in less labile octahedral transition metal complexes.[16,17] For the most part, this evidence tends to be inconclusive because of the existence of complicating side reactions having about the same rate and activation energy as the kinetic process being studied. This is especially true for Co(III) and Pt(IV) complexes where spontaneous and catalyzed internal rearrangements cloud the interpretation of the kinetic data.[16–18]

The measurement of methanol exchange of cobalt(II) complexes is not hindered by side reactions and should, therefore, provide a very useful system for studying kinetic cis and trans effects in octahedral complexes. Poe and coworkers have measured the effect of various ligands on the substitution rates of the trans sites in Rh(III) complexes but have not established whether this is a general labilization effect or a result of a specific trans-directing effect of the ligand.[20]

Finally, this study does provide some insight into the nature of the intermediates or activated complexes for the exchange process. There is a considerable body of information in the literature which tends to indicate that the substitution mechanisms of the first-row transition metal ions are primarily dissociative in nature.[1–3,21] This study and previous work in this laboratory[1,5] indicate that no internal rearrangement takes place when methanol exchanges with monosubstituted cobalt(II) complexes. Taking these two observations into account, it is most likely that the reaction does not proceed by a five-coordinate trigonal-bipyramidal intermediate or activated complex.

Measurements of the methanol-exchange rates of a variety of other Co^{2+} complexes are presently under way in this laboratory.

Registry No. $Co(CH_3OH)_5py^{2+}$, 39208-17-8; $Co(CH_3OH)_6{}^{2+}$, 15276-50-3.

Acknowledgment. We wish to thank the Research Corp. for the Frederick Gardner Cottrel Grant which partially supported this work.

(20) A. J. Poe and K. Shaw, *J. Chem. Soc. A*, 393 (1970), and references therein.

(21) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

Stereochemical Studies of Metal Chelates. X.[1] Preparation and Stereochemistry of Diacidocobalt(III) Complexes Coordinated with (4*R*,5*S*)-Dimethyl-3,6-diaza-1,8-diaminooctane and Its Optically Active Derivatives

MASAFUMI GOTO, HAJIME MATSUSHITA, MASAHIKO SABURI, and SADAO YOSHIKAWA*

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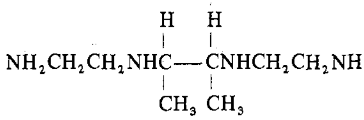
The preparation and characterization of isomers of dichloro- and dinitrocobalt(III) complexes containing (4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane (abbreviated as *meso*-5,6-dmtrien) and (5*R*,6*S*)-dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane [abbreviated as (2*S*,5*R*,6*S*,9*S*)-tmtrien] are reported. One type of cis-β isomer and one type of trans isomer were isolated, and another trans form was detected for the complexes of *meso*-5,6-dmtrien. The stereochemistry of these complexes was studied in detail by means of proton magnetic resonance (pmr) and circular dichroism (CD). The absolute configurations of the coordinated secondary nitrogen atoms were antimeric (*R* and *S*) for the cis-β isomers. The isolated trans isomer had the meso–trans structure, in which the conformation of the central chelate ring was an envelope form. The complexes prepared in this study showed some behaviors in reactivities different from those of triethylenetetramine complexes, owing to the difference in the coordination mode of the secondary amine groups of the ligands.

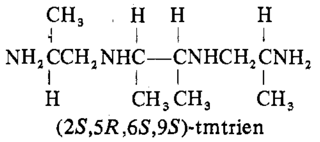
A number of publications have described cobalt(III) complexes containing tetradentate ligands, especially tetramines. It has been observed that several specific geometrical isomers are preferably obtained when the ligands having asymmetric substituents at the carbon atoms of triethylenetetramine (trien) are employed.[1–6] The structures of these complexes have been explained in relation to the configurations and position of the substituents in the trien skeleton. For all the methyl-substituted triens, the methyl group(s) adopted preferentially the equatorial orientation with respect to the gauche five-membered chelate ring.

The ligands prepared in the present study, (4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane (*meso*-5,6-dimethyltriethylenetetramine, abbreviated as *meso*-5,6-dmtrien) and (5*R*,6*S*)-dimethyl-3,7-diaza-(2*S*,9*S*)-diaminodecane [abbreviated as (2*S*,5*R*,6*S*,9*S*)-tmtrien], have two methyl groups derived from *meso*-butane-2,3-diamine (*meso*-bn) in the central chelate ring. The *meso*-bn linkage may coordinate to a



$$NH_2CH_2CH_2NH\underset{CH_3}{\overset{H}{C}}\text{—}\underset{CH_3}{\overset{H}{C}}NHCH_2CH_2NH_2$$

meso-5,6-dmtrien



$$NH_2\underset{H}{\overset{CH_3}{C}}CH_2NH\underset{CH_3}{\overset{H}{C}}\text{—}\underset{CH_3}{\overset{H}{C}}NHCH_2\underset{CH_3}{\overset{H}{C}}NH_2$$

(2*S*,5*R*,6*S*,9*S*)-tmtrien

(1) Part IX: M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, 45, 1443 (1972).

(2) S. Yoshikawa, T. Sekihara, and M. Goto, *Inorg. Chem.*, 6, 169 (1967).

(3) M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, 8, 358 (1969).

(4) M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *Inorg. Chem.*, 9, 1488 (1970).

(5) M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, 45, 806 (1972).

(6) M. Saburi, T. Sawai, and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, 45, 1086 (1972).

metal ion in either of conformations shown in Figure 1. In the δ^7 and λ^7 gauche conformations, which are mirror images and energetically equivalent, one of the methyl groups should be axial with respect to the chelate ring, while both of the methyl groups can locate equatorially in the envelope conformation.

Several diamagnetic metal complexes of *meso*-bn have been examined by means of pmr measurement. It has been concluded that the conversion of δ- and λ-gauche conformation occurs rapidly at room temperature.[8] For the tetramines prepared in this study [*meso*-5,6-dmtrien and (2*S*,5*R*,6*S*,9*S*)-tmtrien], the rapid conformational interconversion of the central *meso*-bn moieties should be prevented when coordinated to the Co(III) ion because of the presence of outer ethylenediamine linkages. If the coordination of all of the four amine groups of a tetramine yielded a particular geometrical form, the isomer brought about by the inversion of the conformation at the central chelate ring should be, in general, energetically different from the original form, due to the differences in nonbonding steric interactions and angular distortions involved. Hence, the conformation of chelate rings should be fixed even for the *meso*-bn moiety of tetramine ligands. Therefore, the complexes with the tetramines of *meso*-bn derivatives are expected to give rise to some interesting isomers, in which one of the methyl groups adopts the uncommon axial orientation or, otherwise, the central chelate ring has an envelope conformation.

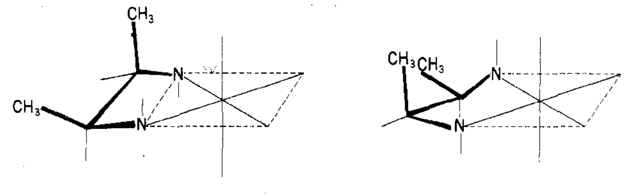
Experimental Section

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu MPS-50L recording spectrophotometer. The circular dichroism curves were measured with a JASCO J-20 recording spectropolarimeter. The infrared spectra were measured with a JASCO DS-301 recording spectrophotometer by means of the KBr disk method. The proton magnetic resonance spectra were measured with a JEOL PS-100 100-MHz spectrometer or with a Hitachi R-20B 60-MHz spectrometer with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard. For the measurements of pmr spectra of the *trans*-dinitro complexes, analytically pure samples of perchlorate salt were converted to chloride salt by shaking the complex suspended in D_2O with an equimolar amount of tetraphenylarsonium chloride. The mixture was then filtered and its pmr spectrum was measured immediately. In the case of *trans*-dichloro complexes, the same method was used in tetradeuterated methanol instead of D_2O.

Materials. A mixture of *meso*- and *rac*-butane-2,3-diamine was obtained by the reduction of dimethylglyoxime with Raney nickel in alkaline solution.[9] The separation of the meso and racemic isomers was performed by the known method.[9] Carbobenzoxy-(*S*)-alanine azide was prepared in ether solution by the method of Erlanger and Brand.[10]

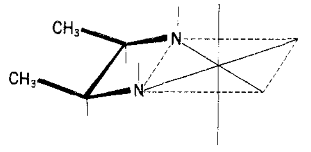
The separation of the *meso*- and *rac*-butane-2,3-diamine as the dihydrochloride[9] was rather difficult and we considered that this method was unsuitable for obtaining sufficient amounts of pure samples of meso isomer. Alternatively, the separation of *meso*- and *rac*-diamine as the *N,N'*-bis(chloroacetyl) derivatives was found to be convenient to the purpose of this study, as follows.

***N,N'*-Bis(chloroacetyl)butane-2,3-diamine. Mixture of Meso and Racemic Forms.** A solution of chloroacetyl chloride (26.4 g) in benzene (100 ml) was added dropwise to a solution of butane-2,3-diamine (10.0 g, a mixture of meso and racemic isomer) in 120 ml of 5 *N* sodium hydroxide, which was cooled in an ice-salt bath, with vigorous stirring by means of a blender. The white precipitate which appeared were filtered off and washed with water several times, yield 25 g.



δ-gauche

λ-gauche



envelope

Figure 1. Structures of *meso*-bn chelate.

Separation of Meso and Racemic Isomers of *N,N'*-Bis(chloroacetyl)butane-2,3-diamine. A mixture of meso and racemic isomers was fractionally recrystallized from hot ethanol. A few less soluble fractions were identical with the meso isomer, which was prepared using the *meso*-butane-2,3-diamine, after repeated recrystallization: mp 214° dec; solubility in ethanol at 25°, 0.78 g/100 ml. *Anal.* Calcd for $C_8H_{14}N_2O_2Cl_2$: C, 39.85; H, 5.85; N, 11.62. Found: C, 39.58; H, 5.85; N, 11.51.

The racemic isomer could be isolated from the filtrate of the meso isomer, mp 157–158°. This product was also identical with the product obtained by employing the *rac*-butane-2,3-diamine as a starting material.

***N,N'*-Bis(glycyl)-*meso*-butane-2,3-diamine Dihydrochloride.** A mixture of bis(chloroacetyl)-*meso*-butane-2,3-diamine (10 g), 28% aqueous ammonia solution (300 ml), methanol (300 ml), and ammonium carbonate (60 g) was allowed to stand for a week. The resultant clear solution was concentrated in a rotary evaporator to dryness. The white residues were recrystallized from methanol and ethanol. *Anal.* Calcd for $C_8H_{18}N_4O_2 \cdot 2HCl$: C, 34.92; H, 7.33; N, 20.30. Found: C, 35.82; H, 7.65; N, 19.83.

(4*R*,5*S*)-Dimethyl-3,6-diaza-1,8-diaminooctane Tetrahydrochloride (*meso*-5,6-Dimethyltriethylenetetramine Tetrahydrochloride, *meso*-5,6-dmtrien·4HCl). Into a 300-ml four-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser attached with a soda lime tube, 150 ml of anhydrous tetrahydrofuran was placed, and 8.35 g of lithium aluminum hydride was added with stirring. Then, dried and pulverized *N,N'*-bis(glycyl)-*meso*-butane-2,3-diamine dihydrochloride (10.0 g) was added in small portions with continuous stirring at room temperature. The mixture was then stirred and heated under reflux for 24 hr, after which time it was cooled to room temperature. Water (15.8 ml) diluted with 20 ml of tetrahydrofuran were added dropwise to the mixture with vigorous stirring. The resultant precipitates were filtered off and washed with tetrahydrofuran. The remaining cake was extracted twice with boiling tetrahydrofuran (100 ml) and filtered. The combined filtrates and washings were concentrated under reduced pressure. The resultant oily residue was taken up into 50 ml of ethanol, and the solution was filtered. Dry hydrogen chloride gas was bubbled into the filtrate, and the precipitates which appeared were filtered off and washed with ethanol and ether, yield 6.3 g. The product was recrystallized from 5 *N* HCl by adding ethanol. *Anal.* Calcd for $C_8H_{22}N_4 \cdot 4HCl$: C, 30.01; H, 8.19; N, 17.50. Found: C, 29.62; H, 8.03; N, 16.80.

***N,N'*-Bis[carbobenzoxy-(*S*)-alanyl]-*meso*-butane-2,3-diamine.** To a solution of carbobenzoxy-(*S*)-alanyl azide prepared from 23.7 g (0.1 mol) of carbobenzoxy-(*S*)-alanine hydrazide in 600 ml of dry ether[10] was added an ethereal solution of *meso*-butane-2,3-diamine (3.1 g, 0.035 mol). The mixture was stirred for 24 hr at ice-bath temperature, and the resultant white precipitates were filtered off and washed with ether. The crude product was recrystallized from ethanol, yield 13.5 g, mp 210–212° (cor). *Anal.* Calcd for $C_{26}H_{34}N_4O_6$: C, 62.63; H, 6.87; N, 11.24. Found: C, 62.73; H, 7.07; N, 11.20.

(5*R*,6*S*)-Dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane Tetrahydrochloride, (2*S*,5*R*,6*S*,9*S*)-tmtrien·4HCl. *N,N'*-Bis[carbobenzoxy-(*S*)-alanyl]-*meso*-butane-2,3-diamine (14.6 g) was added to acetic acid saturated with dry hydrogen bromide (58 g), and the reaction mixture was protected from atmospheric moisture with a calcium chloride drying tube and allowed to stand until carbon dioxide evolution ceased. The resultant solution was then added to anhydrous ether (700 ml) to precipitate the product. The mixture was stored in an

[7] *Inorg. Chem.*, **9**, 1 (1970).

[8] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Chem. Commun.*, 460 (1969).

[9] F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **81**, 4185 (1959).

[10] B. F. Erlanger and E. Brand, *J. Amer. Chem. Soc.*, **73**, 3508 (1951).

ice bath for a few hours, and the precipitates were filtered off and washed with anhydrous ether. To the dried product, *N,N'*-bis[(*S*)-alanyl]-*meso*-butane-2,3-diamine dihydrobromide, suspended in anhydrous tetrahydrofuran (200 ml), lithium aluminum hydride (12.0 g) was added in small portions with stirring at room temperature. The reaction mixture was then stirred and heated under reflux for 24 hr and cooled to room temperature. The following procedures were the same as those for the isolation of *meso*-5,6-dmtrien. The yield of the tetrahydrochloride was about 5 g. This ligand was used without further purification.

***cis*-β-(*RS,SR*)-Dinitro[(4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane]cobalt(III) Chloride Hemihydrate,[11] *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]Cl·0.5H_2O.** A solution containing *meso*-5,6-dmtrien·4HCl (1.60 g), $CoCl_2 \cdot 6H_2O$ (1.19 g), $LiOH \cdot H_2O$ (0.63 g), and $NaNO_2$ (0.735 g) in 80 ml of water was aerated with carbon dioxide free air for 8 hr. The resultant solution was concentrated on a water bath, and the crystals which separated were filtered off and washed with ethanol and acetone, yield 1.5 g. This product was recrystallized from water by adding ethanol. *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]Cl \cdot 0.5H_2O$: C, 26.01; H, 6.22; N, 22.74. Found: C, 25.88; H, 6.21; N, 22.83.

The corresponding iodide salt was also obtained when an aerated solution was concentrated to a volume of 20 ml, followed by filtering and adding solid NaI. The yellow crystals which separated were collected and recrystallized from hot water, yield 1.2 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]I \cdot H_2O$: C, 20.44; H, 5.14; N, 17.88. Found: C, 20.14; H, 5.63; N, 17.60.

Resolution of *cis*-β-(*RS,SR*)-Co(*meso*-5,6-dmtrien)$(NO_2)_2^+$ Ion. *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]I·H_2O (3.46 g, 7.37 mmol) was dissolved in 60 ml of water at 80°. To this solution was added silver α-bromo-*d*-camphor-π-sulfonate (3.08 g, 7.37 mmol) dissolved in 40 ml of water at 80°. The mixture was stirred for a few minutes, and the precipitated AgI was filtered off and washed with water. The filtrate and washings were united and concentrated almost to dryness in a rotary evaporator at 40°. The orange residue was dissolved in a minimum volume of methanol–ethanol mixture (1:1) at 60°. The resultant solution was filtered and allowed to stand at 0° for 24 hr. The orange crystals which separated were collected and washed with ethanol and ether and air-dried: yield 0.4 g; $[\alpha]^{25}D$ −78° (*c* 0.25, water). *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2](C_{10}H_{14}O_4BrS)$: C, 34.02; H, 5.71; N, 13.23. Found: C, 33.78; H, 5.78; N, 13.29.

The diastereoisomer salt obtained as above was ground with a small volume of water, two drops of acetic acid, and an excess amount of $LiClO_4 \cdot 3H_2O$ in a mortar. The orange yellow solids were filtered and washed with aqueous $LiClO_4$ solution and ethanol and air-dired, $[\alpha]^{25}D$ −140° (*c* 0.25, water). *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.62; H, 5.22; N, 19.79. Found: C, 22.76; H, 5.20; N, 18.98.

An attempt to obtain the resolved isomer of this complex from the active diastereoisomeric salt as the iodide salt failed and the optical activity completely vanished after recrystallization from hot water. Hence, the resolved isomer was isolated as the perchlorate, as described above. This product also slowly lost optical activity in aqueous solution, especially at elevated temperatures. Therefore, the isolation of the purely resolved complex was very difficult, and the active perchlorate salt reported here was that showing the highest optical rotation.

***cis*-β-(*RS,SR*)-Dichloro[(4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane]cobalt(III) Chloride Dihydrate, *cis*-β-[Co(*meso*-5,6-dmtrien)Cl_2]Cl·2H_2O.** A mixture of *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]Cl (1.0 g) and concentrated hydrochloric acid (30 ml) was evaporated on a steam bath almost to dryness. The resultant red purple crystals were filtered off and washed with acetone. The crystals were recrystallized from 3 *N* HCl by adding acetone, yield 0.48 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]Cl \cdot 2H_2O$: C, 25.58; H, 6.98; N, 14.92. Found: C, 25.99; H, 7.48; N, 14.58.

***trans*-(*RS*)-Dichloro[(4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane]cobalt(III) Perchlorate, *trans*-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4.** To a solution of *cis*-β-[Co(*meso*-5,6-dmtrien)Cl_2]Cl·2H_2O (0.5 g) in concentrated hydrochloric acid (5 ml), an excess amount of solid $LiClO_4 \cdot 3H_2O$ (1.0 g) was added. The purple solution was allowed to stand for 24 hr at room temperature. The green crystals which separated were collected and recrystallized from methanol saturated with dry hydrogen chloride. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.81; H, 5.50; N, 13.88. Found: C, 23.39; H, 5.37; N, 13.54.

A Mixture of *trans*-(*RS*)- and *trans*-(*RR,SS*)-Dinitro[(4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane]cobalt(III) Perchlorate, *trans*-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4. *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4 was dissolved in hot methanol and a 2-equiv amount of $NaNO_2$ was added. The color of the solution changed from green to red rapidly. To the cooled solution was added an excess of solid $LiClO_4$. The orange-yellow crystals which separated were filtered off and washed with ethanol.

Δ-*cis*-β-(*RS*)-Dinitro[(5*R*,6*S*)-dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane]cobalt(III) Perchlorate Monohydrate, Δ-*cis*-β-(*RS*)-[Co((2*S*,5*R*,6*S*,9*S*)-tmtrien)$(NO_2)_2$]$ClO_4 \cdot H_2O$. A mixture of (2*S*,5*R*,6*S*,9*S*)-tmtrien·4HCl (2.42 g), $CoCl_2 \cdot 6H_2O$ (1.65 g), $LiOH \cdot H_2O$ (0.87 g), and $NaNO_2$ (0.96 g) in 25 ml of water was aerated with carbon dioxide free air for 8 hr. The resultant red solution was concentrated on a water bath to a volume of 15 ml and filtered. To the filtrate an excess amount of $LiClO_4 \cdot 3H_2O$ was added, and the solution was cooled. The yellow brown crystals which separated were filtered off and washed with ethanol, yield 1.10 g. *Anal.* Calcd for $[Co(C_{10}H_{26}N_4)(NO_2)_2]ClO_4 \cdot H_2O$: C, 25.51; H, 5.99; N, 17.85. Found: C, 25.18; H, 6.02; N, 17.76.

Δ-*cis*-β-(*RS*)-Dichloro[(5*R*,6*S*)-dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane]cobalt(III) Perchlorate Monohydrate, Δ-*cis*-β-(*RS*)-[Co((2*S*,5*R*,6*S*,9*S*)-tmtrien)Cl_2]$ClO_4 \cdot H_2O$. Δ-*cis*-β-(*RS*)-[Co((2*S*,5*R*,6*S*,9*S*)-tmtrien)$(NO_2)_2$]ClO_4 dissolved in concentrated hydrochloric acid was gently evaporated on a water bath. The crystals which appeared were collected and washed with ethanol, yield quantitative. *Anal.* Calcd for $[Co(C_{20}H_{26}N_4)Cl_2]ClO_4 \cdot H_2O$: C, 26.71; H, 6.28; N, 12.46. Found: C, 26.77; H, 6.47; N, 12.27.

Results and Discussion

Structures and Rearrangements of *meso*-5,6-dmtrien Complexes. The dinitrocobalt(III) complex of *meso*-5,6-dmtrien obtained by the usual air oxidation method was isolated as the chloride or iodide salt. The electric absorption spectrum of this complex ion is shown in Figure 2. The second peak (NO_2 specific absorption band) was found at 30,900 cm^{-1}, indicating the cis configuration. The absorption maxima for the cis isomers of the $Co(N)_4(NO_2)_2^+$ type were observed at about 31,000 cm^{-1}, while those of the trans isomers were found in the vicinity of 29,000 cm^{-1}.[4,6,12]

The *trans*-dichloro(*meso*-5,6-dmtrien)cobalt(III) complex was isolated as the perchlorate salt by heating the above [Co(*meso*-5,6-dmtrien)$(NO_2)_2$]Cl with concentrated hydrochloric acid, followed by addition of $LiClO_4$. In the absence of $LiClO_4$, purple crystals of *cis*-[Co(*meso*-5,6-dmtrien)Cl_2]Cl were obtained. Further, the perchlorate salt of the *trans*-dichloro complex was also separated from a hydrochloric acid solution of this *cis*-dichloro complex containing $LiClO_4$. Both the trans complexes were shown to be identical. Therefore, the *cis*-dichloro complex should be an intermediate in the conversion from the *cis*-dinitro to the *trans*-dichloro ion. Under the above conditions (in hydrochloric acid), the isomerization reaction from the cis to trans form should proceed with retention of configurations with respect to the secondary N centers.

Three possible isomers of the *trans*-Co(*meso*-5,6-dmtrien)-X_2^+ ion are depicted in Figure 3. The trans-*SS* and trans-*RR* forms are the racemic pair. The trans-*RS* form has an envelope conformation with respect to the central diamine linkage. In this configuration, the two methyl groups should take the equatorial orientations simultaneously. The other possibility that both the methyl groups are situated in the axial orientations at the same time was excluded from a stereochemical point of view. The *trans*-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, obtained by the above-mentioned method, exhibited only one doublet for the *C*-methyl resonance in

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[11] *R* and *S* refer to the configuration about the "angular" and "planar" asymmetric N atoms of triethylenetetramine and its derivatives in that order and follow the rules suggested by R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966). *Cf.* P. A. Marzilli and A. M. Sargeson, *Inorg. Chem.*, 5, 1032 (1967). In the present paper, however, the configurations of the asymmetric secondary N atoms are represented by *R* and *S*, neglecting the substituted methyl groups in trien skeleton. See ref 1, 5, and 6.

[12] F. Basolo, *J. Amer. Chem. Soc.*, 72, 4393 (1950).

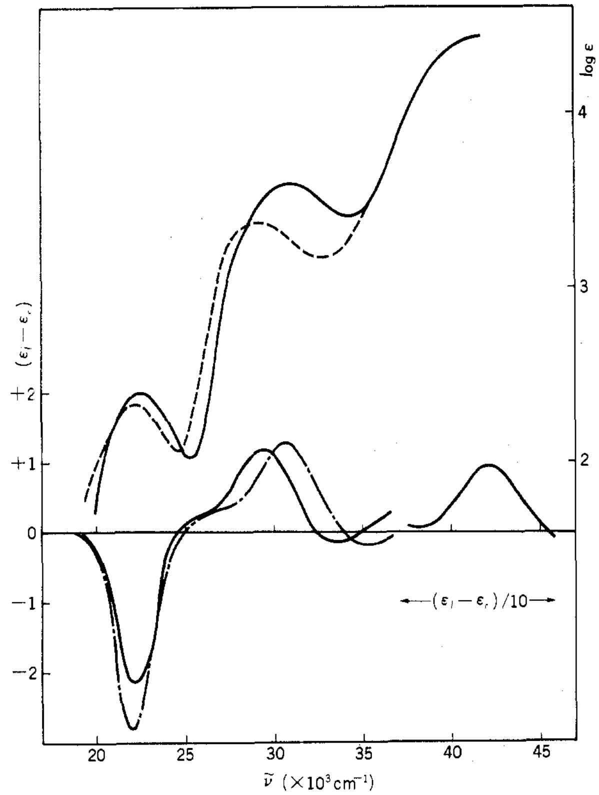


Figure 2. Absorption and CD spectra of the Δ-*cis*-β-(*RS*)-Co(*meso*-5,6-dmtrien)$(NO_2)_2^+$ ion (————), absorption spectrum of the *trans*-Co(*meso*-5,6-dmtrien)$(NO_2)_2^+$ ion (— — —), and CD spectrum of the Δ-*cis*-β-(*RS*)-Co[(2*S*,5*R*,6*S*,9*S*)-tmtrien]$(NO_2)_2^+$ ion (— · — · —).

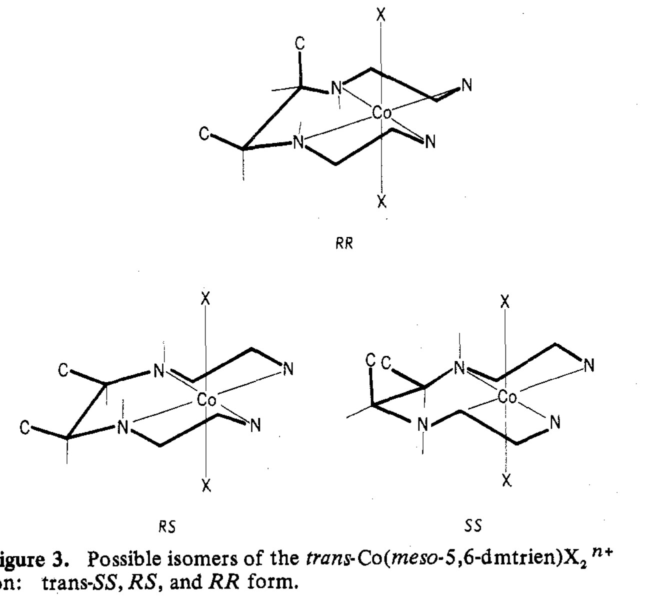


Figure 3. Possible isomers of the *trans*-Co(*meso*-5,6-dmtrien)X_2^{n+} ion: trans-*SS*, *RS*, and *RR* form.

the pmr spectrum as shown in Figure 4a. This demonstrates that the present *trans*-dichloro complex has the trans-*RS* (or meso-trans) configuration. For the racemic trans form (*RR* and *SS*), having the gauche conformation with regard to the central chelate ring, one methyl group will be situated in the equatorial orientation with the other in the axial orientation. These methyl groups can be distinguished by means of pmr.

It is certain that the *cis*-dinitro and *cis*-dichloro complexes, both of which could convert to the *trans*-(*RS*)-dichloro complex in acidic media as described previously, must have the *RS* configuration with respect to the secondary N centers. Further, it is impossible for the cis-α isomer of the trien complex to take the *RS* configuration. Only *RR* and *SS* configurations are possible for the cis-α geometry. Therefore, the *cis*-dinitro and *cis*-dichloro complexes of *meso*-5,6-dmtrien should have the cis-β-*RS*,*SR* geometry.

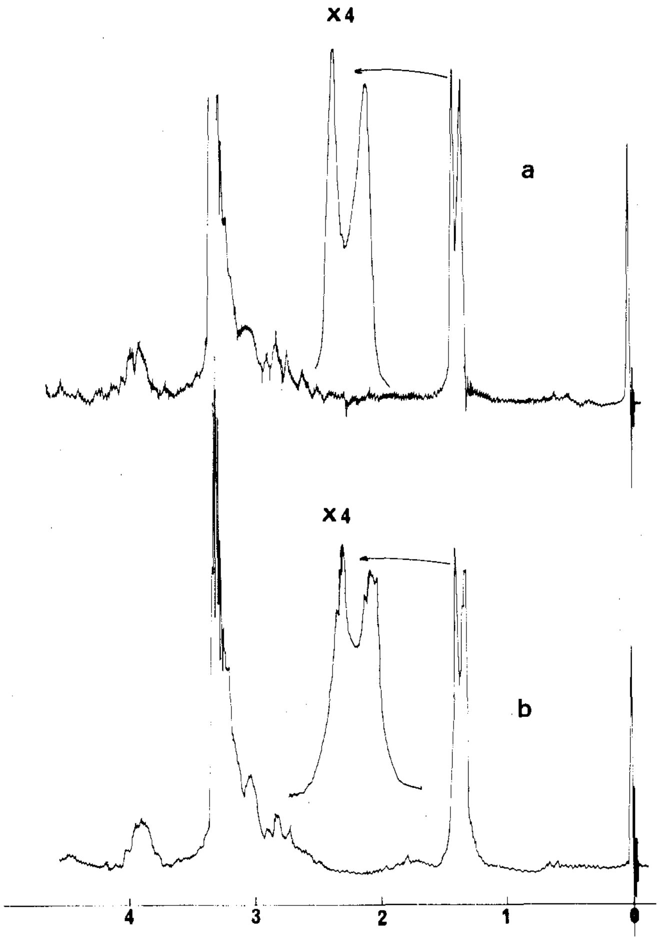


Figure 4. 100-MHz pmr spectra of *trans*-Co(*meso*-5,6-dmtrien)Cl_2^+ complexes: trans-*RS* isomer (a), and a mixture of trans-*RS* and trans-*RR*,*SS* isomers (b).

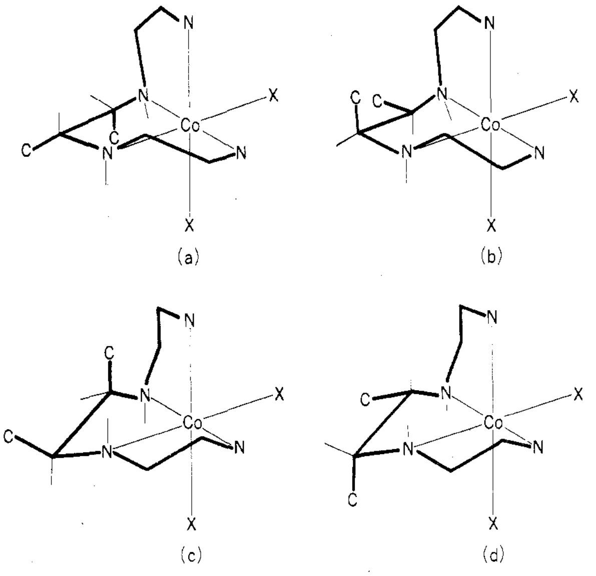


Figure 5. Possible structures of the *cis*-β-Co(*meso*-5,6-dmtrien)X_2^{n+} ion: Δ-cis-β-*RS* forms (a and b); Δ-cis-β-*RR* forms (c and d).

Possible structures for the cis-β geometry of the *meso*-5,6-dmtrien complex are those shown in Figure 5. These structures, all having the Δ absolute configuration, arise from the differences in the combination of the configuration of

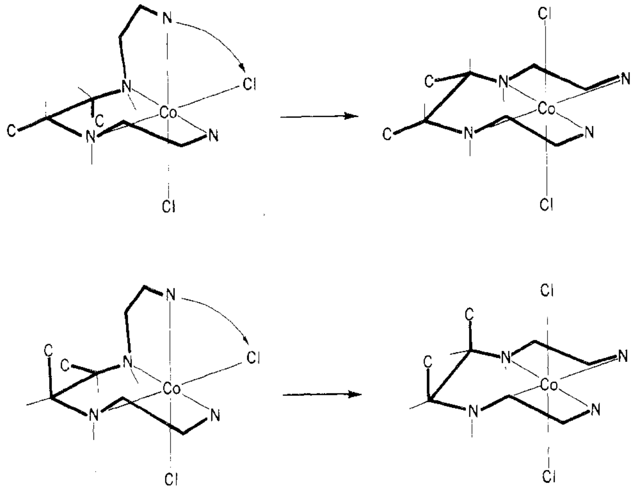


Figure 6. Relationships in the structures between cis-β-*RS* isomers and isomerized trans-*RS* isomers.

secondary N atoms and of the location of the *C*-methyl groups on the central chelate ring. As for the *meso*-5,6-dmtrien complex, either structure a or b (Δ-cis-β-*RR* forms) and its enantiomer are probable.

It is possible to determine the actual structure of the cis-β isomer of the *meso*-5,6-dmtrien complex. If the isomerization from cis-β-*RS,SR* to trans-*RS* isomer proceeds by the edge displacement of the terminal NH_2 group, the isomers illustrated as Figure 5a and b must yield the different trans-*RS* form. As shown in Figure 6, one isomer, corresponding to Figure 5a, gives the trans-*RS* with two equatorial methyl groups, and the other form, corresponding to Figure 5b, converts to the trans-*RS* with two axial methyl groups. The latter case must be very unlikely, as has been described previously. Therefore, the structure illustrated in Figure 3a should be the most probable one for the Δ-cis-β-*RS* configuration.

The isomerization of the Co(*meso*-5,6-dmtrien)Cl_2^+ ion from cis-β-*RS,SR* to the trans form and vice versa was studied in methanol under different conditions. While the recrystallization of *cis*-β-(*RS,SR*)-[Co(*meso*-5,6-dmtrien)Cl_2]Cl from methanol saturated with hydrogen chloride gas yielded the purple original complex, the addition of perchlorate ion caused the separation of green crystals from purple solution. The present trans complex showed a pmr spectrum identical with that of the trans-*RS* isomer (Figure 5a). The trans-*RS* dichloro complex rearranged to the *cis*-β-(*RS,SR*)-dichloro isomer in methanol containing hydrogen chloride gas (the isosbestic points are at 415, 497, and 615 mμ). From these observations, it was concluded that the cis-β-*RS,SR* and trans-*RS* isomers are equilibrated in acidic methanol and that the former is more favored than the latter under the examined conditions. The *trans*-(*RS*)-dichloro perchlorate is, however, much less soluble than the *cis*-β-(*RS,SR*)-dichloro perchlorate and therefore precipitates out of a solution containing the two species in equilibrium. This situations should hold for the phenomena in acidic aqueous solution which have been mentioned earlier.

The *cis*-β-(*RS,SR*)-dinitro complex of *meso*-5,6-dmtrien could be resolved with silver α-bromo-*d*-camphor-π-sulfonate. The (−)D enantiomer, isolated from the less soluble diastereoisomer salt, gave the CD curve shown in Figure 2. The negative CD peak in the first absorption band region indicates the Δ absolute configuration of this enantiomer. Although this isomer has been designated as the Δ-*cis*-β-(*RS*)-Co(*meso*-5,6-dmtrien)$(NO_2)_2^+$ ion,[11] its optical purity is not certain because this complex ion racemizes rather readily in aqueous solution, especially at the elevated temperature.

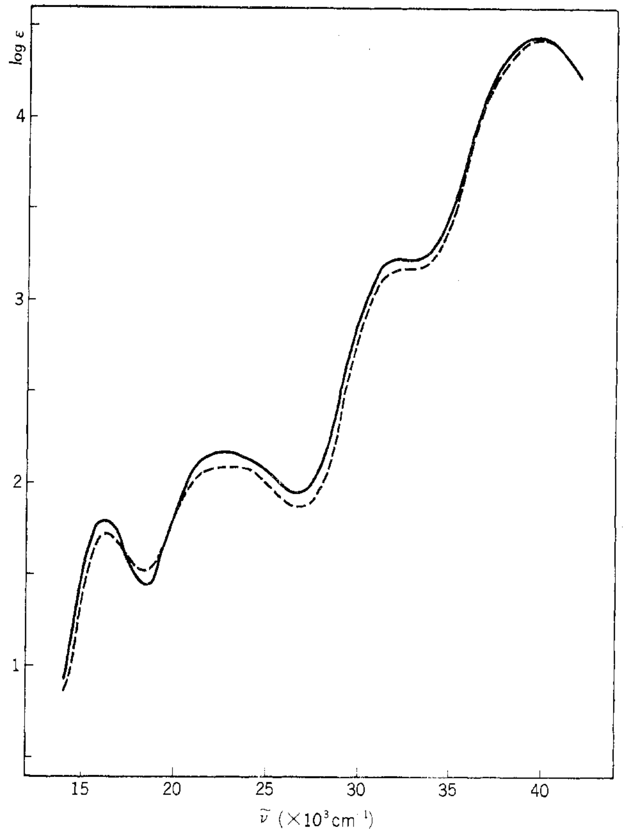


Figure 7. Absorption spectra of the *trans*-(*RS*)-Co(*meso*-5,6-dmtrien)Cl_2^+ ion (———) and a mixture of trans-*RS* and trans-*RR,SS* forms (— — —).

Table I. Chemical Shifts (ppm) for Pmr Spectra[a] of Diacido(L)cobalt(III) Complexes; L = *meso*-5,6-dmtrien

Complexes	C-CH_3	-$NHCH_2$C,	-NHCHCH_3
trans-(*RS*)-Co(L)Cl_2^+ [b]	1.36	2.6	4.0
trans-(*RR,SS*)-Co(L)Cl_2^+ [b]	1.33, 1.40	?	
cis-β-(*RS,SR*)-Co(L)$(NO_2)_2^+$ [c]	1.33, 1.46	2.9	3.7
trans-(*RS*)-Co(L)$(NO_2)_2^+$ [c]	1.48	?	
trans-(*RR,SS*)-Co(L)$(NO_2)_2^+$ [c]	1.09, 1.48	?	

[a] Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was the internal standard reference. [b] In methanol-d_4. [c] In D_2O.

We attempted to obtain the optically active Δ-*cis*-β-(*RS*)-Co(*meso*-5,6-dmtrien)Cl_2^+ ion from the above dinitro complex by the reaction with HCl under a variety of conditions but could not succeed even in methanol solution at −15°. These findings are consistent with the results mentioned above. In acidic media, the Δ-*cis*-β-(*RS*)-dichloro ion, if formed in the initial stage of reaction, must rapidly isomerize, at equilibrium, to the intrinsically optically inactive *trans*-(*RS*)-dichloro ion, and the optical activity of the complex would be lost.

From a methanol solution of *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, green crystals of the trans isomer were recovered after the refluxing of 18 hr. The infrared and electronic absorption spectra of the present trans complex were found to be slightly different from those of the original complex. The absorption curves of these trans complexes are shown in Figure 7. A similar product was also obtained from a methanol solution containing 2% of 2,6-lutidine by a similar procedure. Under these conditions, especially in the latter case, the configuration of secondary N centers is readily inverted. The pmr spectrum of the present trans

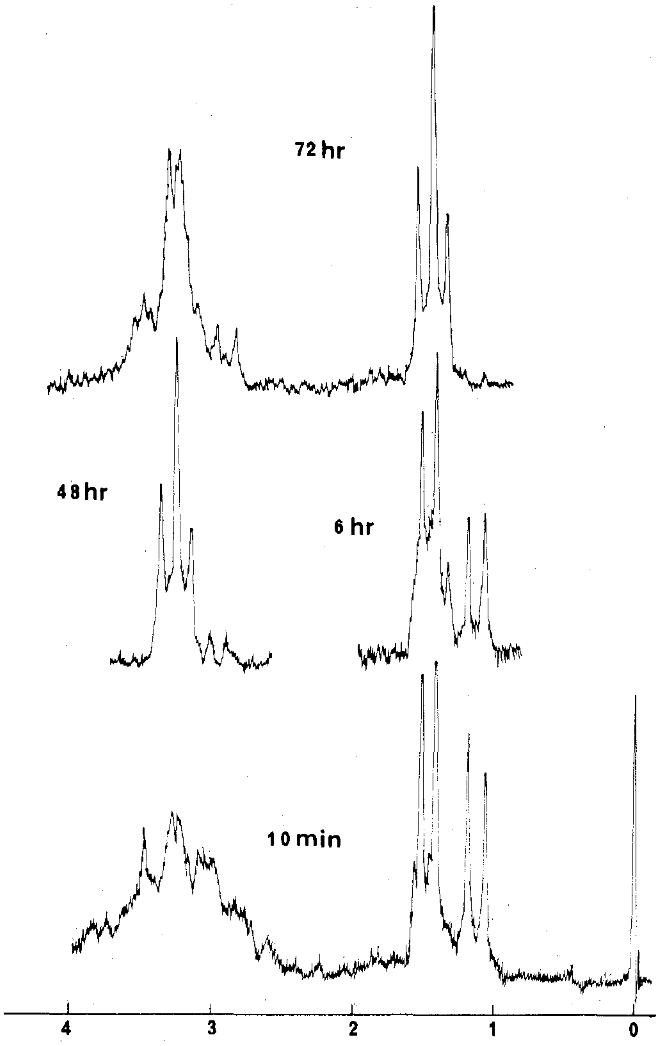


Figure 8. 60-MHz pmr spectrum of a mixture of the *trans*-(*RS*)- and *trans*-(*RR,SS*)-Co(*meso*-5,6-dmtrien)$(NO_2)_2^+$ ion and spectral changes in the isomerization reaction to the cis-β-*RS,SR* form in D_2O.

complex exhibited three doublets in the *C*-methyl resonance region as is shown in Figure 3b. One of the doublets coincided the signals for the trans-*RS* isomer shown in Figure 3a. The other two doublets, with almost equal intensities, could be assigned to the signals for the trans-*SS,RR* isomer. Therefore, the *trans*-(*RS*)-dichloro ion was partially isomerized to the *trans*-(*SS,RR*)-dichloro ion and these ions coexist in neutral or basic methanol solution in equilibrium. The assignments of the pmr signals of *meso*-5,6-dmtrien complexes are summarized in Table I.

The *trans*-(*RS*)-Co(*meso*-5,6-dmtrien)Cl_2^+ complex was converted to the *trans*-dinitro complex by adding $NaNO_2$ in methanol. The absorption curve of the present dinitro complex is shown in Figure 2. The maximum of the second peak was observed at 28,800 cm^{-1}, indicating the trans configuration of nitro groups coordinated. The product, obtained as above, was a mixture of the *trans*-(*RS*)- and *trans*-(*SS,RR*)-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4. The basic properties of $NaNO_2$ should promote the inversion of coordinated secondary amine groups. The pmr spectrum of the *trans*-dinitro complex is shown in Figure 8. The two doublets of large intensity are assigned to the methyl groups of the trans-*SS,RR* isomer, and one methyl doublet of small intensity is assigned to those of the trans-*RS* isomer.

It was further observed that the above trans mixture isomerizes very slowly to the cis-β-*RS,SR* form in aqueous solution. As is shown in Figure 8, the initial three doublets gradually diminished and two doublets, which were overlapped to give three peaks, began to emerge. The final spectrum was the same as that of the *cis*-β-(*RS,SR*)-dinitro complex ion. The relationships of several isomers of the *meso*-5,6-dmtrien complexes are summarized in Scheme I.

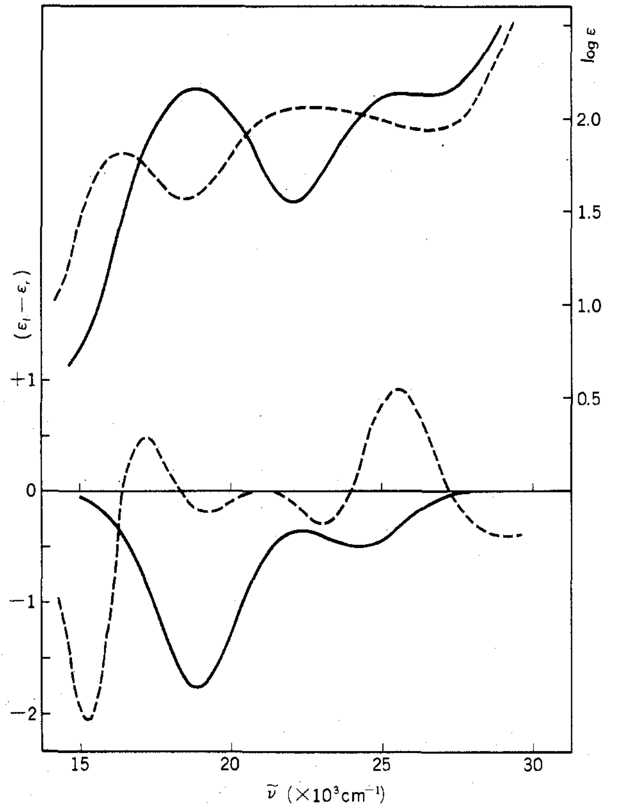
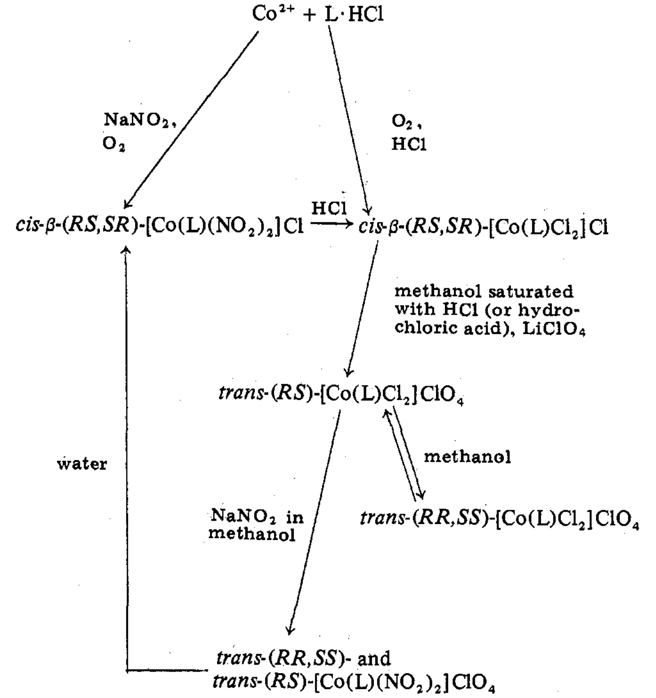


Figure 9. Absorption and CD spectra of the Δ-*cis*-β-(*RS*)-Co[(2*S*,5*R*,6*S*,9*S*)-tmtrien]Cl_2^+ ion (———) in concentrated hydrochloric acid and *trans*-(*SS*)-Co[(2*S*,5*R*,6*S*,9*S*)-tmtrien]Cl_2^+ ion (— — —) in methanol.

Structures and Rearrangements of (2*S*,5*R*,6*S*,9*S*)-tmtrien

Scheme I. Synthetic Routes for Several Cobalt(III) Complexes of *meso*-5,6-dmtrien (L Represents *meso*-5,6-dmtrien)



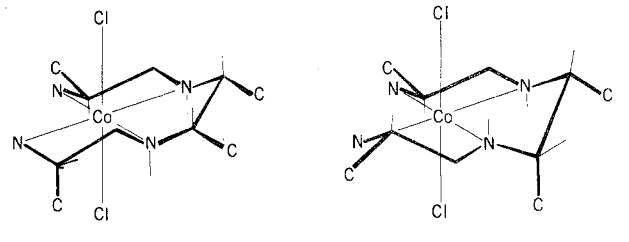
Complexes. In order to compare the geometries and reaction behaviors of the *meso*-5,6-dmtrien complexes, (5*R*,6*S*)-dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane [(2*S*,5*R*,6*S*,9*S*)-tmtrien] was employed. This ligand has the *meso*-bn moiety at the central diamine linkage. The asymmetric carbon centers of both side arms, derived from (*S*)-alanine, have the same *S* configuration. If the methyl groups on the terminal chelate rings favored the equatorial orientation, in a similar manner to the methyl group of propylenediamine chelate[13] or those of methyl substituted triens,[3-6] the terminal chelate rings should adopt the δ conformations. Hence, this tetraamine was expected to take some specific geometries upon coordination.

The CD spectrum of the dinitrocobalt(III) complex with (2*S*,5*R*,6*S*,9*S*)-tmtrien, shown in Figure 2, has a dominant negative peak in the first absorption band region, indicating the Δ absolute configuration. It is most unlikely that the (2*S*,5*R*,6*S*,9*S*)-tmtrien, which prefers the δ configuration with regard to the terminal chelate rings, would coordinate stereospecifically in the Δ-cis-α configuration, since the terminal chelate rings for the Δ-cis-α isomer should have the λ conformations, based on the X-ray analysis data for the cis-α isomers.[14,15] Hence, the dinitrocobalt(III) complex of (2*S*,5*R*,6*S*,9*S*)-tmtrien also has the Δ-cis-β structure, either Δ-β-*RS* or Δ-β-*RR*.

In determining the actual structure of the (2*S*,5*R*,6*S*,9*S*)-tmtrien complex, it was noticed that the conformations of the terminal chelate rings coplanar with the central chelate ring are antimeric between the Δ-cis-β-*RS* and Δ-cis-β-*RR* geometries (*cf.* Figure 5), the δ conformation for the former and the λ for the latter. It is very probable that (2*S*,5*R*,6*S*,9*S*)-tmtrien adopts the Δ-cis-β-*RS* form, because this ligand prefers the δ conformation for the side chelate rings.

The CD curve of the dinitro complex with (2*S*,5*R*,6*S*,9*S*)-tmtrien closely resembles the CD curve for the resolved *meso*-5,6-dmtrien complex (Figure 2). These curves are characterized by a single dominant negative CD peak in the first absorption band region. It has been shown that optically active forms of *cis*-dinitrocobalt(III) complexes with trien or its derivatives, both cis-α and cis-β geometries, exhibit two CD peaks with opposite signs in this region, a dominant peak in the lower wave number side and a small peak in the higher wave number side.[6] The only exception to this rule was the complex with (2*S*,5*S*,9*S*)-trimethyltriethylenetetramine which showed only one negative CD peak in the first absorption band region.[6] The CD pattern of this complex is markedly similar to that of the *meso*-5,6-dmtrien and (2*S*,5*R*,6*S*,9*S*)-tmtrien complexes. We consider that this CD pattern (see Figure 2) may be ascribed to the Δ-cis-β-*RS* configuration which has the axial methyl group on the central diamine linkage. The axial methyl group should orient adjacent to the "angular" secondary N atom, as shown in Figure 5a. Further, it was observed that the Δ-cis-β-*RS* isomers with the axial methyl group show two CD peaks with opposite signs in the NO_2 specific absorption band region;[6] in contrast to that the usual Δ-cis-β-*RS* isomers (with no axial methyl group) show the single dominant positive CD peak in this region.[6] It is interesting to note that the axial methyl group on the chelate ring obviously affects the CD pattern of the complexes.

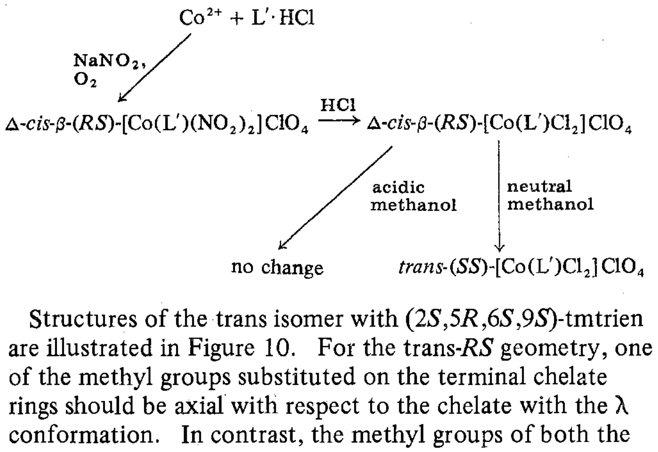
In contrast to the *meso*-5,6-dmtrien complex, the Δ-cis-β-(*RS*)-[Co(2*S*,5*R*,6*S*,9*S*)-tmtrien)$(NO_2)_2$]ClO_4 was converted to the corresponding dichloro complex with full retention of optical activity when treated with concentrated hydrochloric acid. The absorption and CD curves for the *cis*-β-dichloro complex, obtained as above, are shown in Figure 9. The CD pattern of the present complex showed the characteristics for the dichloro complex of Δ-cis-β-*RS* configuration which has been described previously.[5] This cis-β isomer did not change to the trans complex in acidic methanol, and the addition of perchlorate ion yielded perchlorate salt of the original Δ-cis-β isomer. Under neutral or basic conditions, however, the purple methanol solution of this cis-β ion changed to green solution, and the absorption and CD spectra of the solution, shown in Figure 9, suggested that the trans-*SS* had formed, since these curves resembled those of *trans*-(*SS*)-dichloro complexes with trien derivatives.[4] The synthetic routes for the (2*S*,5*R*,6*S*,9*S*)-tmtrien complexes are summarized in Scheme II.



(RS) (SS)

Figure 10. Possible structures of the *trans*-Co[(2*S*,5*R*,6*S*,9*S*)-tmtrien]Cl_2^+ ion trans-*RS* and trans-*SS*.

Scheme II. Synthetic Routes for Several Cobalt(III) Complexes, (2*S*,5*R*,6*S*,9*S*)-tmtrien [L′ Represents (2*S*,5*R*,6*S*,9*S*)-tmtrien]



Structures of the trans isomer with (2*S*,5*R*,6*S*,9*S*)-tmtrien are illustrated in Figure 10. For the trans-*RS* geometry, one of the methyl groups substituted on the terminal chelate rings should be axial with respect to the chelate with the λ conformation. In contrast, the methyl groups of both the terminal diamine rings are situated simultaneously in the equatorial orientation for the trans-*SS* geometry, though one methyl group is axially oriented at the central chelate ring.

In the case of the *meso*-5,6-dmtrien complex, the trans-*RS* and trans-*SS*,*RR* isomers might have comparable stabilities, because the pmr intensities for these isomers are similar for both the dichloro and dinitro complexes (see Figures 4 and 9). Since both additional methyl groups of (2*S*,5*R*,6*S*,9*S*)-tmtrien are situated equatorially, the trans-*SS* form with this ligand would be relatively stable. However, the stability of the trans-*RS* form of the (2*S*,5*R*,6*S*,9*S*)-tmtrien complex would be reduced because of the axial methyl group attached to one of the side diamine linkages. It may be reasonable, therefore, that the trans-*RS* isomer of the Co[(2*S*,5*R*,6*S*,9*S*)-tmtrien]Cl_2^+ ion has not been produced from the Δ-cis-β-*RS* isomer under the acidic condition, which requires the retention of configuration with regard to the secondary N centers in the reaction, and that the trans-*SS* isomer has been ob-

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(13) A. M. Sargeson, *Transition Metal Chem.*, 3, 303 (1966).

(14) M. Dwyer and I. E. Maxwell, *Inorg. Chem.*, 9, 1459 (1970).

(15) M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 28, 457 (1972).

tained from the same starting material under the neutral or basic conditions which permit the inversion of the configuration at the secondary N centers.

Registry No. Chloroacetyl chloride, 79-04-9; butane-2,3-diamine, 563-86-0; *N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-35-2; *meso-N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-36-3; (±)-*N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-37-4; *meso-N,N'*-bis(glycyl)butane-2,3-diamine·2HCl, 39721-38-5; *meso*-5,6-dmtrien·4HCl, 39721-39-6; carbobenzoxy-(*S*)-alanyl azide, 17350-66-2; *meso*-butane-2,3-diamine, 20759-15-3; *N,N'*-bis[carbobenzoxy-(*S*)-alanyl]-*meso*-butane-2,3-diamine, 39721-42-1; (2*S*,5*R*,6*S*,9*S*)-tmtrien·4HCl, 39721-43-2; *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]Cl, 22850-35-7; *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]I, 39721-45-4; [(+)-*cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$] α-bromo-*d*-camphor-π-sulfonate, 39836-74-3; (−)-*cis*-β-[Co(*meso*-5,6-dmtrien$(NO_2)_2$]ClO_4, 39721-14-7; *cis*-β-[Co(*meso*-5,6-dmtrien)Cl_2]Cl, 39721-15-8; *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, 39721-16-9; *trans*-(*RR,SS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, 39721-17-0; *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4, 39721-18-1; *trans*-(*RR,SS*)-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4, 39900-58-8; Δ-*cis*-β-(*RS*)-[Co(tmtrien)$(NO_2)_2$]ClO_4, 39721-19-2; Δ-*cis*-β-(*RS*)-[Co(tmtrien)Cl_2]ClO_4, 39721-20-5; *trans*-(*SS*)-[Co(tmtrien)Cl_2]ClO_4, 39721-21-6.

Contribution from the Evans Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Conformational Studies of Metal Chelates. I. Intra-ring Strain in Five- and Six-Membered Chelate Rings

LOUIS J. DeHAYES and DARYLE H. BUSCH*

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Strain energies are calculated for a series of bidentate chelate species which may be formulated as $M(L)a_4$, where a is chloride and L is ethylenediamine (en), trimethylenediamine (tn), and various *N*- and *C*-methyl-substituted derivatives. Minimum energy conformations are deduced and their conformational enthalpies and free energies are calculated using the Newton–Raphson minimization scheme developed by Boyd. For unsubstituted en, the principal nonbonded repulsions are those between N–H and C–H equatorial–axial pairs. In the pn complex, equatorial orientation of the methyl group leads to a decrease in strain energy as compared to the en complex, because (1) one C–H···N–H repulsion is removed and (2) most of the CH_3 interactions are attractive. An axial CH_3 is destabilized by increases in the torsional bond angle distortion and nonbonded repulsions; the chelate ring is severely flattened; the Co–N and N–C bonds elongated and the Cl–Co–Cl and N–Co–Cl angles distorted. Axial and equatorial *N*-CH_3's are not so strongly distinguished and both produce increased Co–N and N–C bonds. Equatorial *N*-CH_3 increases five-membered ring puckering while axial *N*-CH_3 decreases it. The minimum energy conformations for six-membered rings have larger bond angles and longer bonds. Chair rings are more stable than twist because of torsional distortions in the latter. The distinction between axial and equatorial methyls is greater for six-membered rings. For a twist ring, an axial orientation is favored for *N*-CH_3. Multiple substitution is considered.

Introduction

In the years subsequent to the pioneering work of Corey and Bailar[1] a number of studies have appeared utilizing computational schemes to predict and rationalize the conformational behavior of chelates in metal complexes. The most general of these studies were those of Gollogly and Hawkins on mono-, bis-, and tris-chelate complexes of ethylenediamine, propylenediamine, *N*-methylethylenediamine, and trimethylenediamine.[2]

The approach that they used in their calculations was based on the fact that for a chelate ring there are $3N - 6$ independent variables which specify the exact conformation of the ring. In their calculations they held all bond lengths constant and then systematically varied the other parameters over a given range. At each interval they would calculate an energy for that particular conformation. These energies could then be plotted as a function of the different variables and energy minima located.

There are a number of difficulties with this approach. First, although the variables they chose may be independent of each other, the energy is not an independent function of each individual variable. Second, they have only considered the atoms in the chelate ring skeleton as having the freedom to distort. Hydrogens bound to the chelate ring are not allowed to move independently. An additional criticism is that their energy values cannot be related to experimental energies since they have neglected entropies and, at best, their values are enthalpies not free energies. Despite these criticisms, their work was valuable in that it gave us some feel for the flexibility and range of conformations which are accessible to a chelate.

A second and more rigorous approach to the computation of conformational energies and geometries utilized a Newton–Raphson minimization scheme developed by Boyd[3] and was applied to metal chelates by Snow, *et al.*[4] It is this second approach which we also have chosen to use, with the notable addition of an entropy calculation which allows us to calculate not just conformational enthalpies but relative conformational free energies.

Our aim in using these techniques of conformational analysis in the study of transition metal chelate complexes was (1) to identify those structural features which lead to "preferred" structures and (2) to calculate the relative free energy differences which accompany changes in these particular structural features.

With this dual aim in mind, we undertook a systematic

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(1) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(2) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969); **9**, 576 (1970); **10**, 317 (1971); **11**, 156 (1972).

(3) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

(4) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970); D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *ibid.*, **92**, 3617 (1970).