date(V) complex discussed by Gray and Hare seems to be incompatible with their supposition that only the oxo group makes a substantial contribution to the ground state of the charge-transfer transitions. A choice between placing the σ ligand levels above or below the π levels is more difficult. The portion of the spectrum which would provide the best information with regard to this question is unfortunately obscured by the intense intraligand transitions characteristic of the β-diketone ligands.

No firm assignments have been attempted for the bands beyond 35 kK. The absorption at about 40 kK in the compounds containing phenyl groups is probably the $\pi \rightarrow \pi^*$ transition of the benzene ring, but the spin-allowed $\pi_3 \rightarrow \pi_5$ and $\pi_2 \rightarrow \pi_4$ intraligand transitions may also be found in this region.

Stereochemical Studies of Metal Chelates. III.[1] Preparation and Stereochemistry of Cobalt(III) Complexes with C-Substituted Triethylenetetramines at the Central Ethylenediamine Bridge

BY MASAFUMI GOTO, MASAHIKO SABURI, AND SADAO YOSHIKAWA

The preparation of dichloro- and dinitrocobalt(III) complexes of optically active C-substituted triethylenetetramine at the central ethylenediamine bridge is described. The stereoselective formation of the *cis-β* isomer was observed and the stereochemical details are discussed in terms of the conformation of each chelate ring as well as the configurations of the secondary nitrogen atoms. The rearrangement of *cis-β*-dichloro complexes to *trans* isomers is also reported.

In the past few years, some interesting reactions of cobalt(III) complexes of triethylenetetramine (trien) and its derivatives have been reported, *i.e.*, hydrolysis of the N-terminal peptide bond,[2] formation of a dipeptide ester from amino acid esters,[3,4] and an asymmetric synthesis of α-alanine.[5] Concurrently, studies on the stereochemistry of the cobalt(III) complexes containing trien have been in rapid progress. It was pointed out formerly that three geometrical isomers may exist in diacido trien complexes, namely, *cis-α*, *cis-β*, and *trans* as shown in Figure 1.[6] Sargeson and Searle have succeeded in resolving several *cis-α* and *cis-β* isomers of $Co(trien)X_2^{n+}$[7] and have assigned their absolute configuration on the basis of circular dichroism and rotatory dispersion studies.[8] These authors also indicated that the *trans*-Co(trien)Cl$_2^+$ ion derived from optically active *cis-β* isomer is asymmetric.[9]

Furthermore, the possibility that two different isomers may exist in *cis-β* form was recognized assuming different types of the two asymmetric secondary nitrogen atoms.

In a previous paper,[10] it was reported that L,L-3,8-dimethyltriethylenetetramine (L,L-3,8-dimetrien) was coordinated stereospecifically to the cobalt(III) ion, yielding the optically active *trans*-Co(L,L-3,8-dimetrien)Cl$_2^+$ ion, and that racemic 5-methyltriethylenetetramine (5-metrien) was found to give stereoselectively the *cis-β*-Co(*dl*-5-metrien)Cl$_2^+$ ion. These results indicate that alkyl groups substituted at the carbon atoms adjacent to the secondary nitrogen atom in trien control the geometrical isomer form of dichloro complexes. However, L,L-2,9-dimethyltriethylenetetramine (L,L-2,9-dimetrien),[11] as well as unsubstituted trien, was observed to give the *cis-α* isomer under similar preparative conditions. In order to investigate the effect of position of the substituted group in trien, new optically active trien derivatives containing alkyl groups at the central ethylenediamine bridge have been synthesized; these are shown in Figure 2, and the dichloro- and dinitrocobalt(III) complexes containing these ligands have been prepared. Consequently, it was concluded that these complexes yielded only the *cis-β* isomer and the chirality of the ligands controls stereospecifically the absolute configuration of the complexes. Furthermore, the conformation of each chelate ring in the geometrical isomers will be discussed in detail from the examination of stereomodels.
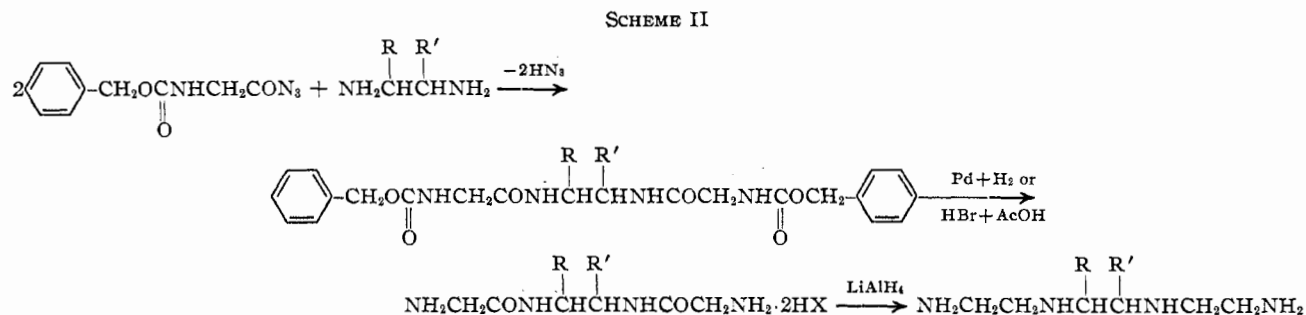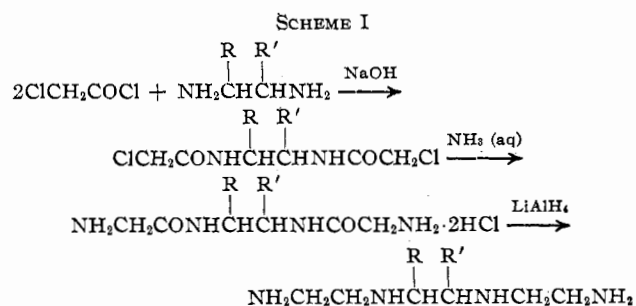
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Experimental Section

Materials.—Commercial grade *dl*-propylenediamine was resolved by the method of Dwyer, *et al.*;[12] $[\alpha]_D$ $-29.8°$ (in benzene). Commercial grade chloroacetyl chloride was used after redistillation. *trans*-Cyclohexane-1,2-diamine was prepared and resolved according to the method of Jaeger and Bijkerk.[13] Its *l*-dihydrochloride salt gave $[\alpha]_D$ $-15.8°$.[14] *dl*-Butane-2,3-diamine was prepared according to the method of Balthis and Bailar[15] and separated after the recrystallization of the dihydrochloride salts from methanol; it was resolved by the method of Lucas, *et al.*;[16] $[\alpha]^{25}_D$ $+30.8°$ (lit.[16] $[\alpha]^{25}_D$ $+29.7°$). Carbobenzoxyglycine azide was prepared by the method of Erlanger and Brand.[17]

Instrumentation.—Visible absorption spectra were measured by a Hitachi recording spectrophotometer. Optical rotatory dispersion and circular dichroism were measured using the Jasco Model ORD/UV-5. Infrared spectra were measured by the Jasco Model DS-301 infrared recording spectrophotometer; using the KBr-disk method by taking 1.2–1.5 mg of the complexes/150 mg of KBr. Proton magnetic resonance spectra were measured using a Japan Electronic Optics Laboratory Model 4H 100-Mc/sec nmr spectrometer with deuterium oxide solutions containing about 40 mg of complex/0.5 ml using sodium trimethylsilylsulfonate as the internal reference.

The ligands, tetramines, were synthesized according to either Scheme I or Scheme II.

SCHEME I

$2ClCH_2COCl + NH_2CHCHNH_2 \xrightarrow{NaOH}$

$ClCH_2CONHCHCHNHCOCH_2Cl \xrightarrow{NH_3 (aq)}$

$NH_2CH_2CONHCHCHNHCOCH_2NH_2 \cdot 2HCl \xrightarrow{LiAlH_4}$

$NH_2CH_2CH_2NHCHCHNHCH_2CH_2NH_2$

SCHEME II

D-N,N'-Bis(chloroacetyl)propylenediamine.—A solution of chloroacetyl chloride (32 g, 0.28 mol) in 100 ml of benzene solution was added dropwise to a solution of D(−)-propylenediamine (10 g, 0.135 mol) in 5 N sodium hydroxide solution (120 ml) cooled in an ice–salt bath and stirred vigorously by a blender. The reaction mixture was filtered and the white precipitate was washed successively with small volumes of ice-cold water, metha-

nol, and acetone and dried under vacuum. This product was recrystallized from ethanol. Yield 28.2 g (91%); mp 128° (cor); $[\alpha]^{25}_D$ $+23.5$ (c 0.5 g/10 ml of water). *Anal.* Calcd for $C_7H_{11}O_2Cl_2$: C, 37.02; H, 5.33; N, 12.34; Cl, 31.22. Found: C, 37.01; H, 5.27; N, 12.04; Cl, 31.32.

D-N,N'-Bis(glycyl)propylenediamine Dihydrochloride.—A mixture of D-N,N'-bis(chloroacetyl)propylenediamine (10 g) and 100 g of ammonium carbonate in 28% aqueous ammonia (200 ml) was allowed to stand for 7 days. It was then evaporated under vacuum, and the oily layer was crystallized by dissolving it in a small volume of water and adding ethanol with occasional stirring. After standing overnight in a refrigerator, the white precipitate was filtered off and washed with ethanol and ether and dried under vacuum. This was recrystallized from water–ethanol; $[\alpha]_D$ $+12.2°$ (c 0.5 g/10 ml of water).

D-N,N'-Bis(β-aminoethyl)propylenediamine Tetrahydrochloride (D-5-Methyltriethylenetetramine Tetrahydrochloride).—Into a 300-ml, four-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser with a soda lime tube, 120 ml of anhydrous tetrahydrofuran was placed, and 8.0 g of pulverized and dried D-N,N'-bis-(glycyl)propylenediamine dihydrochloride was added with stirring. Then 7.2 g of lithium aluminum hydride (0.258 mol) was added in small portions with vigorous stirring while the vessel was kept in an ice-cold bath. After being stirred at this temperature for 30 min, the reaction mixture was refluxed and stirred for 24 hr. The reaction mixture was cooled and 18.6 g (1.03 mol) of water was added dropwise with vigorous stirring while the mixture was kept ice cold. The precipitate was filtered off and the filtered cake was extracted twice with boiling tetrahydrofuran. The combined tetrahydrofuran solution was concentrated under reduced pressure. Concentrated hydrochloric acid was added to the oily residue and the product was crystallized by adding ethanol. Yield 3.96 g (43%); $[\alpha]_D$ $+1.8$ (c 0.5 g/10 ml of water). *Anal.* Calcd for $C_7H_{24}N_4Cl_4 \cdot H_2O$: C, 25.94; H, 8.09; N, 17.29; Cl, 43.75. Found: C, 26.00; H, 8.06; N, 17.05; Cl, 43.81.

***dl*-N,N'-Bis(carbobenzoxyglycyl)butane-2,3-diamine.**—An ether solution (450 ml) of carbobenzoxyglycine azide prepared

from carbobenzoxyglycine hydrazide 30 g (0.135 mol) was added to a 500-ml erlenmeyer flask equipped with a magnetic stirrer. To this solution butane-2,3-diamine (4.5 g, 0.051 mol) in ether was added with vigorous stirring in an ice-cold bath and a white precipitate gradually formed. This mixture was stirred at this temperature for 24 hr, and the precipitate was then filtered and washed with ether; crude yield 17.68 g (70%). This was recrystallized from ethanol several times to give a constant melting point of 142–143° (cor). *Anal.* Calcd for $C_{24}H_{30}N_4O_6$: C, 61.26; H, 6.43; N, 11.91. Found: C, 60.92; H, 6.35; N, 12.17.

***dl*-N,N'-Bis(glycyl)butane-2,3-diamine Dihydrobromide.**—*dl*-N,N'-Bis(carbobenzoxyglycyl)butane-2,3-diamine (16.68 g, 0.035 mol) was added to 50 ml of acetic acid saturated with hydrogen bromide. After 3 hr this reaction mixture was added to 300 ml

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of ether with stirring and the white precipitate was filtered off, washed with ether several times, and dried under vacuum.

dl-N,N'-Bis(glycyl)butane-2,3-diamine Diacetate.—*dl*-N,N'-Bis(glycyl)butane-2,3-diamine dihydrobromide (15.82 g, 0.0435 mol) was added to 87 ml of 1 *N* sodium hydroxide solution and the mixture was evaporated under reduced pressure. To the resulting residue, 200 ml of 1-butanol was added and refluxed for 30 min. This mixture was cooled and filtered to remove sodium bromide; then the filtrate was concentrated to 10 ml, and 50 ml of ether and 5.4 g of acetic acid were added. The white precipitate was collected and dried under vacuum; yield 11.0 g (78%).

dl-N,N'-Bis(β-aminoethyl)butane-2,3-diamine Tetrahydrochloride (*dl*-5,6-Dimethyltriethylenetetramine Tetrahydrochloride).—This was prepared by a procedure similar to that used for D-5-methyltriethylenetetramine tetrahydrochloride; *i.e.*, 10.5 g of *dl*-N,N'-bis(glycyl)butane-2,3-diamine diacetate was reduced with lithium aluminum hydride (10.1 g in 300 ml of tetrahydrofuran); yield 7.8 g (75%). *Anal.* Calcd for $C_8H_{22}N_4 \cdot 4HCl$: C, 30.01; H, 8.19; N, 17.50. Found: C, 30.21; H, 8.14; N, 17.54.

L(−)-N,N'-Bis(carbobenzoxyglycyl)butane-2,3-diamine.— This was prepared by the same procedure as that used for *dl*-N,N'-bis(carbobenzoxyglycyl)butane-2,3-diamine. Crude yield 23.5 g (97%); mp 149–150° (cor); $[\alpha]^{25}$D −5.0° (*c* 0.05 g/10 ml of acetic acid). *Anal.* Calcd for $C_{24}H_{30}N_4O_6$: C, 61.26; H, 6.43; N, 11.91. Found: C, 60.78; H, 6.32; N, 11.89.

L-N,N'-Bis(glycyl)butane-2,3-diamine Diacetate.—Pulverized L-N,N'-bis(carbobenzoxyglycyl)butane-2,3-diamine (9.7 g, 0.021 mol), 250 ml of methanol, and 5 ml of acetic acid were taken into a 500-ml Parr low-pressure apparatus. To this mixture 2 g of palladium black catalyst was added and hydrogen was passed through, occasionally letting the evolved carbon dioxide free. After 1.5 hr, the reaction mixture was filtered and the filtrate was concentrated to 20 ml with a rotatory evaporator. Some product separated from the solution, and the addition of tetrahydrofuran (100 ml) yielded more. The product was filtered off and washed with tetrahydrofuran; yield 4.93 g (78%).

L-N,N'-Bis(β-aminoethyl)butane-2,3-diamine Tetrahydrochloride (L-5,6-Dimethyltriethylenetetramine Tetrahydrochloride).—L-5,6-Bis(glycyl)butane-2,3-diamine diacetate (4.93 g, 0.0154 mol) was reduced with lithium aluminum hydride (4.8 g, 0.13 mol) in 150 ml of tetrahydrofuran. Yield 2.8 g (57%); $[\alpha]^{28}$D +9.96° (*c* 0.61 g/10 ml of water). *Anal.* Calcd for C_8H_{26}-$N_4Cl_4 \cdot H_2O$: C, 30.01; H, 8.22; N, 16.32. Found: C, 28.65; H, 7.46; N, 16.39.

trans-Bis(carbobenzoxyglycyl)cyclohexane-1,2-diamine.—This was prepared from 4.27 g (0.038 mol) of *trans*-cyclohexane-1,2-diamine by the same procedure as that used for *dl*-N,N'-bis-(carbobenzoxyglycyl)butane-2,3-diamine. Yield 17.68 g (75%); mp 196–198° (cor). *Anal.* Calcd for $C_{26}H_{32}O_6N_4$: C, 62.89; H, 6.50; N, 11.28. Found: C, 62.82; H, 6.76; N, 11.35.

trans-N,N'-Bis(glycyl)cyclohexane-1,2-diamine Dihydrobromide.—*trans*-N,N'-Bis(carbobenzoxyglycyl)cyclohexane-1,2-diamine (9.5 g, 0.119 mol) was treated with 70 ml of acetic acid saturated with hydrogen bromide to prepare *dl*-N,N'-bis(glycyl)-butanediamine. The collected precipitate was recrystallized from methanol–ether; yield 6.5 g (87%).

trans-N,N'-Bis(β-aminoethyl)cyclohexane-1,2-diamine Tetrahydrochloride (*dl*-ECE·4HCl).—*trans*-N,N'-Bis(glycyl)cyclohexane-1,2-diamine dihydrobromide (5.85 g, 0.015 mol) was reduced with lithium aluminum hydride (3.20 g, 0.085 mol) in 150 ml of tetrahydrofuran as the preceding tetramine hydrochloride. The crude *trans*-N,N'-bis(β-aminoethyl)cyclohexanediamine tetrahydrochloride could not be recrystallized in any appropriate solvent, so this was used in preparation of cobalt(III) complexes.

D-*trans*-N,N'-Bis(carbobenzoxyglycyl)cyclohexane-1,2-diamine. —This was prepared from 2.5 g (0.022 mol) of D(−)-*trans*-cyclohexane-1,2-diamine by the same procedure as that used for *dl*-N,N'-bis(carbobenzoxyglycyl)butane-2,3-diamine. Yield 9.15 g (84%); mp 169–170° (cor); $[\alpha]^{28}$D +10.2° (*c* 0.05 g/10 ml of acetic acid). *Anal.* Calcd for $C_{26}H_{32}N_4O_6$: C, 62.89; H, 6.50;

N, 11.28. Found: C, 62.87; H, 6.62; N, 11.23.

D-*trans*-N,N'-Bis(glycyl)cyclohexane-1,2-diamine Diacetate.— This was prepared from 6.94 g (0.014 mol) of D-*trans*-N,N'-bis(carbobenzoxyglycyl)cyclohexane-1,2-diamine by the same procedure as that used for L-N,N'-bis(glycyl)butane-2,3-diamine; yield 4.04 g.

D-*trans*-N,N'-Bis(β-aminoethyl)cyclohexane-1,2-diamine Tetrahydrochloride (D-ECE·4HCl).—This was prepared from 4.00 g of L-N,N'-bis(glycyl)cyclohexane-1,2-diamine diacetate by the same procedure as that used for L-5,6-dimethyltriethylenetetramine tetrahydrochloride; $[\alpha]^{28}$D −41° (*c* 0.59 g/10 ml of water). *Anal.* Calcd for $C_{10}H_{28}N_4Cl_4$: C, 34.69; H, 8.15; N, 16.18. Found: C, 34.36; H, 8.09; N, 15.93.

Preparation of Diacidocobalt(III) Complexes. Δ-*cis*-β-Dichloro(D - N,N' - bis(β-aminoethyl)propylenediamine)cobalt(III) Chloride Hemihydrate (Δ-*cis*-β-[Co(D-5-metrien)Cl$_2$]Cl·0.5H$_2$O). —To a mixture of 2.50 g (8.16 × 10^{-3} mol) of D-5-methyltriethylenetetramine tetrahydrochloride and 1.94 g (8.16 × 10^{-3} mol) of cobalt chloride hexahydrate in 80 ml of water was added 1.03 g (24.5 × 10^{-3} mol) of lithium hydroxide monohydrate. The brown solution was aerated for 12 hr with carbon dioxide free air. Then 15 ml of concentrated hydrochloric acid was added and the solution was evaporated on a steam bath until a red-purple product separated. The mixture was cooled to 0° overnight, filtered off, and washed with acetone, ethanol, and ether; yield 2.75 g (97%). This was recrystallized from 3 *N* hydrochloric acid and acetone.

The other dichloro complexes were prepared by procedures similar to that described above, and their elemental analyses are shown in Table I.

Δ-*cis*-β-Dichloro(D-N,N'-bis(β-aminoethyl)cyclohexane-1,2-diamine)cobalt(III) Chloride Hemihydrate (Δ-*cis*-β-[Co(D-ECE)-Cl$_2$]Cl·0.5H$_2$O).—This complex was very soluble in hydrochloric acid and was prepared as described below. To a mixture of 1.68 g (4.9 × 10^{-3} mol) of D-*trans*-N,N'-bis(β-aminoethyl)-cyclohexane-1,2-diamine tetrahydrochloride and 1.16 g (4.86 × 10^{-3} mol) of cobalt chloride hexahydrate in 30 ml of water was added 0.764 g (17.8 × 10^{-3} mol) of lithium hydroxide monohydrate. The brown solution was aerated for 12 hr with carbon dioxide free air. Then 10 ml of concentrated hydrochloric acid was added and the solution was evaporated nearly to dryness on a steam bath. To the purple mixture, ethanol in small portions was added. On scratching the sides of the vessel by a glass rod, purple crystals separated which were collected and washed with acetone. The purple precipitate was dispersed in 100 ml of methanol and dry hydrogen chloride was passed into the mixture; while the mixture was hot, the mixture was filtered off and the filtrate was cooled to 0° overnight. Red-purple crystals were filtered off and washed with acetone and ethanol.

Δ-*cis*-β-Dinitro(D-5-methyltriethylenetetramine)cobalt(III) Chloride Hemihydrate (Δ-*cis*-β-[Co(D-5-metrien)(NO$_2$)$_2$]Cl·0.5-H$_2$O).—To a mixture of 4.6 g (15.0 × 10^{-3} mol) of D-5-methyltriethylenetetramine tetrahydrochloride and 3.56 g (15.0 × 10^{-3} mol) of cobalt chloride hexahydrate in 180 ml of water was added 1.89 g (45.0 × 10^{-3} mol) of lithium hydroxide monohydrate and 2.07 g (30 × 10^{-3} mol) of sodium nitrite. The brown solution was aerated for 12 hr with carbon dioxide free air. The dark red solution was evaporated on a steam bath until the product separated. This mixture was cooled to room temperature and the crystals were filtered off and washed with acetone, ethanol, and ether. The same procedure was repeated twice on the filtrate, and three fractions were obtained (total yield 86.7%). These were recrystallized from water–ethanol. The three fractions described above have the same ORD, and the final filtrate also has the same ORD. This verifies that no other isomer is yielded in this preparation.

The other dinitro complexes were prepared by procedures similar to that described above, and their elemental analyses are shown in Table I.

cis-β-Oxalato-*dl*-5,6-dimethyltriethylenetetraminecobalt(III) Chloride Hemihydrate (*cis*-β-[Co(*dl*-5,6-dimetrien)(ox)]Cl·0.5-H$_2$O).—A mixture of a finely powdered sample of *cis*-β-[Co(*dl*-

TABLE I

ANALYTICAL DATA

Complex	—%C—		—%H—		—%N—	
	Calcd	Found	Calcd	Found	Calcd	Found
Δ-*cis*-β-[Co(D-5-metrien)Cl₂]Cl·0.5H₂O	25.13	25.74	6.33	6.20	16.75	16.68
cis-β-[Co(*dl*-5,6-dimetrien)Cl₂]Cl·0.5H₂O	27.58	28.04	6.65	6.64	16.16	16.17
Δ-*cis*-β-[Co(L-5,6-dimetrien)Cl₂]Cl·H₂O	27.17	26.71	6.84	6.31	15.84	15.76
cis-β-[Co(*dl*-ECE)Cl₂]Cl·0.5H₂O	32.06	32.27	6.73	6.83	14.96	14.83
Δ-*cis*-β-[Co(D-ECE)Cl₂]Cl·0.5H₂O	32.06	32.02	6.73	6.67	14.96	14.42
Δ-*cis*-β-[Co(D-5-metrien)(NO₂)₂]Cl·0.5H₂O	23.64	24.30	5.95	5.76	23.63	23.41
cis-β-[Co(*dl*-5,6-dimetrien)(NO₂)₂]Cl·H₂O	25.37	24.93	6.39	6.41	22.19	22.03
Δ-*cis*-β-[Co(L-5,6-dimetrien)(NO₂)₂]Cl	26.64	27.15	6.15	6.18	23.30	23.28
cis-β-[Co(*dl*-ECE)(NO₂)₂]Cl·H₂O	30.32	29.68	6.42	6.48	21.33	20.76

5,6-dimetrien)Cl₂]Cl·0.5H₂O (0.5 g), K₂C₂O₄·H₂O (265 mg), and 5 ml of water was heated on a water bath to a near dryness. The mixture was dissolved in enough water to give 5 ml of solution and cooled to 0° overnight. The separated red crystals were filtered off, washed with ethanol and ether, and dried under vacuum; yield 350 mg. *Anal.* Calcd for CoC₁₀H₂₂N₄O₄Cl· 0.5H₂O: C, 32.84; H, 6.34; N, 15.32. Found: C, 32.98; H, 6.45; N, 15.42.

Results and Discussion

Visible absorption spectra and rotatory dispersion curves for the dichlorocobalt(III) complexes with quadridentate ligands synthesized in the present study were measured in concentrated hydrochloric acid solutions. (These complexes hydrolyze rapidly to the chloroaquo form in 0.01 *N* perchloric acid solutions.) The visible absorption spectra for the racemic complexes, shown in Figure 3, were found to resemble that for the *cis*-β-Co(trien)Cl₂⁺ ion. The absorption spectra for the complexes with optically active ligands were identical with those for complexes with corresponding inactive ligands. The first absorption bands observed in the region of 530–540 mμ indicate no sign of the existence of any shoulder at the longer wavelength side, which was noticed to be a characteristic of *cis*-α-Co(trien)Cl₂⁺ as compared with the *cis*-β isomer.[8] It is possible on the basis of these results to assign the dichloro complexes of substituted triens to be *cis*-β isomers.

Buckingham and Jones[18] suggested that three infrared absorption bands are useful to distinguish geometrical isomers of some diacido trien complexes, *i.e.*, N–H stretch region, –NH₂ deformation bands, and absorptions in the 1190–990-cm⁻¹ region. It was suggested that *cis*-β isomers, because of their lower symmetry, have more complicated bands than corresponding *cis*-α isomers. For *cis*-β isomers, N–H stretching bands usually consist of four or five peaks and the lowest frequency bands are found near 3000 cm⁻¹, and –NH₂ deformation bands are split into two bands. In the 1190–990-cm⁻¹ region, *cis*-β isomers have four or five bands of medium intensity, whereas *cis*-α isomers have only two intense bands. The N–H stretching bands for the present complexes were fairly complicated and the lowest frequency bands were
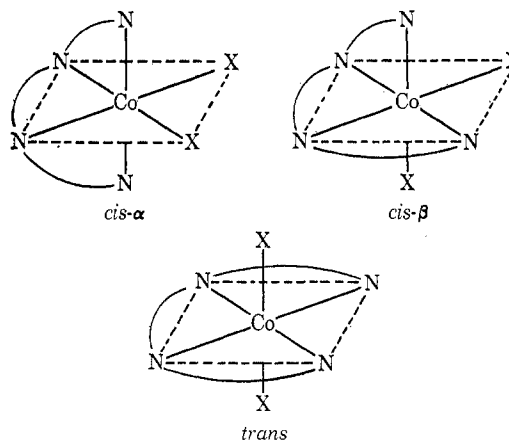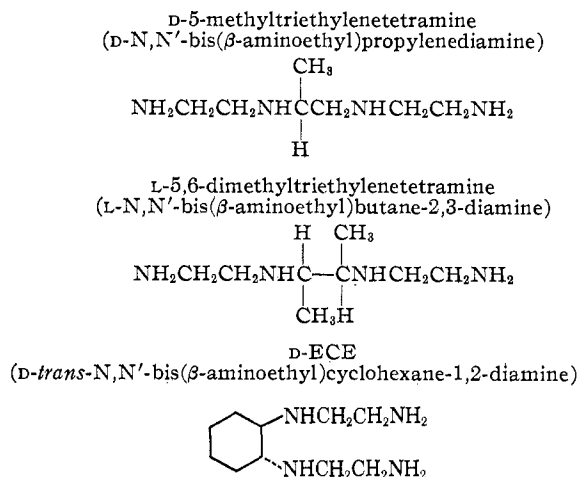
(18) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

Figure 1.—Geometrical isomers of Co(trien)X₂⁺.

D-5-methyltriethylenetetramine
(D-N,N′-bis(β-aminoethyl)propylenediamine)

L-5,6-dimethyltriethylenetetramine
(L-N,N′-bis(β-aminoethyl)butane-2,3-diamine)

D-ECE
(D-*trans*-N,N′-bis(β-aminoethyl)cyclohexane-1,2-diamine)

Figure 2.—The synthesized ligands.

observed near 3000 cm⁻¹. The N–D stretching bands for the deuterated complexes were very similar to one another, and the lowest frequency bands were found at about 2240 cm⁻¹. For the deuterated trien complexes, the corresponding bands are observed at 2308 cm⁻¹ for the *cis*-α isomer and at 2250 cm⁻¹ for the *cis*-β isomer.[18] The characteristics observed for the N–H stretching bands for the complexes with substituted triens are consistent with the supposition that these complexes belong to the *cis*-β isomer.
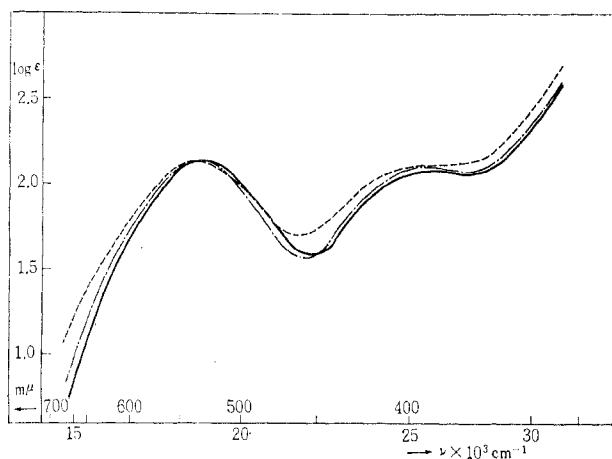
In the –NH₂ deformation region (1500–1600 cm⁻¹),

Figure 3.—Visible absorption spectra for cis-β-Co(dl-5,6-dimetrien)Cl₂⁺ (———), cis-β-Co(dl-ECE)Cl₂⁺ (- - -), and cis-β-Co(trien)Cl₂⁺ (-·-·-), in concentrated hydrochloric acid.
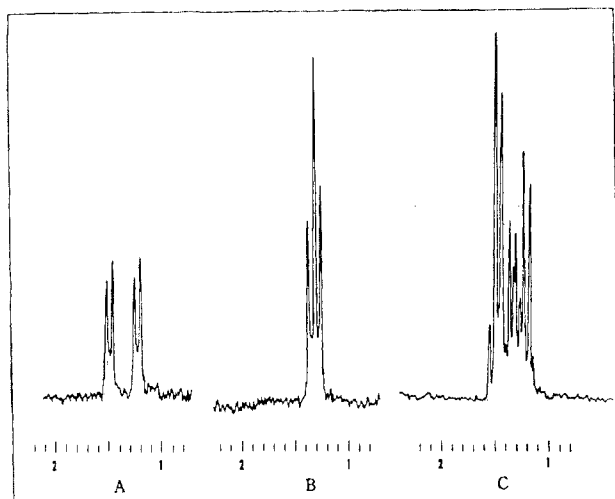

Figure 5.—Optical rotatory dispersion curves of Λ-cis-β-Co(L-5,6-dimetrien)Cl₂⁺ (———), Δ-cis-β-Co(D-5-metrien)Cl₂⁺ (-·-·-), and Δ-cis-β-[Co(D-ECE)Cl₂⁺ (- - -) in hydrochloric acid.

Figure 4.—Pmr spectra (100 Mc) for cis-β-[Co(dl-5,6-dimetrien)(NO₂)₂]Cl·H₂O (A), cis-β-[Co(dl-5,6-dimetrien)(ox)]-Cl·0.5H₂O (B), and cis-β-[Co(dl-5,6-dimetrien)Cl₂]Cl·0.5H₂O (C) in D₂O.

dichlorocobalt(III) complexes of D-5-metrien and dl-5,6-dimetrien showed two bands very similar to those of cis-β-[Co(trien)Cl₂]X, while those of L-5,6-dimetrien and dl- and D-ECE had one band of medium intensity. Dinitro complexes of L-5,6-dimetrien, however, had two bands and the dl-5,6-dimetrien complex showed a single band in this region. These differences may be ascribed chiefly to differences in the hydrogen bonds among the –NH₂ groups, crystalline water, and chloride ion, since the infrared spectra were measured in the solid state (KBr-disk method).

The bands in the 1190–990-cm⁻¹ region were very complicated and were found to vary depending on the substituted groups. It was found that each absorption band in the infrared spectra for both dichloro and dinitro complexes with racemic ligands corresponds to that for the respective optically active ligands. Furthermore, it was discovered that each band in the
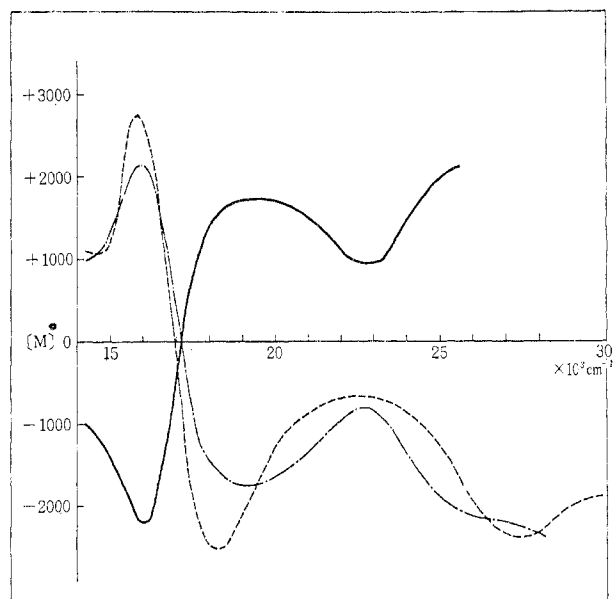
infrared spectrum for the dichloro complex was observed in the corresponding dinitro complex, though a slight shift was found between them, and additional bands for the nitro group were found in the latter complexes. On the basis of infrared spectra, it may be considered that both the racemic and the optically active ligands with the same substituted groups have the same mode of wrapping about the cobalt(III) ion in the dichloro and dinitro complexes, namely, the cis-β form for all of the ligands.

The pmr spectrum for dl-5,6-dimethyltriethylenetetramine tetrahydrochloride showed a doublet at 1.45 ppm (from sodium 2,2-dimethyl-2-silapentanesulfonate as the standard) in D₂O solution, which is due to the methyl protons. An examination of molecular models indicates that methyl groups of dl-5,6-dimetrien complexes can both be located equatorial in relation to the chelate ring, so these methyl groups for the cis-α configuration are in identical chemical environments. Thus, pmr spectra of the methyl groups are expected to show a single doublet for the cis-α isomer and two doublets for the cis-β isomer, theoretically. The corresponding signals for the dichloro-, dinitro-, and oxalato-dl-5,6-dimethyltriethylenetetraminecobalt(III) ion are shown in Figure 4. Two doublets of equal intensity were observed for dinitro and oxalato complexes: 1.22 and 1.49 ppm for the former and 1.33 and 1.39 ppm for the latter, respectively. This confirmed that the dinitro-dl-5,6-dimethyltriethylenetetraminecobalt(III) complex takes the cis-β configuration. In the pmr spectrum for the dichloro complex, however, no less than seven doublet peaks were observed. This indicates that this complex is hydrolyzed to give an equilibrium mixture of one dichloro, two chloroaquo, and one diaquo species in D₂O solution and is also considered to be the cis-β isomer.
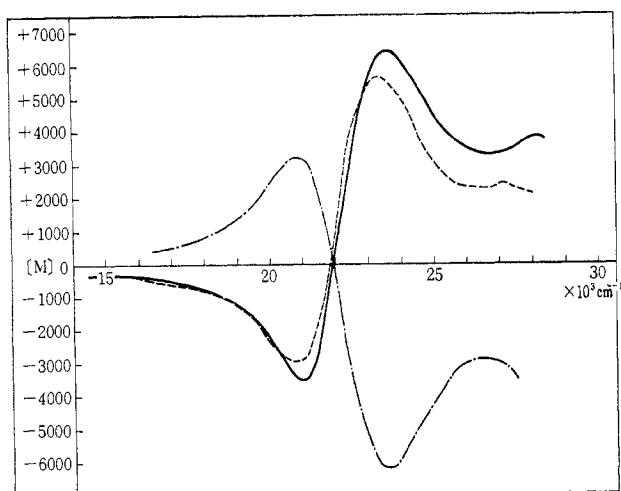
Figure 6.—Optically rotatory dispersion curves of Λ-*cis*-β-Co-(L-5,6-dimetrien)(NO₂)₂⁺ (———), Δ-*cis*-β-Co(D-5-metrien)(NO₂)₂⁺ (–·–·–), and Λ-*cis*-β-Co(L-ECE)(NO₂)₂⁺ (– – – –) in water (L-ECE was prepared from *d*-chxn; [α]D +13.8°).
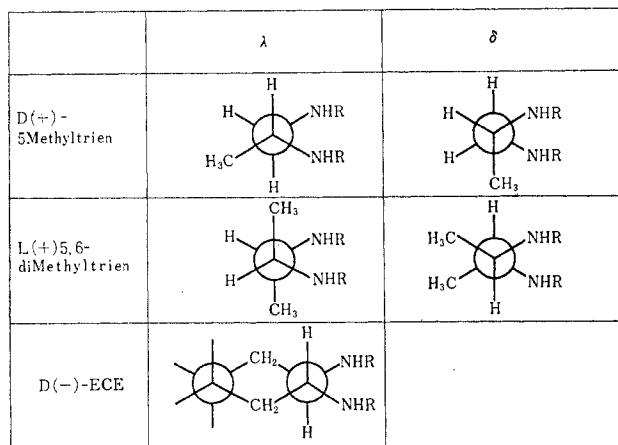

Figure 7.—Two diastereomeric *gauche* forms having central ethylenediamine bridges of the synthesized optically active ligands, represented by Newman projection formula.

The results of the visible absorption, infrared, and pmr spectra indicate consistently that dichloro- and dinitrocobalt(III) complexes with C-substituted triens at the central ethylenediamine bridge adopt the *cis*-β configuration without exception.

The ORD curves for the complexes with optically active ligands also indicate that these complexes are of the *cis*-β form. The ORD curves for the dichloro complexes with active ligands in concentrated hydrochloric acid are shown in Figure 5. A rather small Cotton effect noticed in the ORD curves for the *cis*-α isomer but not for the *cis*-β isomer of the Co(trien)Cl₂⁺ ion[8] was not observed for the present complexes (Figure 5) indicating that these complexes are of *cis*-β form. Considering the signs of the Cotton effect of the first absorption band,[8] the absolute configurations are determined as Δ, Λ, and Δ[19] for the complexes with

(19) Since the complexes discussed here have C₂ or pseudo-C₂ symmetry as do many cobalt(III) complexes, the absolute configurations are related to the configuration of Co(en)₃³⁺ as viewed down a C₂ axis in the manner described by B. E. Douglas, *et al.*, *ibid.*, **6**, 700 (1967).

D-5-metrien, L-5,6-dimetrien, and D-ECE, respectively.

The ORD curves for dinitro complexes are shown in Figure 6. The absolute configuration of these complexes with D-5-metrien, L-5,6-dimetrien, and L-ECE were assigned as Δ, Λ, and Λ, respectively, on the basis of the sign of the Cotton effect of the first absorption band. No other isomers were found in fractional recrystallization of the reaction products of dichloro and dinitro complexes with D-5-metrien.

It seems that the absolute configurations of these complexes are determined by the absolute configurations of the used ligands, which are denoted D, L, and D according to the starting diamines—(−)-propylenediamine,[20] (+)-butane-2,3-diamine,[16] and (−)-cyclohexane-1,2-diamine,[21] respectively. The complexes which contain ligands of the D series adopt the Δ-*cis*-β configuration stereospecifically and *vice versa*. The structures of central ethylenediamine bridges of these ligands in which two amine groups are placed *gauche* are shown in Figure 7, and the optical antipodes of the *gauche* conformations of the diamines are denoted δ or λ.[22] The substituted alkyl groups should prefer the equatorial position to the five-membered chelate ring, since the conformation with the equatorial methyl group is considered to be more stable than that with the axial methyl group in the propylenediamine chelate. Thus, the preferred conformations of the central chelate rings should be λ, δ, and λ for D-5-metrien, L-5,6-dimetrien, and D-ECE, respectively. Therefore, the absolute configurations of the cobalt(III) complexes with trien analogs are determined by the conformations of the central diamine bridges. When the central ethylenediamine bridge is settled to adopt the λ conformation by the asymmetrically substituted alkyl groups (D series), the substituted trien coordinates stereospecifically to the cobalt(III) ion to give the Δ-*cis*-β isomer.

In the puckered structure of the ethylenediamine chelate the diastereomeric relationships of the protons on the N atoms were acknowledged, though their distinction is not so marked as on the C atoms. The β-aminoethyl groups of trien extending from the N atoms of the central chelate ring may be in somewhat different circumstances according to their axial or equatorial nature. In this paper two bonding directions of the N atoms of the ethylenediamine chelate are distinguished as follows. One denoted A corresponds to the pseudo-axial nature and the other, B, corresponds to the pseudo-equatorial nature, which is shown in Figure 8 with some exaggeration. An examination of the Dreiding stereomodels shows that the terminal N atoms of the β-aminoethyl group in the A direction from the N(1) atom can coordinate to the coordination site named 4 in Figure 8, but for the B direction the β-aminoethyl group can coordinate to either the 1 or

(20) H. Reihlen, E. Weinbrenner, and G. V. Hessling, *Ann.*, **494**, 143 (1932).

(21) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(22) According to an IUPAC recommendation pending, the *k* conformation will be designated λ.

the 3 position. In the B direction, these two bonding types are distinguished as B for the latter and as B' for the former. The same extending mode is also possible for N(2) atom.

When the central diamine bridge is fixed in the λ conformation, five isomers arising from the combination of the bonding modes of the β-aminoethyl groups mentioned above may be possible as shown in Figure 9. In these isomers the Λ-*cis*-α form of the B'B' type is a conformational isomer of the Λ-*cis*-α isomer of the AA type (the enantiomorph for Δ-*cis*-α (AA) in Figure 9), since these two isomers are found to interconvert to each other without any bond breaking. For the Δ-*cis*-β isomer two configurational isomers were detected by Sargeson, *et al.*, during the course of a study of the rearrangement of the active *trans*-Co(trien)Cl₂⁺ ion in the presence of the Hg²⁺ ion.[9] The occurrence of these isomers was ascribed to the orientation of the planar secondary amine protons. However, this isomerism is explained in another way as consideration of the conformations of the chelates of trien. The SS-Δ-*cis*-β isomer of the trien complex corresponds to the Δ-*cis*-β isomer of the BB' type and the SR-Δ-*cis*-β isomer of the trien complex corresponds to the Δ-*cis*-β isomer of the AB type (the enantiomorph for Λ-*cis*-β (AB) in Figure 9). It results in the fact that the conformation of the central diamine linkage in the SS-Δ-*cis*-β isomer is λ, whereas that in SR-Δ-*cis*-β is of the δ conformation. Therefore, only SS-Δ-*cis*-β and RS-Λ-*cis*-β forms are possible when the central diamine bridge is fixed in the λ conformation.

Therefore, the sign of the Cotton effect of the first absorption band should indicate the discrimination between SS and SR types of *cis*-β isomers of the complexes with C-substituted triens at the central ethylenediamine bridge of which the conformation is compelled to take the δ or λ form. As mentioned before, the complexes of substituted triens which prefer the λ conformation in central ethylenediamine linkages were found to be of the Δ-*cis*-β form. This means the complexes obtained in the present study belong to the SS type of the *cis*-β isomer.

The molecular model for the Δ-*cis*-β-D-5,6-dimethyl-triethylenetetraminecobalt(III) complex deduced from above consideration is shown in Figure 10, in which both methyl groups are arranged to be distant from the terminal ethylenediamine linkages. For the SS-Δ-*cis*-β (BB' type) form of the D-5-metrien complex two more isomers arising from the difference of the position of the substituted methyl group are possible as shown in Figure 11. Although it is not possible so far to decide which of these two isomers is the real product, some evidence supports the existence of only one isolated species for this complex. The pmr spectrum for the Δ-*cis*-β-Co(D-5-metrien)(NO₂)₂⁺ ion showed a single doublet in the methyl region at 1.26 ppm. In the infrared spectra of dichloro and dinitro complexes of 5-metrien every absorption band is markedly sharp. If two isomeric products coexist, some splitting or broadening of the bands should be
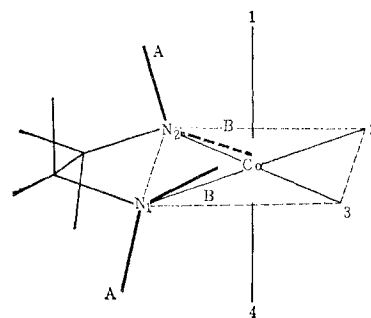

Figure 8.—Two bonding directions of the nitrogen atoms of the coordinated diamine having a λ conformation.
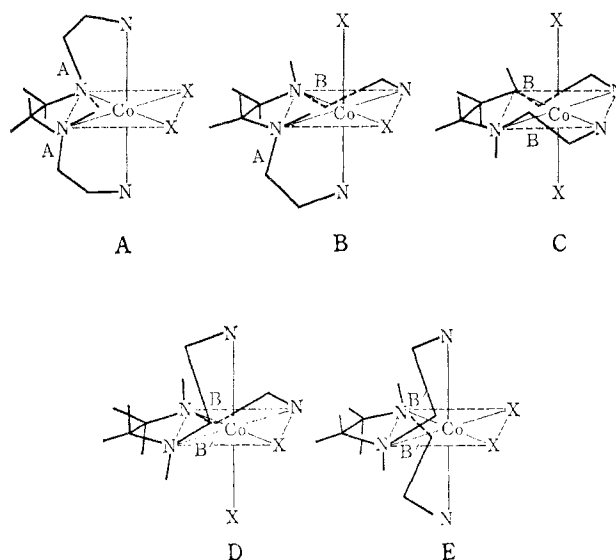

A B C

D E

Figure 9.—Five isomers arising from the combination of the extending modes of β-aminoethyl groups (fixing the conformation of the central linkage as λ): (A) Δ-*cis*-α (AA); (B) Λ-*cis*-β (AB); (C) *trans* (BB); (D) Δ-*cis*-β (BB'); (E) Λ-*cis*-α (B'B').
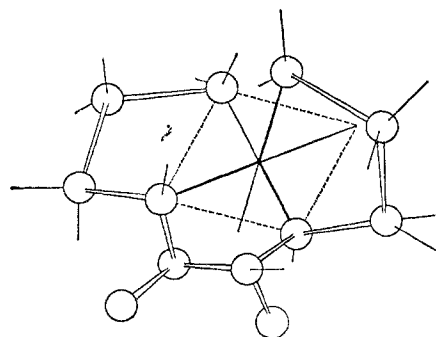

Figure 10.—Molecular model for Δ-*cis*-β-Co(D-5,6-dimetrien)X₂ⁿ⁺.

(A) (B)

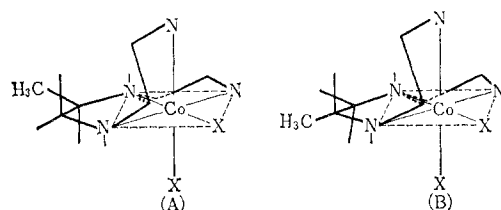Figure 11.—Possible two structures of Δ-*cis*-β-Co(D-5-metrien)-X₂ⁿ⁺ arising from the positions of the substituted methyl group.
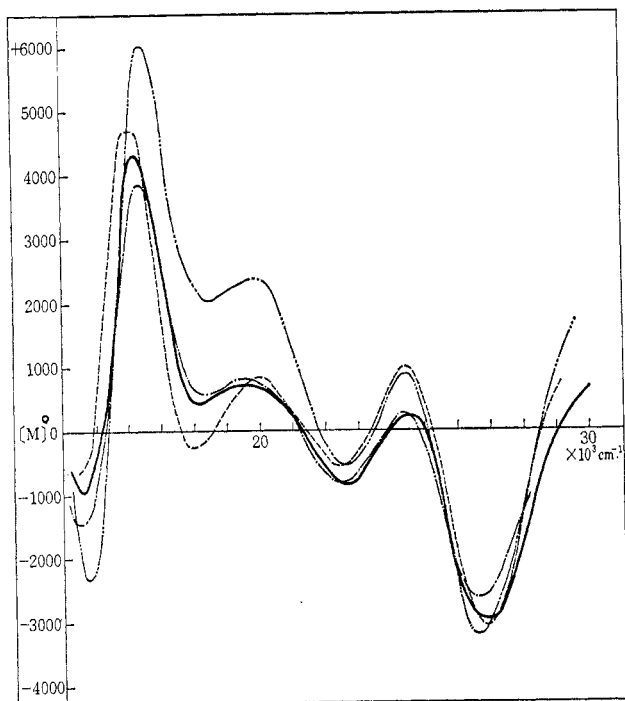
Figure 12.—Optical rotatory dispersion curves for rearranged *trans* isomers in methanol: *trans*-Co(D-5,6-dimetrien)Cl₂⁺ (———); *trans*-Co(D-ECE)Cl₂⁺ (– – –); *trans*-Co(D-5-metrien)Cl₂⁺ (–·–·–); *trans*-Co(L,L-3,8-dimetrien)Cl₂⁺ (–·· –·· –).
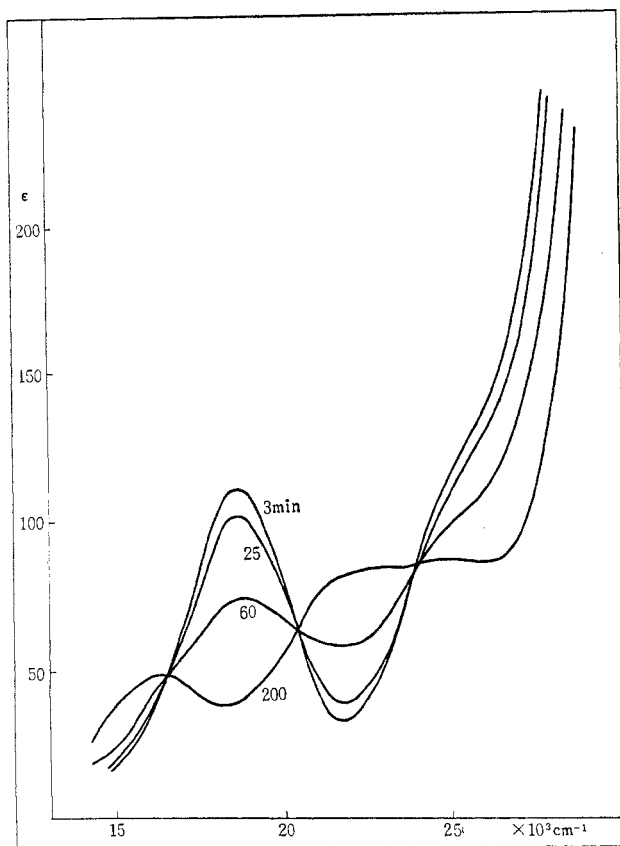

Figure 13.—Spectral change for the rearrangement of Λ-*cis*-β-[Co(L-5,6-dimetrien)Cl₂]Cl·H₂O to *RR*-*trans*-Co(L-5,6-dimetrien)Cl₂⁺ in methanol.

observed. In either case (A) or (B) in Figure 11, the β-aminoethyl group bonded to the N atom adjacent to the carbon atom substituted by the methyl group extends in the B bonding direction. The fact that the *dl*- and L-5,6-dimetrien complexes were obtained in the same structure (*i.e.*, *cis*-β (BB')) as 5-metrien complexes allows the following conclusion. One methyl group substituted for a carbon atom of the central diamine linkage of trien has an important stereochemical influence on the β-aminoethyl group so that the *cis*-β isomers of the *RR* and *SS* forms (*i.e.*, BB' bonding type) are stabilized compared with the *cis*-α isomer or *SR*-*cis*-β isomer (*i.e.*, AB bonding type). The other methyl group in 5,6-dimetrien is found to have no apparent effect at least in determining the topology of the complexes.

Buckingham, Marzilli, and Sargeson[9] have described the stability of two Δ-*cis*-β isomers (*i.e.*, *SS* (BB' type) and *SR* (AB type)) in terms of conformational analysis considering H–H, C–H, N–H, C–C, C–N, and H–Cl nonbonding interactions. There are several significant interactions between C–H and H–H in an *SR*-Δ-*cis*-β (AB type) isomer, and one of the significant interactions has been shown between the equatorial hydrogen at the central diamine linkage and the equatorial hydrogen at the terminal diamine linkage both of which are attached to the carbon atoms adjacent to the secondary nitrogen of A-type bonding. The molecular structure of *cis*-α-[Co(trien)Cl₂]Cl·3H₂O was determined by an X-ray diffraction study.[23a] The structure agreed with one proposed for the *cis*-α isomer, namely, the AA bonding type shown in Figure 9. This mode of coordination derives the same nonbonding interactions between the two hydrogen atoms as those in the *cis*-β isomer (AB type) described above. The distance between these two hydrogens was calculated to be 2.06 Å[23b] from the known geometry using the values of 1.08 Å for the C–H distance and 1.02 Å for the N–H distance and this was the shortest of all of the H–H distances in this ion. Therefore, when an alkyl group is substituted for the carbon atom of the central diamine linkage, this alkyl group prefers to locate the equatorial position and this steric interaction becomes so strong that the complex is compelled to adopt B bonding instead of A bonding. In the case of B or B' bonding, such an interaction should be rather diminished. This effect may be attributed to one of the reasons for the fact that the *cis*-β isomer of the BB' bonding type is preferred to the *cis*-α isomer in the cobalt(III) complexes of triens substituted at the central diamine bridge.

Buckingham, Marzilli, and Sargeson[9] prepared the optically active (+)D-*trans*-Co(trien)Cl₂⁺ ion by heating a suspension of Δ-*cis*-β-[Co(trien)Cl₂]Cl in methanol. The absolute configuration of the active *trans* isomer obtained from the Δ-*cis*-β isomer was assessed as *SS* in relation to the configuration of the secondary nitro-

(23) (a) H. Kimoto, S. Oi, K. Matsumoto, and H. Kuroya, Abstracts, 19th. Annual Meeting of the Chemical Society of Japan, Tokyo, 1966; (b) H. Kuroya and S. Oi, private communication.

gen by comparing the CD curve of this complex with that of the *trans*-Co(L,L-3,8-dimetrien)Cl₂⁺ ion.[24] In the latter complex the conformation of the side diamine linkage is fixed as δ by the substituted methyl groups. The $(+)$D-*trans*-Co(D-5-metrien)Cl₂⁺ complex was prepared from Δ-*cis*-β-[Co(D-5-metrien)Cl₂]Cl by the same procedure as for the trien complex. The ORD curves for this complex shown in Figure 12 resemble that for *trans*-Co(L,L-3,8-dimetrien)Cl₂⁺. It was found that Λ-*cis*-β-Co(L-5,6-dimetrien)Cl₂⁺ and Δ-*cis*-β-Co(D-ECE)Cl₂⁺ (which are soluble enough to measure the visible and ORD curves in methanol) rearrange completely to optically active *trans* isomers in methanol solution. In the course of rearrangement from the *cis*-β to the *trans* isomer, the visible spectrum of the L-5,6-dimetrien complex showed isosbestic points in methanol solution as shown in Figure 13.

The ORD curves for the *trans* isomer are shown in Figure 12. These curves indicate that optically active *trans* isomers in the absolute SS configuration arise for D-5-metrien and D-ECE complexes, and the RR form arises for the L-5,6-dimetrien complex. Thus, it is concluded that the optically active *trans* isomer is obtained by fixing the conformation of the central diamine part; the SS-*trans* isomer is given by the ligands of preferred conformation λ in the central diamine linkage.

As mentioned above, the conformations of the three chelate rings in the SS-*trans* isomer are believed to be δ, λ, and δ. For the other geometrical isomers the conformation of each chelate ring may be determined. The X-ray diffraction studies[23] of the *cis*-α-Co(trien)-Cl₂⁺ ion require the combination of δ, λ, and δ for the Δ-*cis*-α isomer in the solid state. This is supported by the fact that the Δ form was obtained stereospecifically for the *cis*-α-Co(L,L-2,9-dimetrien)Cl₂⁺ ion[11] in which

(24) D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Commun.*, 433 (1967).

the conformations of the side chelates are fixed as δ by the substituted methyl groups. In the case of the SS-Δ-*cis*-β isomer, the conformation of the central chelate ring is λ and that of the side chelate ring coplanar with the central chelate ring is δ. Furthermore, an examination of the Dreiding stereomodel indicates that the other side chelate ring is in the λ conformation. Thus, for the SS-Δ-*cis*-β isomer the combination of the three chelate rings should be denoted as $\delta\lambda\lambda$. The conformation of the central chelate ring of SR-Δ-*cis*-β isomer is δ and that of the side chelate ring coplanar with the central chelate is λ. The conformation of the other side chelate ring is found to be λ, and, consequently, the combination for SR-Δ-*cis*-β isomer may be denoted as $\lambda\delta\lambda$. It is noticed that the conformations of the side chelate rings in SS-Δ-*cis*-β are different, whereas those in SR-Δ-*cis*-β are the same. This suggests that the trien derivative which adopted the same conformation for both of the side chelate rings may coordinate to the cobalt(III) ion to give the RS-*cis*-β form. The Λ-*cis*-β-Co(L,L-2,9-dimetrien)Cl₂⁺ ion synthesized by Asperger and Liu[11] is considered to correspond to this type of isomer. The CD or ORD curve for this complex which is not yet reported should be somewhat different from the corresponding curve for the complexes of the present ligands or unsubstituted trien. Λ-*cis*-β-[Co(L,L-3,8-dimetrien)(NO₂)₂]ClO₄ which shows an ORD curve slightly different from those of the other dinitro complexes was isolated by the present authors and will be reported elsewhere. On the other hand, when the side chelate rings are fixed in different conformations, the SS- and RR-*cis*-β isomers might be formed. *meso*-3,8-dimetrien in which the absolute configuration of the asymmetric carbon atom is reversed was also obtained and the dichlorocobalt(III) complex with this ligand was also of the *cis*-β form. This result will be reported in subsequent papers.