- and β_2-proline complexes compared to the corresponding isomers of the other amino acid complexes. The shift of the absorption bands to longer wavelengths for the S-proline complexes is expected from the lower ligand field strength of the secondary amine group.

The E_a state is predicted to be lower in energy than the A_2 state for C_{4v} or D_3 for both β_1- and β_2-complexes. As shown in Figure 3-8, no evidence for band splitting of the visible absorption spectra was found for any of the amino acid complexes in this study, but the CD spectra show very evident splitting. At least two CD bands could be observed for all resolved β_1– and β_2–[Co(trien)(aa)]$^{2+}$ complex ions in the first ligand field band, *i.e.*, there is either one broad band with tailing in the high energy region or there are two bands within the first ligand field absorption band. These results indicate that the T_{1g} (O_h) state is split into (at least) two states for [Co-(trien)(aa)]$^{2+}$ complex ions (see Table III). The appearance of two CD bands in the first ligand field band region would be consistent with the effective symmetry C_{4v} or D_3.

Absolute configurations were assigned to the β_1- and β_2-isomers of [Co(trien)(aa)]$^{2+}$ complex ions by comparison of their CD spectra with those for the (+)–[Co(en)$_3$]$^{3+}$ ion[16] and the (–)–[Co en$_2$(S–sar)]$^{2+}$ ion for which absolute configurations are known from X-ray studies.[17] The dominant CD peak for these complexes are assigned to the E_a state. Therefore, the complexes are assigned to the Λ-configuration, if the major CD band (E_a) is positive, and the Δ-configuration for a negative CD band (E_a). The assignments of absolute configurations of the β_2 proline complexes have been confirmed by X-ray studies.[9]

The CD spectra for the unresolved complexes show three peaks in the first ligand field band region. Moreover, the CD spectra for both resolved optical isomers of β_1- and β_2-proline complexes show that three components can be resolved in the first ligand field band region. These results indicate that the complexes have symmetry lower than C_{4v} or D_3. The higher symmetry (2 components instead of 3) suggested by the CD spectra for most of the resolved complexes presumably arises from the dominance of one component resulting from a strong configurational contribution. The degeneracy of the T_{1g} (O_h) state would be removed in effective C_{2v}, C_2 or C_1 symmetry. The molecular symmetry is C_1 for [Co-(trien)(aa)]$^{2+}$ complex ions. However, assignments for C_1 symmetry are not significant since the only representation is A.

Stereospecificity and the Assignment of Absolute Configuration. The assignments for the β–RR (or SS)– and β–RS (or SR)– isomers are based primarily on the stereoselectivity of the S-proline complex. Because of the near planarity of the amino acid ring, the optically active amino acid complexes of the type [Co en$_2$(aa)]$^{2+}$ have been considered to have little stereoselectivity.[3,18] Recently Buckingham *et. al*[19] have reported that sarcosine is coordinated stereospecifically in [Co en$_2$(sar)]$^{2+}$ ion. Only the (–)–isomer was isolated for S-sarcosine. An X-ray analysis of the (–)–[Co en$_2$(S–sar)]$^{2+}$ ion[17] indicates that the absolute configuration about Co^{III} ion is Δ for the (–)– isomer. The stereospecific formation of the Δ–(–)–[Co en$_2$(S–sar)]$^{2+}$ ion is attributed to the preferred nonbonded intramolecular interaction between hydrogen atoms of the N-methyl group and those on the adjacent ethylenediamine rings.

More recently, Marzilli and Buckingham have reported that sarcosine is also coordinated stereospecifically in the [Co(trien)(S–sar)]$^{2+}$ ion.[7] Only the (–)–isomer was isolated for S-sarcosine. On the basis of visible, infrared and pmr spectra and the stereospecificity of sarcosine and the negative sign of the Cotton effect (E_a) for the sarcosine complex, they assigned the Δ–(–)–β_2–RR conformation for the S-sarcosine complex. On the basis of the sign of the Cotton effect in comparison to that for the sarcosine complex, they made the assignments Δ–(–)–β_2–RR and Λ–(+)–β_2–SS for the glycine complexes.

S-proline is a cylic amino acid including the five-membered pyrolidine and has a secondary nitrogen atom which becomes asymmetric upon coordination. The steric factors in proline complexes are expected to be more pronounced than those of sarcosine.

Hall and Douglas[18] reported that only one isomer, the (–)$_D$–isomer, was isolated for [Co en$_2$(S–prol)]I$_2$. Denning and Piper[20] reported that three of the possible four isomers of [Co(S–prol)$_2$] were isolated successfully but the fourth isomer was either not formed or formed in very small amount. Yasui *et al.*[21] were able to isolate only one isomer of the complex [Co-(S–prol)$_3$].

In the present study, only the (–)–isomer was isolated for the [Co(trien)(S–prol)]$^{2+}$ ion in the preparation by the first method. The visible absorption spectrum for the (–)–[Co(trien)(S–prol)]$^{2+}$ ion is very similar to that of the Δ–(––)–β_2–RR–[Co(trien)(S-sar)]$^{2+}$ ion. Its CD spectrum shows one broad band in the visible region with a shoulder near 510 mμ. This CD band has the same sign of the Cotton effect as the (–)–isomer of sarcosine, so it is presumed to have the Δ–(–)–β_2–RR configuration. Framework molecular models reveal that the repulsive interactions are at a minimum in the proline complex for Δ–(–)–β_2–RR–[Co(trien)(S–prol)]I$_2$. The structures reveal more distortion for the Λ–(+)–isomer, but the preparative method used for that work showed little stereoselectivity. The stereoselectivity observed in method 1 is presumed to be kinetically controlled. The corresponding assignments, Δ–(–)–β_2–RR or Λ–(+)-

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(17) J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 324 (1967).
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(19) D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg Chem.*, *5*, 1649 (1966).
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Table III. Data from Absorption and Circular Dichroism Spectra and Assigned Ring Conformations

Complex	Excited State	Absorption Spectra ν_{max} (cm^{-1})	ε_{max}	CD Spectra ν_{max} (cm^{-1})	$\Delta\varepsilon_{max}$	Conformation [a]
Λ—(+)—β_1—SS—[Co(trien)(gly)]$I_2 \cdot H_2O$	^1E_a	20,400	166	19,550	+2.30	δ|λ|δδ
	^1E_b	28,580	115	26,200	+0.20	
	$^1A_1$			29,200	−0.13	
Λ—(+)—β_2—SS—[Co(trien)(gly)]$I_2 \cdot H_2O$	^1E_a	20,950	136	20,500	+2.13	δ|λ|λδ
	^1E_b	28,950	155	29,500	−0.15	
Λ—(+)—β_2—SR—[Co(trien)(gly)]$I_2 \cdot H_2O$	^1E_a	20,950	138	20,500	+1.92	λ|δ|δδ
	^1E_b	28,950	165	29,500	−0.13	
Λ—(+)—β_1—SS—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,400	163	19,950	+2.02	δ|λ|δδ
	^1E_b	28,580	139	26,400	+0.08	
	$^1A_1$			29,300	−0.15	
Δ—(−)—β_1—RR—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,400	163	19,350	−2.07	λ|δ|λδ
	^1E_b	28,580	139	26,100	−0.18	
	$^1A_1$			29,300	−0.13	
Unresolved—β_1—(RR and SS)—[Co(trien)(S—ala)]$I_2 \cdot H_2O$		20,400	163	19,100	−0.25	
				20,750	+0.18	
				23,100	−0.06	
		28,580	139	30,000	−0.08	
					(very broad)	
Λ—(+)—β_2—SS—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	142	20,350	+2.38	δ|λ|δδ
	^1E_b	28,950	153	27,000	+0.05	
	$^1A_1$			29,700	−0.10	
Δ—(−)—β_2—RR—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	142	21,000	−2.37	λ|δ|δδ
	^1E_b	28,950	153	28,700	+0.30	
Unresolved—β_2—(RR and SS)—[Co(trien)(S—ala)]$I_2 \cdot H_2O$		20,950	142	18,570	−0.05	
				20,300	+0.35	
				22,200	−0.60	
		28,950	153	29,000	+0.05	
					(very broad)	
Λ—(+)—β_2—SS—[Co(trien)(R—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	142	21,000	+2.37	δ|λ|λλ
	^1E_b	28,950	153	28,700	−0.30	
Δ—(−)—β_2—RR—[Co(trien)(R—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	142	20,350	−2.38	λ|δ|λλ
	^1E_b	28,950	153	27,000	−0.05	
	$^1A_1$			29,700	−0.10	
Unresolved—β_2—(RR and SS)—[Co(trien)(R—ala)]$I_2 \cdot H_2O$		20,950	142	18,570	+0.05	
				20,300	−0.35	
				22,200	+0.60	
		28,950	153	29,000	−0.05	
					(very broad)	
Λ—(+)—β_2—SR—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	136	20,500	+1.83	λ|δ|δδ
	^1E_b	28,950	155	29,500	−0.08	
Δ—(−)—β_2—RS—[Co(trien)(S—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	136	20,500	−2.04	δ|λ|λδ
	^1E_b	28,950	155	29,500	+0.10	
Unresolved—β_2—(RS and SR)—[Co(trien)(S—ala)]$I_2 \cdot H_2O$		20,950	136	20,500	−0.10	
		28,950	155		(very broad)	
Λ—(+)—β_2—SR—[Co(trien)(R—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	136	20,500	+2.04	λ|δ|δλ
	^1E_b	28,950	155	29,500	−0.10	
Δ—(−)—β_2—RS—[Co(trien)(R—ala)]$I_2 \cdot H_2O$	^1E_a	20,950	136	20,500	−1.83	δ|λ|λλ
	^1E_b	28,950	135	29,500	+0.08	
Unresolved—β_2—(RS and SR)—[Co(trien)(R—ala)]$I_2 \cdot H_2O$		20,950	136	20,500	+0.10	
		28,950	155		(very broad)	
Λ—(+)—β_1—SS—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,400	165	20,000	+1.95	δ|λ|δδ
	^1E_b	28,580	135	26,000	+0.08	
	$^1A_1$			29,300	−0.24	
Δ—(−)—β_1—RR—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,400	164	19,600	−2.05	λ|δ|λδ
	^1E_b	28,580	135	26,000	−0.18	
	$^1A_1$			28,700	−0.08	
Unresolved—β_1—(RR and SS)—[Co(trien)(S—meth)]$I_2 \cdot H_2O$		20,400	165	19,100	−0.25	
				20,700	+0.15	
				26,000	−0.10	
		28,580	135	29,000	−0.10	
					(very broad)	
Λ—(+)—β_2—SS—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,950	137	20,650	+2.38	δ|λ|δδ
	^1E_b	28,950	160	29,500	−0.15	
Δ—(−)—β_2—RR—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,950	137	21,150	−2.20	λ|δ|δδ
	^1E_b	28,950	160	28,800	+0.26	
(±)—β_2—(RR and SS)—[Co(trien)(S—meth)]$I_2 \cdot H_2O$ [b]		20,950	137	18,400	−0.08	
				20,200	+0.28	
				22,500	−0.68	
		28,950	160	28,500	+0.07	
Λ—(+)—β_2—SR—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,950	149	20,850	+1.90	λ|δ|δδ
	^1E_b	28,950	171	29,000	−0.15	
Δ—(−)—β_2—RS—[Co(trien)(S—meth)]$I_2 \cdot H_2O$	^1E_a	20,950	149	20,850	−2.03	δ|λ|λδ
	^1E_b	28,950	171	29,000	+0.15	

Table III. (Continued)

	Excited State	Absorption Spectra ν_{max} (cm^{-1})	ε_{max}	CD Spectra ν_{max} (cm^{-1})	$\Delta\varepsilon_{max}$	
Unresolved—β_2—(RS and SR)—[Co(trien)(S—meth)]$I_2 \cdot H_2O$		20,950	149	20,500	−0.10	
		28,950	171			
Λ—(+)—β_1—SS—[Co(trien)(S—prol)]$I_2 \cdot H_2O$	$^1A_2$ ^1E_a $^1B_2$	20,200	174	18,550	−0.23	δ|λ|δδ
	$^1B_1$			20,500	+1.80	
	^1E_b	28,580	160	28,700	−0.28	
Δ—(—)—β_1—RR—[Co(trien)(S—prol)]$I_2 \cdot H_2O$	^1E_a	20,200	174	19,150	−1.90	λ|δ|λδ
	$^1A_2$			22,850	−0.08	
	^1E_b	28,580	160	26,600	−0.23	
(±)—β_1—(RR and SS)—[Co(trien)(S—prol)]$I_2 \cdot H_2O$ [b]		20,200	174	18,900	−0.86	
				20,750	+0.64	
		28,580	160	27,100	−0.25	
Λ—(+)—β_2—SS—[Co(trien)(S—prol)]$I_2 \cdot H_2O$	$^1A_2$ ^1E_a $^1B_2$	20,600	158	18,050	−0.27	δ|λ|δδ
	$^1B_1$			20,300	+2.45	
	^1E_b	28,500	175	28,900	−0.36	
Δ—(—)—β_2—RR—[Co(trien)(S—prol)]$I_2 \cdot H_2O$	^1E_a	20,600	158	20,300	−1.43	λ|δ|δδ
	$^1A_2$			21,400	−1.53	
	^1E_b	28,500	175	28,500	+0.18	
(±)—β_2—(RR and SS)—[Co(trien)(S—prol)]$I_2 \cdot H_2O$ [b]		20,600	158	18,600	−.36	
				20,200	+0.50	
				22,500	−0.43	
		28,500	175		−0.08 (very broad)	

[a] |δ| (or |λ|): ring conformation of the central diamine ring in trien. Last δ (or λ): ring conformation of the amino acid chelate ring. [b] CD data are for the curve obtained as the average of the curves for the (+)— and (—)—isomers.

—β_2—SS, were made for the complexes of the other amino acids obtained by the same method in this work.

The isomers isolated by the second method are interpreted as the Λ—(+)—β_2—SR and Δ—(—)—β_2—RS—conformers for all amino acids except proline They were assigned as β_2 isomers on the basis of visible, infrared, and pmr spectra, but the CD curves indicated that they were not Δ—RR or Λ—SS isomers. Two isomers were obtained for the proline complex either with or without a resolving agent. The (—)—isomer was identical to that obtained by the first method and was presumed to belong to that series. The major CD band in the visible region for the (+)—isomer is opposite in sign to that of the (—)—isomer, therefore, it was assigned as Λ—(+)—β_2—SS—[Co(trien)(S-prol)]I_2, another member of the first series.

Four isomers were isolated with proline in the preparation by the third method. Two of them were identical to those obtained by the second method, the Λ—(+)—β_2—SS— and Δ—(—)—β_2—RR—conformers. The other two were not β_2—isomers. On the basis of the visible, infrared, and pmr spectra, they were assigned the β_1-configuration. Only two β_1-isomers were isolated for each of the trien-amino acid complexes. Models clearly show strong steric interaction involving the proline ring of both β_1-RS and β_1SR isomers, so the isomers obtained were assigned as β_1-RR and β_1-SS conformers. According to the sign of the Cotton effect of the major CD peak for both (+)— and (—)—isomers, they were assigned as Λ—(+)—β_1—SS— and Δ—(—)—β_1—RR—[Co(trien)(S-prol]I_2, respectively (Figure 8). The other amino acid complexes with the β_1-configuration are also assigned the Λ—(+)—β_1—SS and Δ—(—)—β_1—RR conformations on the basis of comparing the «vicinal effect» CD curves of RR (or SS) and RS (or SR) conformations (Figures 5, 6, and 7) and the similarity in the CD spectra of the (—)—β_1—isomers for all of the amino acid complexes.

Vicinal Effect and Conformational Isomers of the Trien Chelate Ring. The «vicinal effect»[22] has been pointed out to be useful for elucidating the origin of optical activity and the electronic structure of the dissymmetric transition metal in the visible absorption region.[23] The shapes of the «vicinal effect» CD curves for complexes were suggested not to be characteristic of particular optically active ligands, but to be determined primarily by the total molecular symmetry of the complex. Three types of «vicinal effect» CD curves are found for β—[Co(trien)(S—aa)]I_2 complexes in the present study. As shown in Figures 5, 6, and 7, the CD spectra for «racemic» β_2—RR (and SS)—[Co(trien)(S—aa)]I_2 with S-alanine and S-methionine are similar to those of [Co en_2(S—aa)]I_2[3,18] complex for which three CD peaks (—,+,—) are found in the first ligand field band, except the intensities for three peaks are relatively higher for trien complexes. The β_1-isomers, with S-alanine and S-methionine also show three CD peaks (—,+,—) in the first ligand field band region. The CD curves for the β_1—S—methionine complex are similar to those shown in Figure 7 for the corresponding S—alanine complex. Their intensities are comparable to those of the [Co-en_2(S—aa)]I_2 complexes, but the two negative CD peaks are reversed in order of relative intensities for

(22) Y. Shimura, *Bull. Chem. Soc. Japan, 31,* 315 (1958).
(23) J. Fujita and Y. Shimura, Optical Rotatory Dispersion and Circular Dichroism, in « Spectroscopy and Structure of Metal Chelate Compounds », K. Nakamoto and P. J. McCarthy, Eds., John Wiley and Sons, Inc., New York, 1968, p. 156.

β_1–[Co(trien)(S–aa)]I_2 and [Coen$_2$(S–aa)]I_2complexes Only one weak, broad, negative peak is observed in the first ligand field band region (Figure 6) in the CD spectra for the unresolved β_2–RS(and SR)–[Co(trien)-(S–aa)]I_2.

It has been pointed out that the sign and magnitude of a CD band of an asymmetrically perturbed symmetric chormophore is largely determined by the chirality of the perturbing environment.[24] Three factors are considered as controlling the CD of the «racemic» complexes: (1) the asymmetric center of the amino acid ligand (the true vicinal effect), (2) the conformation of each chelate, and (3) the asymmetric secondary amine groups. To separate these factors from the observed CD curves is rather difficult, because at least two of these are operative for all of the complexes under consideration.

S-proline has two asymmetric centers, at the α-carbon atom and the N-atom. More significant differences in CD curves are observed for (±)–β_1–[Co(trien)-(S–prol)]I_2 and (±)–β_2–[Co(trien)(S–prol)]I_2 (Figure 8) (where ± refers to an equimolar mixture of the (+)– and (–)–isomers) in comparison to the curves of the other amino acid complexes. The β_2–isomer shows CD peaks (–,+,–) of equal intensity in the first ligand field band region and the β_1–isomer shows two CD peaks (–,+) with a tailing in the second peak in this region, suggesting the presence of a third peak. The intensities of both peaks are higher than any of the other β_2–isomers. The vicinal effect CD curves are expected to be different for both conformational isomers (Λ–SS and Λ–SR) for each series of β–isomers, since the different arrangement on the «planar» secondary nitrogen would give different ring conformations and different interaction with the asymmetric center of the optically active ligand within the complex. The visible, infrared and pmr spectra for both β_2–RR (or SS) and β_2–RS (or SR) (Figure 3) with glycine are similar, but the former has slightly higher CD intensities than the latter. The CD spectra for both series of conformers with optically active amino acids (*i.e.*, R– and S–alanine and S–methionine) are very different (Figure 4). The CD spectra for R–alanine complexes are mirror images of those of the enantiomeric isomers of S–alanine complexes. No interconversion was found for either series of conformers in aqueous media.

Optical Activity and Ring Conformations. There are many considerations concerning the origin of the optical activity exhibited by *d-d* absorption bands in the visible region for dissymetric transition metal complexes. Experimentally, it has been shown that there are three contributions to the optical activity of chelate complexes: (1) the configurational effect (contribution from the right or left spiral of chelate rings about the metal ion), (2) the conformational effect (contribution from the conformations of each chelate ring), and (3) the vicinal effect (contribution from asymmetric centers of the ligands). Among these three factors, it has been concluded[25,26] that the optical activity of the metal complexes in the first ligand field band region is governed mainly by the configuration of the chelate rings around the Co^{III} ions. The conformational and vicinal effects are only minor factors in this region. These effects might be expected to be additive and separable.[25,26] However, in fact, to distinguish the vicinal effect from the conformational effect is rather difficult, since the absolute configuration of the ligand determines the preferred chelate ring conformation.

A limited degree of additivity is found for the Co^{III}-diamine complexes.[25] This additivity was questioned by Mason *et al.*[26] since the en rings may not have a preferred conformation in a tris-diamine Co^{III} complexes, or the differences between the visible CD of the (+)–[Co(+)–pn$_3$]$^{3+}$ and (+)–[Co en$_3$]$^{3+}$ ions, *i.e.*, the larger $^1A_2$ CD band of the former complex, may be due to the asymmetric centers of the pn rings or arise from a different frequency interval between the $^1A_2$ and ^1E_a transitions for those two complexes. Moreover, Mason *et al.*[26] have shown that when one or more of the chelate rings in (+)–[Co(+)–pn$_3$]$^{3+}$ are substituted by (–)–pn (*i.e.*, ring conformation changes from δ^4 to λ, the major positive CD band (^1E_a) remains positive and has a similar magnitude while the minor negative CD band ($^1A_2$) is eliminated. They suggest that the disappearance of the $^1A_2$ CD band is probably caused by a reduction in the frequency interval between the ^1E_a and $^1A_2$ transitions, so that the negative $^1A_2$ CD band is completely masked by the stronger positive ^1E_a CD band, or may be caused by the conformational change. The most probable factor here may be the conformational change in the tris-diamine Co^{III} complexes, because (+)–pn and (–)–pn have the same ligand field strength and the major factors that cause the differences in the CD spectra for (–)–pn and (+)–pn complexes would be the conformational and vicinal effects. Ogino, Murano, and Fujita[27] found an error in the CD data reported earlier[28] and confirmed the additivity of configurational and conformational contributions.

In the present study, the conformations of the chelate rings are assigned on the basis of analyzing the observed CD spectra. The conformations of the two « in plane » chelate rings are fixed by configuration of the « planar » asymmetric N atom of trien. The conformational and vicinal effects have been separated on this basis. Ring conformational assignments are given in Table III. In the previous section, it was mentioned the disappearance of the second negative CD band ($^1A_2$) might result from the ring conformational change from δ to λ. Good examples to examine this possibility might be the [Co en$_2$(aa)]I_2 complexes. The CD spectra for both isomers of [Co en$_2$(gly)]I_2 [3] show a single intense peak in the first ligand field band region. However, Smith and Douglas[29] have shown that a second CD peak of opposite sign appears in this region when electrolytes are added. Moreover, this second peak is apparent for the (+)–isomer of the corresponding complexes

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(25) B. E. Douglas, *Inorg. Chem.*, *4*, 1813 (1965).
(26) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.* (A), 1304 (1968).
(27) K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Letters*, *4*, 351 (1968).
(28) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).
(29) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, *5*, 784 (1966).

of S-alanine, S-phenylalanine, S-leucine[3] and S-methionine[18] without the addition of electrolytes. Only one broader peak is found for the (−)–isomer in this region.

The absolute configuration of an S-amino acid is known and the chelate ring formed by the α-amino acid is slightly puckered. From the conformational analysis, C-substituents are expected to adopt the more stable equatorial position. Hall and Douglas[18] assigned the chelate ring conformations as δδδ for (+)–[Co en$_2$(aa)]$_2$ (where aa = glycine or S-amino acid anions). The ring conformations for the (−)–isomers of S-amino acid complexes have been assumed to involve mixing of δ and λ conformations (*i.e.*, λδδ or or λλδ, where the conformation of the amino acid is given last). The X-ray analysis for the (−)–[Co-en$_2$(sar)]$^{2+}$ ion[12] shows that the Co-sar chelate ring is slightly puckered and the two en chelate rings are puckered with opposite conformations. Therefore, the ring conformations may be assigned as λδδ (or δλδ). The degree of planarity of the chelate rings is expected to be in the order: glycine > S-amino acid > en > (+)–pn. Therefore, one might expect that the second negative CD band ($^1A_2$) is most pronounced for (+)–[Co(+)–pn$_3$]$^{3+}$, less pronounced for [Co en$_2$(S-aa)]$^{2+}$ and completely disappears for the [Co en$_2$(gly)]$^{2+}$ ion. The spiral configuration of a complex has a dominant effect on the CD band of E parentage so that the weaker band (A_2) reflects conformational changes to a greater extent.

The intensities of the CD peaks for the [Co(trien)-(aa)]I$_2$ complexes (Figures 3 and 4) are comparable to those of the corresponding [Co en$_2$(aa)]I$_2$ complexes, so that the addition of another chelate ring and the presence of two asymmetric N centers do not make significant contributions. The CD spectra for both isomers of β$_1$–SS (or RR)–[Co(trien)(gly)]I$_2$ (Figure 3) are very similar to those of [Co en$_2$(gly)]I$_2$ isomers.[3] Therefore, it is presumed that the two isomers of β$_1$–SS (or RR)–[Co(trien)(gly)]$_2$ with the same absolute configurations as the respective isomers of [Co en$_2$(gly)]I$_2$ [3] have the same chelate ring conformations. They are assigned as Λ–(+)–β$_1$–(δδδ) for the (+)–isomer and Δ–(−)–β$_1$–(λλλ) for the (−)–isomer (the central diamine ring in trien is neglected in this assignment). From the model, the conformations for both isomers are assigned as Λ–(+)–β$_1$–(δ|λ|δδ) and Δ–(−)–β$_1$–(λ|δ|λλ) where |λ| and |δ| mean the conformations of the central diamine ring of trien).

The CD spectra for both isomers of β$_2$–RR (or SS)–[Co(trien)(gly)]I$_2$ and β$_2$–RS (or SR)–[Co(trien)-(gly)]$_2$ Figure 3) are very similar except the former has slightly higher CD intensities. Only one broad band is observed for both β$_2$-conformational isomers in the first ligand field band region. The differences in the CD spectra for β$_1$ and β$_2$-glycine complexes (Figure 3) could be caused by the different ring conformations or the reduction of the frequency interval of ^1E_a and $^1A_2$ transitions for the β$_2$isomers. This could cause the weaker component to be completely masked by the stronger ^1E_a CD band. However, the latter argument may be refuted by the CD spectra of optically active amino acid complexes. The CD spectra for the (+)–isomers of both β$_1$–SS and β$_2$–SS with S-alanine (Figure 4) and S-methionine (not shown, similar to the curve for the S-alanine complex) are very similar to that of β$_1$–(+)–SS–[Co(trien)(gly)]I$_2$ (Figure 3), therefore the ring conformations for both β$_1$–SS and β$_2$–SS–[Co(trien)(S–aa)]I$_2$ are presumed to be the same as those of β$_1$–(+)–SS–[Co(trien)(gly)]I$_2$. However, the CD spectra for the (+)–isomers of β$_2$–SR–[Co(trien)(S–ala)]I$_2$ with S-alanine (Figure 6) and S-methionine (similar to that of the corresponding complex of S-alanine) are different from those of (+)–isomers of β$_1$–SS– and β$_2$–SS–[Co(trien)(S–aa)]I$_2$ (Figures 5 and 7). These results indicate that the reduction of frequency interval ^1E_a to $^1A_2$ for the β$_2$-isomers is not responsible for the observed results. Since the ligand field splittings for both the β$_2$–SS– and β$_2$–SR– complexes are the same (electronic spectra for both conformational isomers are identical), therefore, the differences in the CD spectra for β$_2$–SS– and β$_2$–SR– conformers are probably due to the different ring conformations of the two conformers.

One broad CD peak is observed for the (−)–isomers of β$_2$–RR and β$_2$–RS conformers with glycine, S-alanine (Figures 5 and 6) and S-methionine (curves similar to those of S-alanine). These CD peaks are very similar to that of the β$_2$–(−)–RR–[Co(trien)-(S–sar)]$^{2+}$ ion[7] and the (−)–[Co en$_2$(S–sar]$^{2+}$ ion[19] for which the absolute configuration and ring conformations have been determined by X-ray analysis.[17] Therefore these (−)–β$_2$– (RR or RS) conformers and the (−)–[Co en$_2$(S–sar)]$^{2+}$ ion are assumed to have the same conformations in solution (*i.e.*, λδδ for the three propeller chelate rings, where the last conformational notation, δ designates for the ring conformation of the amino acid chelate ring and the central diamine ring in trien is neglected). On the basis of the CD curves and molecular models, conformations of chelate rings and absolute configurations of complexes are assigned as given in Table III. The assigned conformations of the central diamine chelate ring of trien complexes are the same as those of the respective L–5,6–dimethyl trien complexes which were reported to be stereospecific.[30]

The amino acid chelate ring is known to be less puckered than a diamine chelate ring. The CD spectra for the (+)–isomers of β$_1$–SS– and β$_2$–SS–[Co(trien)(S–aa)]I$_2$ with S-alanine (Figure 4) and S-methionine (similar to Figure 4) reveal a single intense peak in the first ligand-field band region. A second peak is apparent for the (+)–isomer of [Co en$_2$(S–aa)]I$_2$.[15,16] As was mentioned earlier, the intensity of the second CD peak ($^1A_2$) depends greatly upon the conformation of the chelate rings. If the two terminal ethylene-diamine rings of trien have the same conformations as those of the en rings of [Co(en)$_2$XY]$^{2+}$ complexes, one may expect that the amino acid chelate ring in Co-trien complexes (no $^1A_2$ peak apparent) would be less puckered than those of [Co en$_2$(S–aa)]I$_2$ complexes. Framework molecular models show that for minimizing the non-bonded intramolecular interaction between the trien

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rings and the C-substituents of α–S–amino acids, the amino acid chelate ring is less puckered for [Co(trien)-(S–aa)]I_2 than that of [Co en_2(S–aa)]I_2.

The S-proline chelate ring is expected to be less puckered than those of the other S-amino acid complexes and the chelate ring for S-azet (S-azetidine-2-carboxylic acid) is expected to be planar. The CD spectra for (+)–isomers of both S-proline and S-azet complexes[31] reveal a tailing of the positive CD band on the short wavelength side with no indication of a significant contribution of opposite sign ($^1A_2$) as would be expected if the chelate rings were puckered. The fact that the trien complexes of other amino acids give CD curves more similar to those of the complexes containing the nearly planar proline and azet chelate rings, leads one to conclude that, in general, amino acid chelate rings are more nearly planar in [Co(trien)(aa)]I_2 complexes than in [Co en_2(aa)]I_2 complexes. Therefore, it can be assumed that the optical activity derived from an S-amino acid chelate ring is largely due to the vicinal effect (asymmetric center of the optically active amino acid), rather than from the conformation of the chelate ring of the amino acid.

If the CD curves for the first ligand-field band region of Λ–(+)–β_1–SS– [Co(trien)(S–ala)]I_2 and Δ–(–)–β_1–RR –[Co(trien)(S–ala)]$_2$ (Figure 7) are averaged, so that configurational and conformational effects are eliminated (assuming that the amino acid chelate ring is nearly planar), the resultant CD curve of the unresolved complex [*i.e.*, $1/2(\Lambda(\delta|\lambda|\delta\underline{\delta}V)+\Delta(\lambda|\delta|\lambda\underline{\delta}V)\cong V$, where V represents the vicinal effect, $|\lambda|$ and $|\delta|$ represent the conformations of the central diamine ring of trien, and the last $\underline{\delta}$ represents the conformation of amino acid chelate ring which is assumed to be nearly planar and is neglected]. If the CD spectra in the visible region for Λ–(+)–β_2–SR–[Co(trien)(S–ala)]I_2 and Δ–(–)–β_2–RS–[Co(trien)-(S–ala)]I_2 (Figure 6) are averaged, so that configurational and conformational effects are eliminated, the resultant curve closely resembles that for the unresolved curve (Figure 6) [*i.e.*, $1/2(\Lambda(\lambda|\delta|\delta\underline{\delta}V)+\Delta(\delta|\lambda|\lambda\underline{\delta}V))\cong V$]. However, if the visible region CD spectra of Λ–(+)–β_2–SS –[Co(trien)(S–ala)]I_2 and Δ–(–)–β_2–RR –[Co(trien)(S–ala)]I_2 (Figure 5) are averaged to give a curve similar to that for the unresolved complex, the configurational effect is eliminated, but the resultant curve includes the CD contribution from the conformational effect of one ethylenediamine ring of trien and the vicinal effect of the S-amino acid (Figure 5) [*i.e.*, $1/2(\Lambda(\delta|\lambda|\delta\underline{\delta}V+\Delta(\lambda|\delta|\delta\underline{\delta}V))\cong\delta+V$].

These results indicate: (1) the additivity is generally valid for complexes with a diastereoisomeric relationship, (2) the general shape of the CD curve for the vicinal effect is determined by the overall molecular structure of the complex and is not characteristic of a particular ligand, and (3) the resultant curve obtained by adding CD curves of optical isomers is not generally a true vicinal effect CD curve, but a composite of conformational and vicinal effects.

(31) B. E. Douglas and C. Y. Lin, results to be published.