Stereochemical Studies of Metal Chelates. V.[1] Preparation and Circular Dichroism of *trans*-Diacido(2,5,8,11-tetraazadodecane)cobalt(III) Ion and Its Optically Active Derivatives

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The preparation, isolation, and characterization of a series of Co(III) complexes containing the tetramine ligands 2,5,8,11-tetraazadodecane, its optically active methyl derivatives, and 2,5,9,12-tetraazatridecane are reported. All these tetramines yield *trans*-dinitro- and *trans*-dichlorocobalt(III) complexes. The absolute configurations of the optically active *trans* complexes are assigned with the pmr spectra and the known configuration of the ligands.

Introduction

The study of stereochemistry of metal chelates containing multidentate ligands is an attractive problem because of the large number of possible geometrical isomers owing to the wrapping modes of the ligands. The stability of these geometrical isomers is dependent on the structure of the ligand. A large number of publications have described cobalt(III) complexes containing tetradentate ligands, especially tetramines. Sargeson and Searle[2] have reported that *cis* isomers (*cis*-α and *cis*-β) are more stable than the *trans* isomer for dinitrotriethylenetetramine cobalt(III) ion. The present authors found that a different geometrical isomer is obtained preferably from the ligands which have an asymmetric substituent at the carbon atom(s) in the backbone of trien.[3,4] This stereospecificity has been explained in terms of nonbonded atomic interactions.[4]

The straight-chain tetramine 2,5,8,11-tetraazadodecane (1,10-dimethyltriethylenetetramine, 1,10-Me$_2$trien) is a methyl-substituted trien at terminal N atoms. This substitution of methyl groups may considerably affect the stability of the possible geometrical isomers of the diacidocobalt(III) complexes.

The (+)-D-*trans*-Co(trien)Cl$_2$+ ion has three circular dichroism bands in the region of the first absorption band.[5] The absolute configuration of this ion was deduced from the absolute configurations of the secondary amine of the starting material, Λ-*cis*-β-Co(trien)-Cl$_2$+, and has been confirmed by comparing the CD curve of the (+)-D-*trans*-Co(LL-3,8-Me$_2$trien)Cl$_2$+ ion.[3,6] Recently *trans*-Co(N-Meen)$_2$X$_2$+ (X = Cl or NO$_2$) have been resolved and their absolute configurations deduced from the sign of the CD band near 22,000 cm^{-1} with X = Cl.[7] However, this assignment was inconsistent with the result of *trans*-Co(N-Mepn)-

X$_2$+ (X = Cl or NO$_2$; Mepn = CH$_3$NHCHCH$_3$CH$_2$NH$_2$) ions where the absolute configuration of N-methylpropylenediamine was known.[8] The origin of optical activity is not well understood so far, but the result described above indicates that the sign of CD bands is not solely determined by the conformation(s) of the chelate ring for the *trans*-CoN$_4$X$_2$+ ion. This fact stimulates us to investigate the correlation between optical activity and structure of the metal chelate (conformation(s) of chelate ring(s) and asymmetric N center are most desirable at this stage). To clarify this point, some asymmetrically methyl-substituted 1,10-Me$_2$trien ligands of known absolute configuration have been synthesized and the CD curves measured for *trans*-dichloro- and *trans*-dinitrocobalt(III) complexes containing these ligands.

A homolog of trien, 1,4,8,11-tetraazaundecane (2,3,2-tet), has been reported to yield the *trans*-dichloro isomer instead of the *cis* isomers.[9,10] The difference in coordination behavior between trien and 2,3,2-tet was explained in terms of two secondary amine configurations based on the different number of atoms in the chelate ring.[11] Similar properties will be also shown for *trans*-dinitro- and *trans*-dichlorocobalt(III) complexes containing 2,5,9,12-tetraazatridecane (1,11-Me$_2$-2,3,2-tet).

Experimental Section

Materials.—Commercial grade *dl*-propylenediamine was resolved by the method of Dwyer, *et al.*,[12] [α]D −31° (in benzene). Carbobenzoxyalanine azide was prepared by the method of Erlanger and Brand.[13]

Instrumentation.—Visible and ultraviolet absorption spectra were measured with a Shimadzu QV-50 spectrophotometer. Circular dichroism curves were measured with a Shimadzu QV-50 spectrophotometer with its CD attachment or the JASCO Model ORD/UV-5 recording spectropolarimeter. Infrared spectra were measured with the JASCO Model DS-301 infrared recording spectrophotometer using the KBr-disk method. Proton magnetic resonance spectra were measured using the Japan Electronic

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Optics Laboratory Model C-60H 60-Mcps nmr spectrometer with NaOD– or D_2SO_4–deuterium oxide solution and sodium trimethylsilylpropanesulfonate as the internal standard reference. For *trans*-[Co(1,3,8,10-Me₄trien)(NO₂)₂]Cl and *trans*-[Co(1,2,9,-10-Me₄trien)(NO₂)₂]Cl, analytically pure samples of the perchlorate salts were converted to chloride salts by shaking an aqueous suspension with an equimolar amount of tetraphenylarsonium chloride. The solutions were then filtered and evaporated to dryness. For *trans*-[Co(1,10-Me₂trien)(NO₂)₂]ClO₄ and *trans*-[Co(D-1,5,10-Me₃trien)(NO₂)₂]ClO₄, analytically pure samples of the salts were converted to chloride by shaking a deuterium oxide suspension with an equimolar amount of tetraphenylarsonium chloride. The solutions were filtered and measured immediately.

Preparation of Tetramines.—The ligands, tetramines, were synthesized according to one of the following procedures
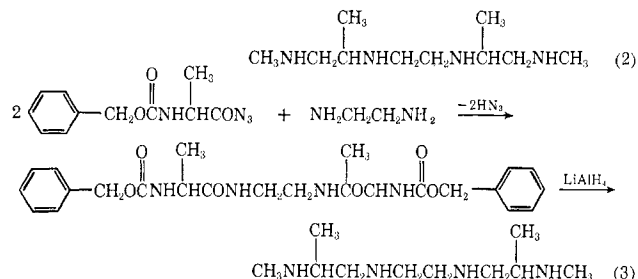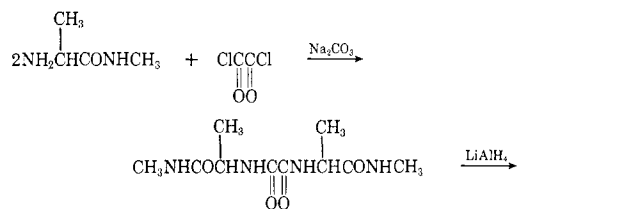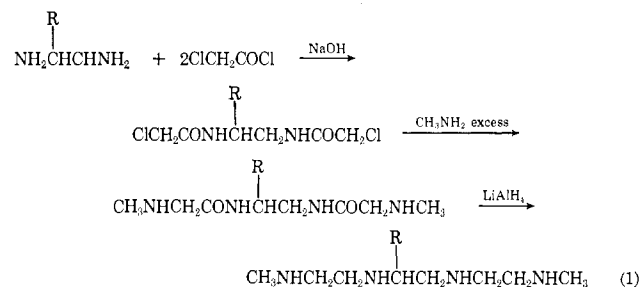
N,N'-Bis(chloroacetyl)ethylenediamine.—A solution of chloroacetyl chloride (32 g, 0.28 mol) in 50 ml of benzene was added dropwise to a solution of ethylenediamine (8.1 g, 0.135 mol) and 120 ml of 5 *N* sodium hydroxide solution in an ice–salt bath with vigorous stirring with a blender. The separated white precipitate was filtered and washed several times with water. This was recrystallized from ethanol; yield 25–26 g (85%); mp 175° (lit.[14] mp 175°).

N,N'-Bis(N-methylglycyl)ethylenediamine Dihydrochloride.—A dried and pulverized sample of N,N'-bis(chloroacetyl)ethylenediamine (19 g, 0.82 mol) was added to a mixture of methanol (200 ml) and 40% monomethylamine aqueous solution (400 ml). The reaction mixture was allowed to stand for 1 week. Then the mixture was concentrated to dryness with a rotatory evaporator under reduced pressure. This was crystallized from a small amount of water and ethanol; yield 21 g (89%).

2,5,8,11-Tetraazadodecane Tetrahydrochloride (1,10-Dimethyltriethylenetetramine Tetrahydrochloride; 1,10-Me₂trien· 4HCl).—Into a 500-ml four-necked round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser with a soda lime tube, 300 ml of anhydrous tetrahydrofuran was placed, and 17 g (0.45 mol) of lithium aluminum hydride was added with stirring. Then dried and pul-

(14) T. L. Cottrell and J. E. Gill, *J. Chem. Soc.*, 129 (1947).

verized bis(N-methylglycyl)ethylenediamine (26 g, 0.105 mol) was added with vigorous stirring in an ice–salt bath. After stirring at room temperature for 30 min, the reaction mixture was refluxed and stirred for 24 hr. The reaction mixture was cooled and 33.7 g (1.87 mol) of water was added dropwise with vigorous stirring in an ice–bath. The separated precipitate was filtered off and the filtered cake was extracted twice with boiling tetrahydrofuran. The combined tetrahydrofuran was concentrated under reduced pressure. Concentrated hydrochloric acid was added to a mixture of the oily residue and the product was crystallized by adding ethanol; yield 17.2 g (34%). *Anal.* Calcd for $C_8H_{22}N_4·4HCl$: C, 30.01; H, 8.19; N, 17.50. Found: C, 30.01; H, 7.94; N, 17.16.

D-N,N'-Bis(N-methylglycyl)propylenediamine Dihydrochloride. —Dried and pulverized D-bis(chloroacetyl)propylenediamine[4] was treated with aqueous methylamine solution as for N,N'-bis(N-methylglycyl)ethylenediamine. This was used for the next synthesis without recrystallization.

D-6-Methyl-2,5,8,11-tetraazadodecane Tetrahydrochloride (D-1,5,10-Trimethyltriethylenetetramine Tetrahydrochloride, D-1,5,-10-Me₃trien·4HCl).—This was prepared by the same method as that used for 1,10-Me₂trien·4HCl. However when concentrated hydrochloric acid was added to the oily residue diluted with ethanol, the mixture became very dark red. The separated crystals were filtered and washed with ethanol thoroughly and recrystallized with water–ethanol several times to remove the color; $[\alpha]^{20}$D −0.6° (*c* 0.5 g/10 ml of water). *Anal.* Calcd for $C_9H_{24}N_4·4HCl$: C, 32.35; H, 8.44; N, 16.77. Found: C, 31.75; H, 8.66; N, 16.81.

Bis(L-N-methylalanyl)oxamide (4(R),9(R)-dimethyl-2,5,8,11-tetraaza-3,6,7,10-tetraoxododecane).—A solution of oxalyl chloride (10.0 g, 0.079 mol) and 70 ml of benzene was added dropwise to a solution of L-alanine methylamide (24 g, 0.24 mol) and Na_2CO_3 (10 g) in 100 ml of water with vigorous stirring with a blender in an ice–salt bath. The separated precipitate was filtered and washed with water, ethanol, and ether successively. This was recrystallized from ethanol; yield 13.8 g (70%).

LL-4,9-Dimethyl-2,5,8,11-tetraazadodecane (LL-1,3,8,10-Tetramethyltriethylenetetramine, LL-1,3,8,10-Me₄trien).—The above described tetramide (13.8 g) was reduced with 12.2 g of lithium aluminum hydride in 300 ml of tetrahydrofuran by a similar method as that used for 1,10-Me₂trien·4HCl. The oily layer was distilled under reduced pressure in a nitrogen atmosphere (3 mm, 98–109°); yield 5.0 g; $[\alpha]^{20}$D +13° (*c* 0.35 g/10 ml of water). *Anal.* Calcd for $C_{10}H_{26}N_4·4HCl·H_2O$: C, 32.80; H, 8.81. Found: C, 32.20; H, 8.86.

Bis(carbobenzoxy-L-alanyl)ethylenediamine.—The condensation of ethylenediamine (1.8 g, 0.03 mol) with the azide prepared from 17.8 g (0.075 mol) of carbobenzoxy-L-alanine hydrazide was carried out in 400 ml of ether with a magnetic stirrer for 24 hr in an ice bath. The resulting white precipitate of N,N'-bis(carbobenzoyl-L-alanyl)ethylenediamine was filtered and washed with ether. This was recrystallized from ethanol; yield 6.0 g (42%); mp 194–195° (cor); $[\alpha]^{25}_{436}$ −22.0° (*c* 1.09 g/100 ml of acetic acid). *Anal.* Calcd for $C_{24}H_{30}N_4O_6$: C, 61.26; N, 11.91. Found: C, 61.02; N, 11.75.

LL-3,10-Dimethyl-2,5,8,11-tetraazadodecane Tetrahydrochloride (LL-1,2,9,10-Tetramethyltriethylenetetramine Tetrahydrochloride, LL-1,2,9,10-Me₄trien·4HCl).—A dried and pulverized sample (9.4 g, 0.02 mol) of N,N'-bis(carbobenzoyl-L-alanyl)-ethylenediamine was reduced by 12.9 g (0.34 mol) of lithium aluminum hydride in 250 ml of tetrahydrofuran following the same procedure used for 1,10-Me₂trien·4HCl; $[\alpha]^{25}_{436}$ +3.7° (*c* 34.3 mg/10 ml of water). *Anal.* Calcd for $C_{10}H_{30}N_4Cl_4$: C, 34.50; H, 8.68; N, 16.09. Found: C, 34.19; H, 8.60; N, 15.47.

2,5,9,12-Tetraazatridecane Tetrahydrochloride (1,11-Me₂-2,3,-2-tet·4HCl).—This was prepared by the same procedure as 1,10-Me₂trien·4HCl with trimethylenediamine as the starting material instead of ethylenediamine. For N,N'-bis(chloroacetyl)trimethylenediamine the yield was 60%. *Anal.* Calcd for $C_7H_{12}N_2O_2$: C, 37.02; H, 5.33; N, 12.34. Found: C, 37.17; H,

TABLE I
ANALYTICAL DATA

|	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
trans-[Co(1,10-Me₂trien)Cl₂]Cl·HCl	25.55	26.03	6.16	5.90	14.89	14.91
trans-[Co(1,10-Me₂trien)(NO₂)₂]ClO₄	22.62	22.62	5.22	5.14	19.79	20.60
cis-[Co(1-Metrien)Cl₂]Cl	25.82	25.61	6.19	6.34	17.21	17.35
cis-[Co(1-Metrien)(NO₂)₂]I	19.19	19.92	4.60	4.84	19.18	19.35
trans-[Co(D-1,5,10-Me₃trien)Cl₂]ClO₄	25.88	25.88	5.79	6.19	13.42	13.70
trans-[Co(D-1,5,10-Me₃trien)(NO₂)₂]ClO₄	24.64	24.45	5.51	5.26	19.16	18.61 / 19.87
trans-[Co(LL-1,3,8,10-Me₄trien)Cl₂]ClO₄	27.83	27.58	6.07	6.21	12.98	12.42
trans-[Co(LL-1,3,8,10-Me₄trien)(NO₂)₂]ClO₄	26.53	26.59	5.79	5.79	18.56	18.35
trans-[Co(LL-1,2,9,10-Me₄trien)Cl₂]Cl·2HCl	27.26	27.07	6.41	6.12	12.72	12.53
trans-[Co(LL-1,2,9,10-Me₄trien)(NO₂)₂]ClO₄	26.53	26.76	5.79	5.83	18.56	19.12
trans-[Co(2,3,2-tet)(NO₂)₂]ClO₄	20.47	20.50	4.91	4.89	20.47	20.36
cis-[Co(2,3,2-tet)(NO₂)₂]I	19.19	19.56	4.60	4.94	19.18	18.71
trans-[Co(1,11-Me₂-2,3,2-tet)Cl₂]ClO₄	25.83	25.69	5.79	5.75	13.42	13.19
trans-[Co(1,11-Me₂-2,3,2-tet)(NO₂)₂]ClO₄	24.64	24.49	5.51	5.53	19.16	18.75
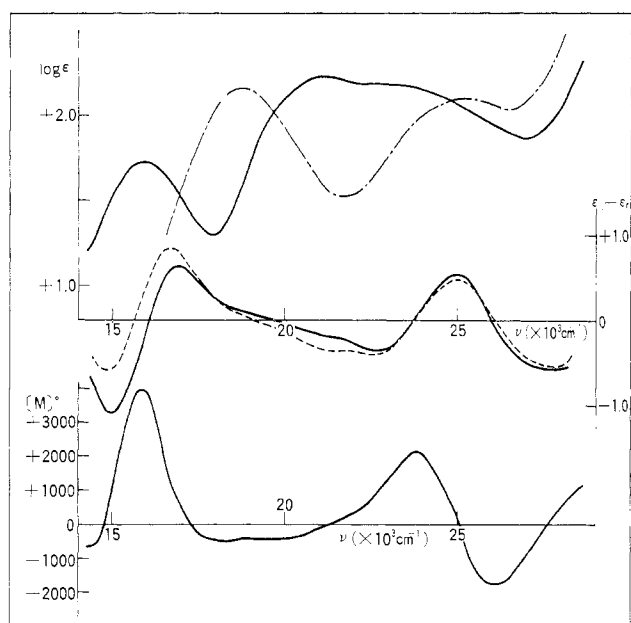
Figure 1.—Visible absorption, circular dichroism, and optical rotatory dispersion spectra for *trans*-Co(LL-1,3,8,10-Me₄trien)-Cl₂⁺ (———), visible absorption spectrum for *cis*-[Co(1-Me(trien)]-Cl₂⁺ (— — —), and circular dichroism spectrum for *trans*-Co(D-1,5,10-Me₃trien)Cl₂⁺ (— - — - —).

5.17; N, 12.27. N,N'-Bis(N-methylglycyl)trimethylenediamine was recrystallized from water–ethanol. For 2,5,9,12-tetra-azatridecane tetrahydrochloride (1,11-Me₂-2,3,2-tet·4HCl) the yield was 30%. *Anal.* Calcd for C₉H₂₄N₄·4HCl: C, 32.35; H, 8.45; N, 16.77; Cl, 42.44. Found: C, 32.29; H, 8.39; N, 16.07; Cl, 42.72.

Preparation of Dichloro- and Dinitrotetraminecobalt(III) Complexes. *trans*-Dichloro(1,10-dimethyltriethylenetetramine)-cobalt(III) Chloride Hydrochloride, *trans*-[Co(1,10-Me₂trien)-Cl₂]Cl·HCl.—A mixture of 1,10-Me₂trien·4HCl (3.20 g, 0.01 mol), CoCl₂·6H₂O (2.38 g), and LiOH·H₂O (1.26 g) in 80 ml of water was aerated with CO₂-free air for 12 hr. The brown solution was evaporated with blowing air at room temperature till crystals began to separate. Concentrated hydrochloric acid (1.5 ml) was added and the mixture was evaporated to near dryness. The separated crystals were filtered and washed with acetone thoroughly. The mixture was extracted with ethanol repeatedly until the extract showed no green color. The green ethanol solution was concentrated to 50 ml and 80 ml of acetone was added and the separated crystals were filtered and washed with acetone and ether; yield 760 mg (20%). For analysis, see Table I.

cis-Dichloro(1-methyltriethylenetetramine)cobalt(III) Chloride, *cis*-[Co(1-Metrien)Cl₂]Cl.—The purple residue after the extract described above contained ligand tetrahydrochloride and was washed with small portions of cold 3 N hydrochloric acid. The purple residue was recrystallized from 3 N hydrochloric acid and acetone. For analysis, see Table I.

trans-Dichloro(tetramine)cobalt(III) Perchlorate (tetramine = 1,10-Me₂trien, LL-1,2,9,10-Me₄trien, D-1,5,10-Me₃trien, 1,11-Me₂-2,3,2-tet).—A mixture of tetramine·4HCl (0.01 mol) and CoCl₂·6H₂O (0.01 mol, 2.38 g) was dissolved in 50 ml of water, and LiOH·H₂O (0.03 mol, 1.2 g) was added to this mixture. The mixture was aerated with CO₂-free air for 12 hr, concentrated hydrochloric acid (2.0 ml) was added, and the mixture was concentrated to the volume of 10 ml. A large excess of lithium perchlorate was added and separated crystals were filtered and washed with acetone and ethanol. Yield: for 1,10-Me₂trien, 30%; for D-1,5,10-Me₃trien, 20%; for 1,11-Me₂-2,3,2-tet, 82%. For analyses, see Table I.

trans-Dichloro(LL-1,3,8,10-tetramethyltriethylenetetramine)-cobalt(III) Perchlorate.—This was prepared by a method similar to that described above. The initial mixtures were prepared with LL-1,3,8,10-Me₄trien (0.01 mol) and 1 N HCl (10 ml) cobalt chloride hexahydrate (0.01 mol); yield 30%. For analysis, see Table I.

trans-Dinitro(tetramine)cobalt(III) Perchlorate (tetramine = 1,10-Me₂trien, LL-1,2,9,10-Me₄trien, 1,11-Me₂-2,3,2-tet).—These compounds were prepared as follows. A mixture of tetramine·4HCl (0.01 mol), CoCl₂·6H₂O (0.01 mol), LiOH·H₂O (0.03 mol), and NaNO₂ (0.02 mol) in 80 ml of water was aerated with CO₂-free air for 8 hr. The mixture was concentrated on a steam bath to 50 ml, a large excess of lithium perchlorate was added, and the mixture was cooled at 0° overnight. The separated crystals were filtered and washed with acetone, ethanol, and ether and air dried. Yield: for 1,10-Me₂trien, 70%; for 1,11-Me₂-2,3,2-tet, 58%. For analyses, see Table I.

trans-Dinitro(D-1,5,10-trimethyltriethylenetetramine)cobalt-(III) Perchlorate.—A mixture of D-1,5,10-trimethyltriethylene-tetramine tetrahydrochloride (3.34 g, 0.01 mol), CoCl₂·6H₂O (2.38 g, 0.01 mol), LiOH·H₂O (1.26 g, 0.03 mol), and NaNO₂ (1.39 g, 0.02 mol) in 100 ml of water was aerated with CO₂-free air for 12 hr. The red solution was concentrated on a steam bath to 10 ml and lithium perchlorate trihydrate (1.06 g, 0.01 mol) was added and allowed to stand overnight. The separated crystals were filtered off and washed with ethanol and acetone; yield 3.23 g (76%). Fractional recrystallizations was carried for this crystal and seven fractions were obtained. These fractions were found to have identical infrared spectra and optical dispersion curves but the final filtrate had a different dispersion which showed a positive Cotton effect in the region of first absorption band.

trans-Dinitro(tetramine)cobalt(III) Perchlorate (tetramine = 1,3,8,10-Me₄trien, 2,3,2-tet).—A mixture of tetramine (0.01

TABLE II

SPECTRAL DATA OF THE DINITRO(TETRAMINE)COBALT(III) IONS[a]

	I		II		III	
	ν_{max}	(log ϵ_{max})	ν_{max}	(log ϵ_{max})	ν_{max}	(log ϵ_{max})
trans-Co(1,10-Me₂trien)(NO₂)₂⁺	22.2	(2.47)	28.8	(3.48)	39.5	(4.40)
trans-Co(D-1,5,10-Me₃trien)(NO₂)₂⁺	22.1	(2.44)	28.6	(3.44)	39.4	(4.40)
trans-Co(LL-1,3,8,10-Me₄trien)(NO₂)₂⁺	22.0	(2.49)	28.7	(3.40)	39.5	(4.39)
trans-Co(LL-1,2,9,10-Me₄trien)(NO₂)₂⁺	22.0	(2.50)	28.5	(3.44)	39.6	(4.40)
trans-Co(LL-3,8-Me₂trien)(NO₂)₂⁺	22.5	(2.46)	29.0	(3.50)	39.8	(4.36)
cis-Co(2,3,2-tet)(NO₂)₂⁺	22.4	(2.41)	30.2	(3.46)	40.0	(4.37)
trans-Co(2,3,2-tet)(NO₂)₂⁺	22.5	(2.39)	28.6	(3.44)	39.2	(4.34)
trans-Co(1,11-Me₂-2,3,2-tet)(NO₂)₂⁺	21.7	(2.22)	28.3	(3.42)	39.3	(4.41)

[a] All energies in 10^3 cm⁻¹, in water.

mol), CoCl₂·6H₂O (0.01 mol), HCl (0.01 mol), and NaNO₂ (0.02 mol) in 80 ml of water was aerated with CO₂-free air for 8 hr. The red solution was concentrated on a steam bath to a volume of 10 ml and a large excess of LiClO₄ was added and the mixture was allowed to stand overnight. The separated crystals were filtered off, washed with acetone and ethanol, and air dried. The yield for 2,3,2-tet was 65%. For analyses, see Table I.

cis-Dinitro(1,4,8,11-tetraazaundecane)cobalt(III) Iodide.—A mixture of *trans*-[Co(2,3,2-tet)Cl₂]Cl (4 g)[9,10] and lithium carbonate (4 g) in 50 ml of water was digested on a steam bath for 30 min and the still undissolved lithium carbonate was filtered off while still hot. To the filtrate 3 *N* HCl (4.5 ml) and sodium nitrite (2 g) were added and the mixture was warmed at 60° for 15 min, sodium iodide (2 g) was added, and the mixture was cooled in a refrigerator overnight. The separated crystals were filtered and washed with aqueous sodium iodide solution, ethanol, and acetone thoroughly; yield 1.75 g.

trans-Dichloro(LL-3,8-dimethyltriethylenetetramine)cobalt(III) Perchlorate.—LL-3,8-Me₂trien·4HCl[3] (3.40 g) and lithium hydroxide monohydrate (1.25 g) were dissolved in 30 ml of water, followed by CoCl₂·6H₂O (2·38 g). The resultant solution was aerated for 12 hr with CO₂-free air and filtered. After 10 ml of concentrated hydrochloric acid was added, the filtrate was evaporated on a steam bath until a small amount of green crystals separated. Perchloric acid (60%, 3 ml) was added to the solution and the mixture was cooled to 5° for 1 hr. The green crystals which separated were collected, washed with methanol and acetone, and dried under vacuum; yield 1.5 g. *Anal.* Calcd for [Co(C₈H₂₂N₄)Cl₂]ClO₄: C, 23.81; H, 5.50; N, 13.88. Found: C, 23.70; H, 5.47; N, 13.35.

trans-Dinitro(LL-3,8-dimethyltriethylenetetramine)cobalt(III) Perchlorate Hemihydrate.—A 0.60-g sample of *trans*-[Co(LL-3,8-Me₂trien)Cl₂]ClO₄ was dissolved in a minimum volume of boiling anhydrous methanol (~150 ml) and NaNO₂ (0.21 g) was added. After the color of the solution changed from green to yellow-brown, the solution was cooled in an ice bath for 1 hr and the crystals that separated were collected, washed with methanol and ether, and dried under vacuum; yield 0.50 g. The product was recrystallized from warm water. *Anal.* Calcd for [Co(C₈H₂₂N₄)(NO₂)₂]ClO₄·0.5H₂O: C, 22.15; H, 5.34; N, 19.38. Found: C, 22.44; H, 5.35; N, 19.27.

Results

The structures of the synthesized ligands were confirmed with the pmr spectra of their tetrahydrochloride salts.

Preparations of the Dichloro- and Dinitrocobalt(III) Ions.—The preparation of the dichloro complexes from the aerial oxidation of a mixture of Co²⁺ (1 mol), L·4HCl (L ligand) (1 mol), and LiOH (3 mol) in water yields the *trans* isomer for 1,10-Me₂trien and its derivatives. A small amount of purple crystals was isolated in the preparation of *trans*-[Co(1,10-Me₂trien)Cl₂]Cl·HCl. These crystals were found to be *cis*-[Co(1-Metrien)Cl₂]Cl from elemental analysis
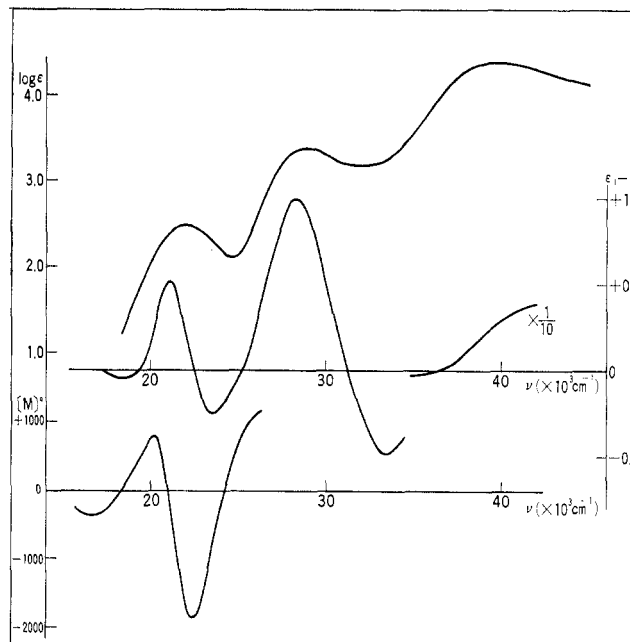

Figure 2.—Absorption, circular dichroism, and optical rotatory dispersion spectra for *trans*-Co(LL-1,3,8,10-Me₄trien)(NO₂)₂⁺.

and the infrared spectrum. This material was derived from a small amount of ammonia in the aqueous monomethylamine solution.

The dinitro complexes from the aerial oxidation of a mixture of Co²⁺ (1 mol), L·HCl (1 mol), LiOH (3 mol), and NaNO₂ (2 mol) in water were isolated as perchlorate salts, [Co(D-1,5,10-Me₃trien)(NO₂)₂]-ClO₄. All seven fractions (total yield 74%) were identical species as determined from ir spectra and ORD measurement; no other isomers could be detected. The *cis*-Co(2,3,2-tet)(NO₂)₂⁺ ion was prepared as the iodide salt, because the *cis*-Co(2,3,2-tet)(NO₂)₂⁺ ion isomerizes to the corresponding *trans* isomer in a weak acid solution, and the solubility of the *trans* isomer is lower for the perchlorate salt than the iodide. The *cis*-Co(1-Metrien)(NO₂)₂⁺ ion was obtained by the treatment of NaNO₂ with aqueous *cis*-[Co(1-Metrien)Cl₂]Cl.

Absorption Spectra, Rotatory Dispersion, and Circular Dichroism Curves.—For *trans*-Co(LL-1,3,8,10-Me₄trien)(NO₂)₂⁺, *trans*-Co(LL-1,3,8,10-Me₄trien)Cl₂⁺, and *cis*-Co(1-Metrien)Cl₂⁺, these are given in Figures 1 and 2. For the complexes isolated in this study, the spectral and CD data were shown in Tables II–IV.

TABLE III

SPECTRAL DATA OF THE DICHLORO(TETRAMINE)COBALT(III) ION[a]

L	Ia ν_{max}	Ia (ϵ_{max})	Ib ν_{max}	Ib (ϵ_{max})	ΔDq(amine)[e]
trans-Co(1,10-Me₂trien)Cl₂⁺	16.0	(45)	21.3	(204)	25.0
trans-Co(D-1,5,10-Me₃trien)Cl₂⁺	16.0	(54)	21.3	(165)	25.0
trans-Co(LL-1,3,8,10-Me₄trien)Cl₂⁺	15.9	(54)	21.1	(166)	24.8
trans-Co(LL-1,2,9,10-Me₄trien)Cl₂⁺	15.9	(50)	21.3	(166)	24.8
trans-Co(trien)Cl₂⁺ [b]	16.3	(36)	22.2		25.6
trans-Co(2,3,2-tet)Cl₂⁺ [c]	16.1	(35)	23.4		25.2
trans-Co(1,11-Me₂-2,3,2-tet)Cl₂⁺	15.8	(36)	21.0		24.6
trans-Co(cyclam)Cl₂⁺ [d]	15.7	(32)	22.7		24.4
cis-Co(1-Metrien)Cl₂⁺			18.7 (125)		

[a] All energies in 10^3 cm⁻¹, in methanol. [b] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963). [c] H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, 5, 2060 (1966). [d] B. Bosnich, C. K. Poon, and M. L. Tobe, *ibid.*, 4, 1102 (1965). [e] Calculated by the procedure of Wentworth and Piper[f] as modified Sadasivan, Kernohan, and Endicott:[g] ΔDq(amine) = $2Dq(I_a) + 2C - \Delta Dq(Cl^-)$, where C is given the value 3800 cm⁻¹ and $\Delta Dq(Cl^-)$ the value 14,600 cm⁻¹; *i.e.*, ΔDq(amine) = $(2Dq(I_a) - 7000)$ cm⁻¹. [f] R. A. D Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 709 (1965). [g] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *ibid.*, 6, 770 (1967).

TABLE IV

CIRCULAR DICHROISM BANDS FOR *trans*-CoLX₂
IN THE REGION OF THE FIRST ABSORPTION BAND

L	X = Cl[a] Absorpn band ν_{max}	X = Cl[a] CD max[c] ($\epsilon_l - \epsilon_r$)[d]	X = NO₂[b] Absorpn band ν_{max}[c]	X = NO₂[b] CD max[c] ($\epsilon_l - \epsilon_r$)[d]
D-1,5,10-Me₃trien	16.0	14.9 (−0.60)	22.1	18.4 (−0.02)
		16.7 (+0.85)		21.2 (+0.42)
	21.2	21.5 (−0.36)		23.8 (−0.28)
		22.5 (−0.40)		
LL-1,2,9,10-Me₄trien	15.9	14.9 (−0.81)		18.6 (−0.04)
		16.8 (+0.61)	22.0	21.1 (+0.47)
	21.6	21.6 (−0.61)		23.3 (−0.40)
LL-1,3,8,10-Me₄trien	15.9	14.9 (−1.10)	22.0	18.5 (−0.05)
		16.9 (+0.64)		21.1 (+0.52)
	21.2	22.7 (−0.36)		23.7 (−0.25)

[a] In methanol. [b] In water. [c] In 10^3 cm⁻¹. [d] CD maxima ($\epsilon_l - \epsilon_r$) in parentheses.

Pmr Spectra.—Proton magnetic spectra for the *trans*-Co(1,10-Me₂trien)(NO₂)₂⁺ and *trans*-Co(LL-1,2,-9,10-Me₄trien)(NO₂)₂⁺ ions in D₃O⁺ and OD⁻ are given in Figure 3. The absorptions are assigned as indicated in Table V. The N protons in these complexes are deuterated in D₂O and OD⁻ solutions causing a sharpening in the CH₂ absorptions and reduction from a doublet to a single sharp resonance for the N–CH₃ protons. If the filtrate was evaporated to dryness, with the conversion from perchlorate salts to chloride salts for *trans*-Co(1,10-Me₂trien)(NO₂)₂⁺ and *trans*-Co(D-1,5,10-Me₃trien)(NO₂)₂⁺, considerable isomerization from *trans* to *cis* structures occurred. The *cis*- and *trans*-Co(1,10-Me₂trien)(NO₂)₂⁺ mixture obtained in D₃O⁺ is shown in Figure 3 also. The pmr spectra for *trans*-Co(1,10-Me₂trien)(NO₂)₂⁺ (Figure 3A) shows two N–H resonances at 6.72 and 7.32 ppm. The two N–H signals diminished at different rates; *i.e.*, the lower field N–H signal diminished completely while the higher field N–H signal and the N-methyl group doublet both still remained after 1 day after dissolving in 0.02 N D₂SO₄ solution. In deuterioxide solution the N-methyl signal is expected to change from a doublet to a singlet due to the H–D exchange at the amine group. Therefore, the N–H signals in higher and lower magnetic fields are assigned, respectively,

to the N–H resonance at the terminal position (1,10) and the middle position (4,7) of the ligand.

Infrared Spectra.—Infrared spectra for *trans*-[Co-(1,10-Me₂trien)(NO₂)₂]ClO₄, *trans*-[Co(2,3,2-tet)(NO₂)-₂]ClO₄, and other *trans*-dinitro complexes prepared in this study all have one strong band at 1300–1360 cm⁻¹, while *cis*-[Co(2,3,2-tet)(NO₂)₂]I has two bands of near intensity at 1310 and 1340 cm⁻¹ in the KBr method. All the *trans*-dinitro (trien substituted at terminal amines) cobalt(III) complexes have one or two strong bands in the N–H stretching region. *cis*-[Co(1-Metrien)Cl₂]Cl and *cis*-[Co(1-Metrien)-(NO₂)₂]I showed sharp medium absorptions in the N–H₂ deformation region, *i.e.*, 1572 cm⁻¹ for the former and 1574 cm⁻¹ for the latter.

Discussion

Spectra.—The absorption spectra, Table II, verify that all of the isolated dinitro complexes except *cis*-Co(2,3,2-tet)(NO₂)₂⁺ and *cis*-Co(1-Metrien)(NO₂)₂⁺ have *trans* configurations. The second band for Co-(N)₄(NO₂)₂⁺ has been useful in distinguishing the *trans* and *cis* configurations. The absorption maxima for the *trans* configuration were found at about 28,800 and 29,500 cm⁻¹ and those for the *cis* configuration were found at 30,800 and 31,100 cm⁻¹ when N₄ was (NH₃)₄ and (en)₂.[15] The *trans* isomer isolated in the present study has absorption maxima at (28.3–28.8) × 10^3 cm⁻¹ and *cis*-Co(2,3,2-tet)(NO₂)₂⁺ at 30.2 × 10^3 cm⁻¹. N-Methylation causes the first band to shift to lower energy—800 and 500 cm⁻¹ for *trans*-Co(2,3,2-tet)(NO₂)₂⁺ and *trans*-Co(LL-3,8-Me₂trien)-(NO₂)₂⁺, respectively. However N-methylation causes the second band to shift slightly, *i.e.*, about 300 cm⁻¹ for both *trans*-Co(2,3,2-tet)(NO₂)₂⁺ and *trans*-Co(LL-3,8-Me₂trien)(NO₂)₂⁺ ions. This slight shift confirms the utility of the second band in assigning the configurations of the Co(N)₄(NO₂)₂⁺ systems.

The *trans*-dichloro complexes (Table III) have the absorption for the I_a band ($A_{1g} \rightarrow E_g$ for D₄ symmetry) at 16,000 and 15,800 cm⁻¹ for *trans*-Co(1,10-Me₂-trien)Cl₂⁺ and *trans*-Co(1,11-Me₂-2,3,2-tet)Cl₂⁺, respectively. The ΔDq(amine) values obtained by the

(15) F. Basolo, *J. Am. Chem. Soc.*, 72, 4393 (1950).

<div align="center">

TABLE V

ASSIGNMENTS OF CHEMICAL SHIFTS (PPM)[a] FOR PMR SPECTRA OF DINITRO COMPLEXES

</div>

	N–H	CH₃‑NCH₂CH₂N or NCHCH₂N	N–CH₃	C–CH₃
trans-Co(1,10-Me₂trien)(NO₂)₂⁺	6.72	2.69–4.00	2.35	
	7.31			
trans-Co(D-1,5,10-Me₃trien)(NO₂)₂⁺	6.60	2.54–3.79	2.31	1.46
	7.27			
trans-Co(LL-1,3,8,10-Me₄trien)(NO₂)₂⁺	6.45	2.47–3.74	2.24	1.34
	6.86			
trans-Co(LL-1,2,9,10-Me₄trien)(NO₂)₂⁺	5.93	2.48–3.53	2.29	1.44
	7.27			

[a] Sodium trimethylsilylpropanesulfonate as standard reference.

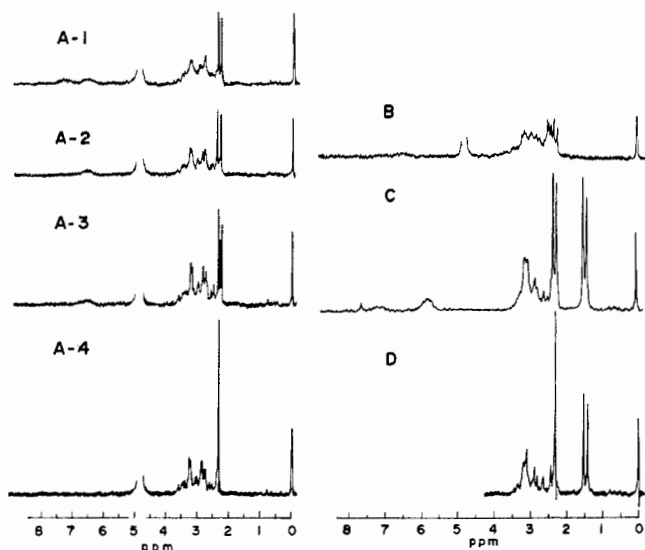Figure 3.—Pmr spectra: A, *trans*-Co(1,10-Me₂trien)(NO₂)₂⁺ (A-1, in 0.02 *N* D₂SO₄ after 2 hr; A-2, in 0.02 *N* D₂SO₄ after 2 days; A-3, in 0.01 *N* NaOD after 2 hr; A-4, in 0.01 *N* NaOD after 2 days); B, *cis–trans* mixtures of Co(1,10-Me₂trien)(NO₂)₂⁺ in 0.02 *N* D₂SO₄ after 2 hr; C, *trans*-Co(LL-1,2,9,10-Me₄trien)-(NO₂)₂⁺ in 0.02 *N* D₂SO₄; D, *trans*-Co(LL-1,2,9,10-Me₄trien)-(NO₂)₂⁺ in 0.01 *N* NaOD.

procedure described by Wentworth and Piper,[16] as modified by Sadasivan, Kernohan, and Endicott,[17] were 25.0 and 24.6 for the above ions, respectively. The ligand field strength of 1,10-dimethyltriethylenetetramine is similar to those of 2,3,2-tet, (en)₂, and (NH₃)₄ and that of 1,11-Me₂-2,3,2-tet is similar to those of cyclic tetramines (tet *a*,[18] tet *b*,[18] and cyclam[19]). The first absorption band of *cis*-[Co(1-Metrien)-Cl₂]Cl shows no sign of the existence of any shoulder at the longer wavelength side, characteristic of *cis*-α-Co(trien)Cl₂⁺ as compared with the *cis*-β isomer. However the donor atoms of trien and 1-Metrien complexes were somewhat different, *i.e.*, two primary amine and two secondary amine for the former and three secondary amine and one primary amine for the latter. This difference disturbs the assignment of the configuration of *cis*-Co(1-Metrien)Cl₂⁺ based only

(16) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).
(17) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *ibid.*, **6**, 770 (1967).
(18) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).
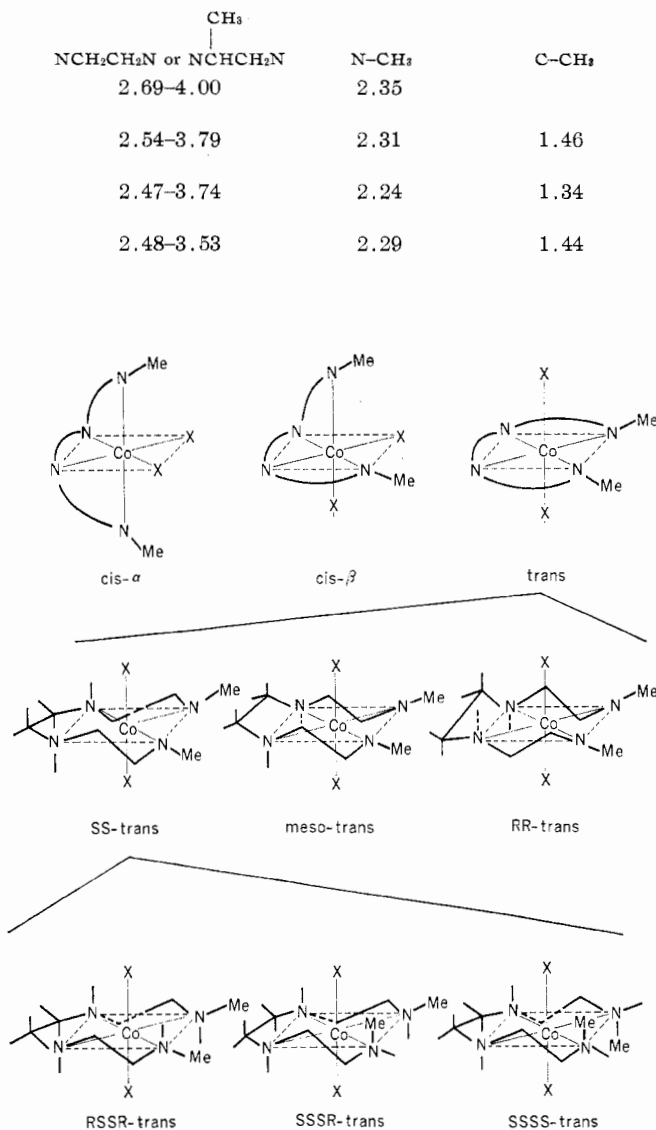(19) B. Boshnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965).

Figure 4.—Possible structures of *trans*-Co(1,10-Me₂trien)X₂ⁿ⁺.

on the absorption spectrum. The ORD and CD curves of the complexes containing asymmetric ligands are very similar to each other. The relation between the CD curves and configurations of complex ions will be discussed in a later section.

The infrared spectrum for the *trans*-dinitro complexes shows one strong band near the 1330-cm⁻¹ region which has been assigned as the NO₂ symmetrically stretching vibration. *cis*-[Co(2,3,2-tet)(NO₂)₂]I has two bands of nearly equal intensity. This difference in the number of NO₂ symmetrically stretching bands has been used to assign the *cis–trans* configurations of [Co(NH₃)₄(NO₂)]X[20] and [Co(en)₂(NO₂)₂]X.[21]

ORD and CD Curves. The Configuration of *trans*-Diacido(1,10-dimethyltriethylenetetramine)cobalt(III) Ions.—In the *trans* complex the configurations about the secondary N atoms give rise to three possible isomers for trien complexes as shown in Figure 4. The

(20) J. R. Beattie and H. J. V. Tyrrell, *J. Chem. Soc.*, 1954 (1956).
(21) J. P. Faust and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 5346 (1954).

1,10-(CH$_3$)$_2$trien   CH$_3$–NH–CH$_2$CH$_2$–NH–CH$_2$CH$_2$–NH–CH$_2$CH$_2$–NH–CH$_3$

LL-1,3,8,10-(CH$_3$)$_4$trien

$$\text{CH}_3\text{-NH-CH}_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-NH-CH}_2\text{CH}_2\text{-NH-CH}_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-NH-CH}_3$$

LL-1,2,9,10-(CH$_3$)$_4$trien

$$\text{CH}_3\text{-NH-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-CH}_2\text{-NH-CH}_2\text{CH}_2\text{-NH-CH}_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-NH-CH}_3$$

D-1,5,10-(CH$_3$)$_3$trien

$$\text{CH}_3\text{-NH-CH}_2\text{CH}_2\text{-NH-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-CH}_2\text{-NH-CH}_2\text{CH}_2\text{-NH-CH}_3$$

1,11-(CH$_3$)$_2$2,3,2-tet   CH$_3$–NH–CH$_2$CH$_2$–NH–CH$_2$CH$_2$CH$_2$–NH–CH$_2$CH$_2$–NH–CH$_3$
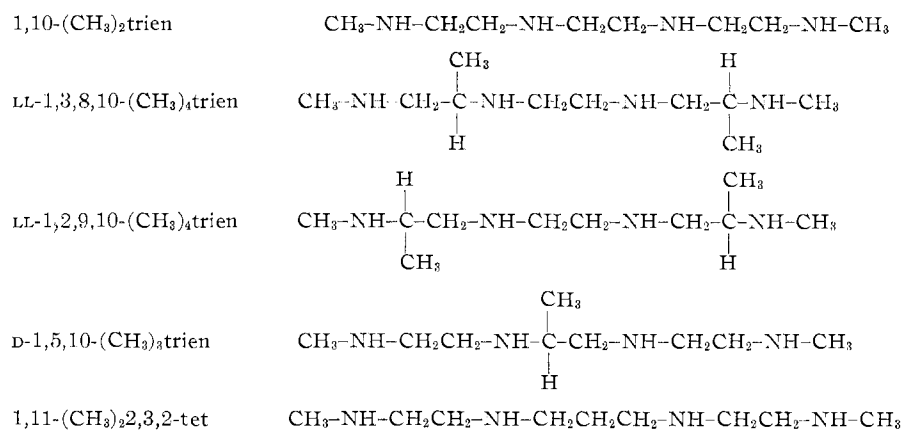
Figure 5.—The structures of the ligands prepared in this study.

RR and *SS* forms have three *gauche* ring conformations precisely decided by the configurations about the secondary N atoms. The absolute configuration of (+)D-*trans*-Co(trien)Cl$_2$$^+$ has been confirmed as *SS* in relation to the configuration of secondary nitrogen by comparing the CD curve of this complex with that of the *trans*-Co(LL-3,8-Me$_2$trien)Cl$_2$$^+$ ion. In the latter complex the side ethylenediamine linkage is forced to assume the δ conformation by the substituted methyl groups.
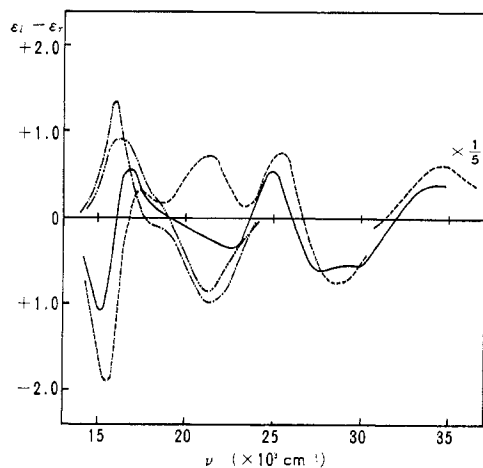

Figure 6.—Circular dichroism spectra for *trans*-Co(LL-1,3,8,10-Me$_4$trien)Cl$_2$$^+$ (——), *trans*-Co(LL-3,8-Me$_2$trien)Cl$^+$ (– – – –), the composite curve for *trans*-Co(LL-1,3,8,10-Me$_4$trien)Cl$_2$$^+$ − *trans*-Co(LL-3,8-Me$_2$trien)Cl$_2$$^+$ (–·—·—·–), and the contribution from the (*R*)-asymmetric nitrogen suggested by Hawkins' composite curve for (−)D-*trans*-Co(N-Meen)$_2$Cl$_2$$^+$− *trans*-Co(*l*-pn)$_2Cl_2$$^+$(–··—··—··—).

The tetramine ligands prepared in this study, LL-1,3,8,10-Me$_4$trien and D-1,5,10-Me$_3$trien, bear the asymmetric methyl substitution. LL-1,3,8,10-Me$_4$trien and LL-1,2,9,10-Me$_4$trien have the enantiomeric forms derived from L-alanine. The ligand D-1,5,10-Me$_3$trien has an asymmetric central ethylene linkage derived from (−)-propylenediamine of which the absolute configuration was determined as D.[22] These asymmetrically substituted methyl groups are expected to assume an equatorial position with regard to the

chelate ring(s), which requires the conformation(s) of the outer diamine linkage to be δ[23] for LL-1,3,8,10-Me$_4$trien and LL-1,2,9,10-Me$_4$trien and the conformation of the central diamine linkage to be λ for D-1,5,10-Me$_3$trien. The structure of the synthesized ligand is shown in Figure 5.

The fact that all dinitro- and dichlorocobalt(III) complexes containing these ligands have similar ORD and CD curves shows these complexes to have similar structures. They will be shown to have (δ,λ,δ) chelate ring conformations and *SS* configurations about the secondary amine groups. The three possible structures which arise from the configurations of the N-methyl group at the terminal amine group are shown in Figure 4. The proton magnetic resonance spectra of *trans*-Co(1,10-Me$_2$trien)(NO$_2$)$_2$$^+$, *trans*-Co(D-1,5,10-Me$_4$trien)(NO$_2$)$_2$$^+$, *trans*-Co(LL-1,3,8,10-Me$_4$trien)-(NO$_2$)$_2$$^+$, and *trans*-Co(LL-1,2,9,10-Me$_4$trien)(NO$_2$)$_2$$^+$ showed only one N-methyl signal. Thus these complex ions have either the *SSSS* or *RSSR* geometry, since the N-methyl groups in the *SSSR* geometry are environmentally different. The stability of a coordinated secondary amine group has been studied by Buckingham and his coworkers.[7] It has been shown that the axial N-methyl group is less stable by about 5 kcal/mol than an equatorial N-methyl group owing to the nonbonded interactions in the ligands. The present *SSSS* and *RSSR* isomers have axial and equatorial methyl groups, respectively, and the *RSSR* geometry should be the most stable structure.

The CD curves of *trans*-CoN$_4$X$_2$$^+$ ions were measured with ligands *l*-pn,[24,25] *l*-chxn,[26] LL-3,8-Me$_2$trien,[3] and N-Meen[7] where X = Cl. Absorption spectra of these ions have the first absorption band ($^1A_1$ → $^1T_{1g}$ in O$_h$) near 16,000 cm^{-1} (I$_a$ band) and 22,000 cm^{-1} (I$_b$ band) which is ascribed to the $^1A_1$ → ^1Eg and $^1A_1$ → $^1A_2$ transition in D$_{4h}$ symmetry, and two CD bands and one CD band, respectively, are found in these transitions. The CD curves of these ions were explained to be due to their chiral structure. *trans-*

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

(23) The nomenclature of the conformation of a diamine chelate ring is designated based on the proposal in *Inorg. Chem.*, **9**, 1 (1970).

(24) R. A. D. Wentworth and T. S. Piper, *ibid.*, **4**, 262 (1965).

(25) C. J. Hawkins, E. Larsen, and I. I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

(26) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

$Co((+)pn)_2Cl_2^+$, *trans*-$Co((+)chxn)_2Cl_2^+$, and *trans*-$Co(LL-3,8-Me_2trien)Cl_2^+$ have a positive CD band in the $^1A_1 \rightarrow {}^1A_2$ transition and the dominant negative band and the less significant positive band in the $^1A_1 \rightarrow {}^1E$ transition. These results agreed with the fact that all the chelate conformations (terminal for LL-3,8-Me$_2$trien) have the same conformation, *i.e.*, δ. The trien ligands with methyl substitution at the terminal N center, D-1,5,10-Me$_3$trien, LL-1,2,9,10-Me$_4$trien, and LL-1,3,8,10-Me$_4$trien, yield the *trans* complexes in which the terminal chelate ring conformation is δ. However, these dichloro complexes have a CD band near 21,500 cm^{-1} whose sign is opposite that of *trans*-$Co(LL-3,8-Me_2trien)Cl_2$ and curves in the region of 15,000–17,000 cm^{-1} similar to those of the *trans*-$Co(LL-3,8-Me_2trien)Cl_2^+$ ion as shown in Figure 6. The CD band near 22,000 cm^{-1} is ascribed to the $^1A_1 \rightarrow {}^1A_2(D_{4h})$ transition because the ligand field difference between these ions should be small. Therefore it is concluded that the CD band of the I$_b$ band has opposite signs for *trans*-$Co(LL-1,3,-8,10-Me_4trien)Cl_2^+$ and *trans*-$Co(LL-3,8-Me_2trien)Cl_2^+$ ions where the difference in structure is only that the former ions bear methyl groups at terminal nitrogen atoms. The similarity in the shapes of the CD bands (I$_a$ band) of *trans*-$Co(LL-3,8-Me_2trien)Cl_2^+$ and *trans*-$Co(LL-1,3,8,10-Me_4trien)Cl_2^+$ is explainable either as two essentially similar CD bands (two CD bands with the same transitions and same signs) or as CD bands in which the two transitions derived from $^1A_1 \rightarrow {}^1E$ change places in the energy resulting in CD bands which appear similar, because these two transitions cannot be assigned definitely at present.

The dinitro complexes, *trans*-$Co(LL-1,3,8,10-Me_4-trien)(NO_2)_2^+$ and *trans*-$Co(LL-3,8-Me_2trien)(NO_2)_2^+$, have apparently opposite CD bands in the visible and ultraviolet regions as shown in Figure 7. In the first absorption band, the *trans*-$Co(LL-1,3,8,10-Me_4trien)-(NO_2)_2^+$ complexes have three CD maxima. These CD bands should be assigned to the corresponding electronic transitions according to the theory of Yamatera[27] by comparison with the corresponding *trans*-dichloro complex. However the two CD maxima in *trans*-$Co(LL-3,8-Me_2trien)_2(NO_2)_2^+$ make the assignment unreliable with respect to the signs of the CD bands. The overlapping band in these absorptions make this situation complicated.

From the above discussions, it is concluded that the sign of the CD band of the $^1A_1 \rightarrow {}^1A_2$ transition is not essentially determined by the chirality of chelate ring(s) but that N-methylation causes a severe change in CD curves.

The circular dichroism for $(-)$D-*trans*-Co(N-Meen)-Cl_2^+ has been interpreted with the aid of the hexadecadal rule by Mason.[28] The regional sign depicted in Figure 8 indicates the sign of the Cotton effect induced by substituents in the $+z$ hemisphere for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component; the signs given (Figure 8)
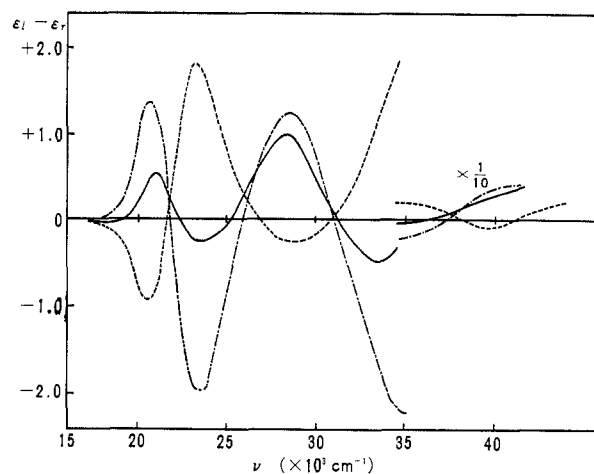

Figure 7.—Circular dichroism spectra for *trans*-$Co(LL-1,3,8,10-Me_4trien)(NO_2)_2^+$ (——), *trans*-$Co(LL-3,8-Me_2trien)$ $(NO_2)_2$ (————), and the composite curve for *trans*-$Co(LL-1,3,8,10-Me_4trien)-(NO_2)_2^+$ — *trans*-$Co(LL-3,8-Me_2trien)(NO_2)_2^+$ (—·—·—).
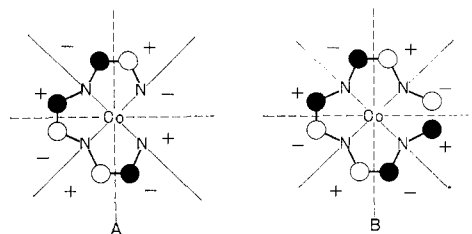

Figure 8.—The structures of *trans*-$Co(LL-3,8-Me_2trien)X_2$ (A) and *trans*-$Co(LL-1,3,8,10-Me_4$ trien)X_2 (B), the location of the carbon atoms in chelate ring below the CoN$_4$ plane (●) and above the CoN$_4$ plane (○), and the hexadecadal regional sign suggested by Mason.[29]

are reversed for substituents in the $-z$ hemisphere for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ component. The Co(tetramine)-Cl_2^+ ion studied here has chelate rings and N-methyl substituents as shown in Figure 8. Carbon atoms in the $+z$ hemisphere are indicated with open circles and carbon atoms in the $-z$ hemisphere with full circles. It is observed that CH$_2$ and CHCH$_3$ groups of the chelate rings in the side chelate ring lie in positive sectors whereas N–CH$_3$ groups and CH$_2$ groups in the central chelate ring lie in negative sectors. The dissymmetric potential, $xyz(x^2 - y^2)$, has a larger absolute value for the N–CH$_3$ group than for the CH$_2$ and CHCH$_3$ groups of the tetramine rings. As a result, the Cotton effect for the $A_{1g} \rightarrow A_{2g}$ component is positive for *trans*-$Co(LL-3,8-Me_2trien)Cl_2^+$ and negative for *trans*-$Co(LL-1,3,8,10-Me_4trien)Cl_2^+$ and for the other two Co(tetramine)Cl_2^+ complexes prepared in this study.

Recently Hawkins[29] also interpreted the circular dichroism spectra of the complexes *trans*-$Co(d-pn)_2Cl_2^+$ and $(-)$D-*trans*-$Co(N-Meen)_2Cl_2^+$ as arising principally from the conformational effect and the vicinal effect. The vicinal effect from the (R)-asymmetric nitrogen has a positive effect dominating the E$_g$ transition and a negative band for the A$_2$ component.

The present synthesized *trans*-Co(tetramine)Cl_2^+

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complex has an (R)-asymmetric nitrogen at the end of chelate ring. The vicinal effect from this (R)-asymmetric nitrogen has been obtained from the circular dichroism spectra of *trans*-Co(LL-1,3,8,10-Me₄trien)Cl₂⁺ and *trans*-Co(LL-3,8-Me₂trien)Cl₂⁺ and is represented in Figure 6 with that[29] from $(-)$D-*trans*-Co(N-Meen)Cl₂⁺ and *trans*-Co(d-pn)₂Cl₂⁺. These two vicinal effects are very similar and have a positive Cotton effect for the $A_{1g} \rightarrow E_g(D_{4h})$ component and a negative Cotton effect for the $^1A_1 \rightarrow {}^1A_2$ component. This result indicates that the vicinal effect from (R)-asymmetric nitrogen does not depend on the positions of the two (R)-asymmetric nitrogen (*i.e.*, *trans* for *trans*-Co(N-Meen)₂Cl₂⁺ and *cis* for *trans*-Co(LL-1,3,8,10-Me₄trien)Cl₂⁺), as well as the fact that this effect is essentially similar for these two *trans*-CoN₄Cl₂⁺ ions which have (R)-asymmetric nitrogen.

The difference in the circular dichroism for *trans*-Co-(LL-1,3,8,10-Me₄trien)(NO₂)₂⁺ and *trans*-Co(LL-3,8-Me₂trien)(NO₂)₂⁺ should have been determined by the vicinal effect from the (R)-asymmetric nitrogen. This effect is shown in Figure 7 also and this vicinal effect has positive Cotton effects near 20,800 and 23,500 cm⁻¹. From the Yamatera theory, the lower energy band may be the $^1A_1 \rightarrow {}^1A_2(D_{4h})$ component and the higher energy band may be the $^1A_1 \rightarrow {}^1E(D_{4h})$ component of the $^1A_1 \rightarrow {}^1T_1(O_h)$ d–d transition. The signs of the Cotton effects induced from the (R)-asymmetric nitrogen are different for the corresponding component of the *trans*-CoN₄Cl₂⁺ and *trans*-CoN₄(NO₂)₂⁺ chromophores.

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The Triamines of Cobalt(III). I. Geometrical Isomers of Trinitrotriamminecobalt(III)[1a]

By ROBERT B. HAGEL[1b] and LEONARD F. DRUDING

A number of preparations from the literature for trinitrotriamminecobalt(III) were examined for their structural arrangement. Evidence for the existence of the facial and meridial isomers was established by proton magnetic resonance spectra and thin layer chromatography and by comparison with other cobalt(III) triamines of known geometry. Additional properties of these isomers studied included their infrared and ultraviolet spectra.

Introduction

In Alfred Werner's classic explanation of the theory of structure of coordination complexes, he submitted considerable evidence for an octahedral arrangement of groups for coordination number of 6. Most important evidence for this structural assignment was that for octahedral complexes containing two different ligands A and B in the general formula MA_nB_{6-n} where $n = 2$, 3, or 4, only two geometrical isomers are possible. Where $n = 2$ (and the equivalent case of $n = 4$), many hundreds of *cis–trans* isomer pairs have been prepared and characterized. However, for $n = 3$, or MA_3B_3, only five such sets of geometrical isomers[2] have been firmly identified: Ru(H₂O)₃Cl₃,[3,4] Pt-(NH₃)Br₃⁺,[5] Pt(NH₃)₃I₃⁺,[6] Ir(H₂O)₃Cl₃,[7] and Rh(CH₃-

CN)₃Cl₃.[8] Less clear has been the situation with trinitrotriamminecobalt(III), which was first prepared in 1866 by Erdmann;[9] later preparations were reported by Werner[10] and Jorgensen.[11] No evidence was then given for the structures of these compounds or even whether different isomers were represented. The first study of the various preparations of Co(NH₃)₃(NO₂)₃ was reported in 1938[12] by Duval, who examined five methods of preparation by visible, ultraviolet, and infrared spectroscopy, refractive index of aqueous solutions, conductivity, and X-ray powder diffraction. These measurements indicated that two different products resulted when the Werner and Jorgensen preparations were compared. Duval assumed that these were the two geometrical isomers of the complex but he did not assign configurations from his data. In 1952, Tanito, Saito, and Kuroya[13] determined the crystal structure of the product of the Jorgensen preparation to be that of the meridial isomer.

(1) (a) Presented at the 158th National Meeting of the American Chemical Society, Sept 7–12, New York, N. Y., 1969. (b) Abstracted from the Ph.D. dissertation of R. B. Hagel, Rutgers University, 1969.

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