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Preparation and Stereochemistry of a New Isomer (Λ-*cis*-β) of Cobalt(III) Complexes with (3*S*,8*S*)-3,8-Dimethyl-1,4,7,10-tetraazadecane[1]

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Carbonatocobalt(III) complex of (3*S*,8*S*)-3,8-dimethyl-1,4,7,10-tetraazadecane((3*S*,8*S*)-dimetrien) was prepared from *trans*-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$ by treating with carbonate or hydrogencarbonate ion. The carbonato complex was assigned to the Λ-*cis*-β configuration, a novel geometry for the (3*S*,8*S*)-dimetrien complexes. The visible absorption, circular dichroism, and proton magnetic resonance data were obtained for the Λ-β and other carbonato complexes. Preparation and assignment of dinitrocobalt(III) complex with (3*S*,8*S*)-dimetrien are given. The relative stabilities of the four isomers of (3*S*,8*S*)-dimetrien complexes (Λ-*cis*-α, Λ-*cis*-β, Δ-*cis*-β, and *trans*) are discussed qualitatively.

Five stereoisomers are possible for the dianionocobalt(III) complexes of triethylenetetramine, one *cis*-α, two *cis*-β, and two *trans*. Of these isomers, the central metal ion is a chiral center except for one of the *trans* isomers (*meso-trans*). When a chiral tetramine obtained by introducing methyl group(s) into the carbon chain of trien is employed, the stereoisomers of cobalt(III) complex are sufficiently affected by the steric effects of the methyl substituents and give rise to the isomers of particular geometry and chirality.[2–5] Three isolated isomers of dichloro- and dinitrocobalt(III) complexes with (3*S*,8*S*)-3,8-dimethyl-1,4,7,10-tetraazadecane (abbreviated as (3*S*,8*S*)-dimetrien), for instance, have the Λ-*cis*-α, Δ-*cis*-β and *trans* geometries, in which the absolute configurations of the two coordinated secondary nitrogen atoms have the combination of (*R*,*R*),[6] (*R*,*S*), and (*S*,*S*), respectively.[2,3]

The stereoselectivity found in the formation of the (3*S*,8*S*)-dimetrien complexes has been ascribed to the preferential equatorial orientation of the methyl groups with respect to the five-membered chelate rings.[2,3] X-Ray diffraction studies demonstrated the preference of equatorial orientation of the methyl groups for the three isomers of dinitrocobalt(III) complexes.[7–9] So far as the stereoisomers with the equatorial methyl groups are concerned, the possible isomers of (3*S*,8*S*)-dimetriencobalt(III) complex are those mentioned above (Λ-*cis*-α, Δ-*cis*-β and *trans*).

In the course of attempts to convert the *trans*-dichlorocobalt(III) of (3*S*,8*S*)-dimetrien into either of the *cis*-dichloro isomers, we have isolated a carbonato complex, which could be assigned to the Λ-*cis*-β configuration based on the data of circular dichloism (CD) and proton magnetic resonance (PMR). In the present report, the preparation and stereochemistry of the carbonatocobalt(III) complex of (3*S*,8*S*)-dimetrien will be described.

Experimental

Λ-β-Carbonato((3S,8S)-3,8-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate(Λ-β-[CoCO$_3$((3S,8S)-dimetrien)]ClO$_4$). To a solution of *trans*-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$[2] (0.50 g) in water (10 ml) was added lithium carbonate (0.20 g) and the mixture was heated for 30 min on a water bath (80 °C). Excess lithium carbonate was filtered off and the filtrate was evaporated to about 5 ml on a water bath. Five ml of methanol was added and the resultant precipitates were immediately removed by filtration. Solid lithium perchlorate (1.5 g) was added and dissolved. The sides of the vessel were scratched with a glass rod until red-violet crystals appeared. After being cooled in a refrigerator overnight, the crystals were collected, washed with methanol and ether, and air-dried. Yield, 0.25—0.30 g. The product was recrystallized from a small volume of water by adding methanol. Found: C, 27.32; H, 5.77; N, 13.75%. Calcd for [CoCO$_3$(C$_8$H$_{22}$N$_4$)]ClO$_4$: C, 27.57; H, 5.65; N, 14.27%.

This carbonato complex can be obtained in acidic condition as follows:

trans-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$ (0.40 g) was dissolved in water (10 ml) and aquated for 30 min on a water bath (60 °C). To the resultant orange-red solution was added NaHCO$_3$ (0.20 g), the solution being left to stand at room temperature for 15 min. It was then evaporated to a volume of 5 ml, and methanol (5 ml) and solid lithium perchlorate (1.0 g) were added in succession. After being left to stand in a refrigerator overnight, the crystals which separated were filtered off, washed with methanol and ether, and air-dried. Yield, 0.25 g.

Δ-β-Carbonato((3S,8S)-3,8-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Perchlorate (Δ-β-[CoCO$_3$((3S,8S)-dimetrien)]ClO$_4$·2H$_2$O. Crude Δ-*cis*-β-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$[2] (1.30 g) was added to 20 ml of 0.01 M HClO$_4$ and dissolved by vigorous shaking. After shaking for 3 min, the undissolved materials (mainly Λ-*cis*-α-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$) were removed by filtration. The filtrate was heated for 5 min on a water bath (70 °C), and 0.60 g of NaHCO$_3$ was added in small portions. Solid sodium perchlorate (1.0 g) was added and the deep-red solution was kept in a refrigerator overnight. Deep-red crystals were collected, washed with cold water and ethanol, and air-dried. Yield, 0.58 g. More crystals were recovered from the above filtrate by evaporating on a rotary evaporator. (0.20 g). All the products were recrystallized from warm water. Found: C, 25.33; H, 6.08; N, 13.28%. Calcd for [CoCO$_3$(C$_8$H$_{22}$N$_4$)]ClO$_4$·2H$_2$O: C 25.21; H, 6.11; N, 13.07%.

Λ-β-[CoCO$_3$((3S,8S)-dimetrien)]ClO$_4$→trans-[CoCl$_2$((3S,8S)-dimetrien)]ClO$_4$. Λ-β-[CoCO$_3$((3*S*,8*S*)-dimetrien)]ClO$_4$ (0.20 g) was dissolved in 5 M HCl (5 ml) and LiClO$_4$ (0.5 g) was added. Green needle-like crystals were obtained on standing at room temperature. The product was identified with *trans*-[CoCl$_2$((3*S*,8*S*)-dimetrien)]ClO$_4$.

Λ-β-[CoCO$_3$((3S,8S)-dimetrien)]ClO$_4$ → trans-[Co(NO$_2$)$_2$-((3S,8S)-dimetrien)]ClO$_4$. Λ-β-[CoCO$_3$((3*S*,8*S*)-dimetrien)]ClO$_4$ (1.20 g) was added in small portions to 5 ml of 2 M HClO$_4$. The complex dissolved with effervescence to give an orange-red solution. Sodium nitrite (0.50 g) was added in small portions, and the solution was heated for 5 min on

a water bath (70 °C). After being cooled to room temperature, solid lithium perchlorate (1.0 g) was added and dissolved. The resultant solution was allowed to stand in a refrigerator overnight and the crystals separated were filtered off, washed with water, ethanol, and acetone. Yield, 0.50 g. The product recrystallized from warm water was identified with *trans*-$[Co(NO_2)_2((3S,8S)$-dimetrien$)]ClO_4$.

Trans-*$CoCl_2((3S,8S)$-dimetrien$)^+ \rightarrow$ Λ-β-$CoCO_3((3S,8S)$-dimetrien$)^+$.* A weighed sample (*ca.* 25 mg) of *trans*-$[CoCl_2((3S,8S)$-dimetrien$)]ClO_4$ was dissolved in 20 ml of 0.01 M $HClO_4$ in a 25 ml volumetric flask. After the solution had been kept at room temperature for 1 h, 0.050 g of $NaHCO_3$ was added and dissolved. After 30 min the final volume was adjusted to 25 ml by adding water, and the visible absorption and CD spectra of the solution were recorded. The spectra agreed with those of the isolated Λ-β-$[CoCO_3((3S,8S)$-dimetrien$)]ClO_4$ within experimental error.

*Δ-*cis*-β-$CoCl_2((3S,8S)$-dimetrien$)^+ \rightarrow$ Δ-β-$CoCO_3((3S,8S)$-dimetrien$)^+$.* A weighed sample (*ca.* 17 mg) of Δ-*cis*-β-$[CoCl_2((3S,8S)$-dimetrien$)]ClO_4$ was dissolved in 20 ml of 0.01 M $HClO_4$ in a 25 ml volumetric flask, and the solution was stood at room temperature for 15 min. 0.050 g of $NaHCO_3$ was added and the volume was adjusted to 25 ml by adding water. After being left to stand for 30 min, the visible absorption and CD spectra of the resultant solution were recorded. The spectral data were almost identical with those for the isolated Δ-β-$[CoCO_3((3S,8S)$-dimetrien$)]ClO_4 \cdot 2H_2O$.

*Λ-*cis*-α-$CoCl_2((3S,8S)$-dimetrien$)^+ \rightarrow$ Λ-α-$CoCO_3((3S,8S)$-dimetrien$)^+$.* A weighed sample (*ca.* 17 mg) of Λ-*cis*-α-$[CoCl_2((3S,8S)$-dimetrien$)]ClO_4$ was dissolved in 20 ml of 0.01 M $HClO_4$ in a 25 ml volumetric flask. The solution was allowed to stand for 16 h at room temperature, followed by the addition of 0.050 g of $NaHCO_3$. The final volume was adjusted to 25 ml by adding water, and the visible absorption and CD spectra of the solution were measured.

*Λ-*cis*-β-Dinitro((3S,8S)-3,8-dimethyl-1,4,7,10-tetraazadecane)-cobalt(III) Chloride (Λ-*cis*-β-$[Co(NO_2)_2((3S,8S)$-dimetrien$)]Cl \cdot 0.5\,H_2O \cdot 0.5\,CH_3OH$).* (3*S*,8*S*)-Dimetrien·4HCl (1.60 g), $LiOH \cdot H_2O$ (0.63 g), $CoCl_2 \cdot 6H_2O$ (1.09 g) and $NaNO_2$ (0.70 g) were dissolved successively in 50 ml of methanol and the resultant sulution was aerated for 1 h at room temperature. The white precipitates which appeared were filtered off, and the filtrate was transferred into a beaker and heated on a water bath at 80 °C. In a few minutes the solution began to boil and brown crystals began to separate. Boiling was continued for 30 min, with occasional addition of a few mililiters of methanol to maintain the volume at *ca.* 50 ml. The mixture was cooled to room temperature, and then stored in a refrigerator overnight. The crystals separated were collected and washed with methanol. Yield, 1.02 g. The crude product was dissolved in water (15—20 ml) at 70 °C, and the undissolved impurities were removed by filtration. An equal volume of methanol was added to the filtrate, and cooled in a refrigerator overnight. The brown crystals were filtered off, washed with methanol, and air-dried. Yield, 0.70 g. Found: C, 26.87; H, 6.43; N, 21.21%. Calcd for $[Co(NO_2)_2(C_8H_{22}N_4)]Cl \cdot 0.5H_2O \cdot 0.5(CH_4O)$: C, 26.50; H, 6.41; N, 21.82%.

Measurements. The absorption spectra were obtained with a Shimadzu MPS-50 L Spectrophotometer. The circular dichroism spectra were measured with a JASCO J-20 automatic spectropolarimeter. The 60 MHz proton magnetic resonance spectra were obtained with a Hitachi R-20 B spectrometer in D_2O solutions using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.

Results and Discussion

It is necessary to adopt basic reaction conditions in order to convert the *trans*(*S*,*S*)-$[CoCl_2((3S,8S)$-dimetrien$)]^+$ ion into either the Λ-α(*R*,*R*)- or the Δ-β(*R*,*S*)-$[CoCl_2((3S,8S)$-dimetrien$)]^+$ ion, since the reaction proceeds with the inversion of configuration at the coordinated secondary nitrogen center, which is usually promoted by base. We thus applied the method employed by Sargeson and Searle for the conversion of the *cis*-α-$[CoCl_2(trien)]^+$ into the β-$[CoCO_3(trien)]^+$ ion with carbonate ion.[10]

The carbonato complex, $[CoCO_3((3S,8S)$-dimetrien$)]ClO_4$, complex (I), was obtained by the reaction of *trans*-$[CoCl_2((3S,8S)$-dimetrien$)]ClO_4$ with excess Li_2CO_3. Its visible absorption and circular dichroism (CD) spectra are given in Fig. 1. The CD curve exhibits only a large positive band in the first absorption band region, which can be ascribed to the Λ configuration about the central cobalt(III) atom. This leads to the conclusion that complex (I) has the Λ-α configuration, if the possible isomers of *cis* geometry are restricted to Λ-α and Δ-β.

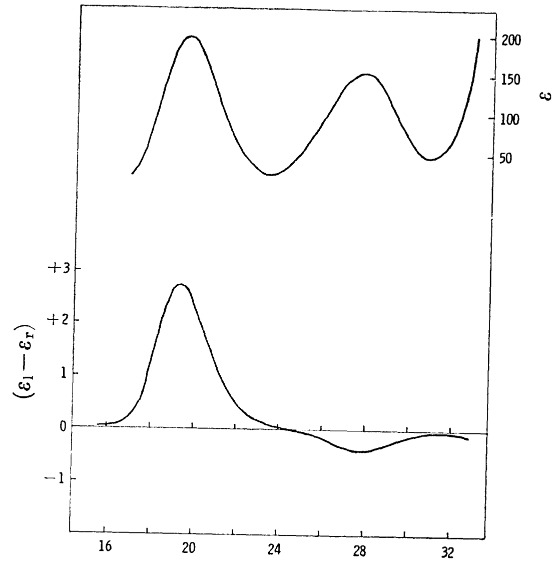

Fig. 1. Visible absorption and CD spectra of complex (I) (Λ-β-$[CoCO_3((3S,8S)$-dimetrien$)]ClO_4$).

However, attempts to obtain the Λ-*cis*-α isomer of dichloro and dinitro complex, (Eqs. (1) and (2)), were found to give the corresponding *trans* isomer. Under the acidic conditions in (1) and (2), the configuration of the coordinated secondary N centers should be difinitely retained. This indicates that the secondary N atoms of complex (I) take the same configurations as the *trans* isomers, *i.e.* (*S*,*S*).

$$\text{Complex (I)} \xrightarrow{\text{HCl}} \xrightarrow{(\text{LiClO}_4)} trans\text{-}[CoCl_2((3S,8S)\text{-dimetrien})]ClO_4 \qquad (1)$$

$$\text{Complex (I)} \xrightarrow{\text{HClO}_4} \xrightarrow{\text{NaNO}_2} \xrightarrow{(\text{LiClO}_4)} trans\text{-}[Co(NO_2)_2((3S,8S)\text{-dimetrien})]ClO_4 \qquad (2)$$

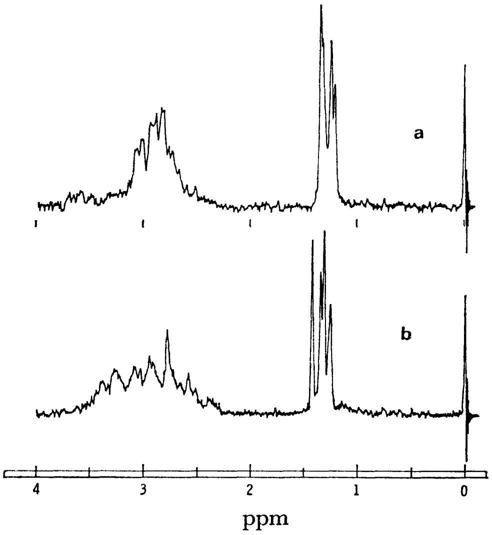

Fig. 2. PMR spectra of $[CoCO_3((3S,8S)\text{-dimetrien})]^+$ ion; (a) Λ-β isomer, and (b) Δ-β isomer.

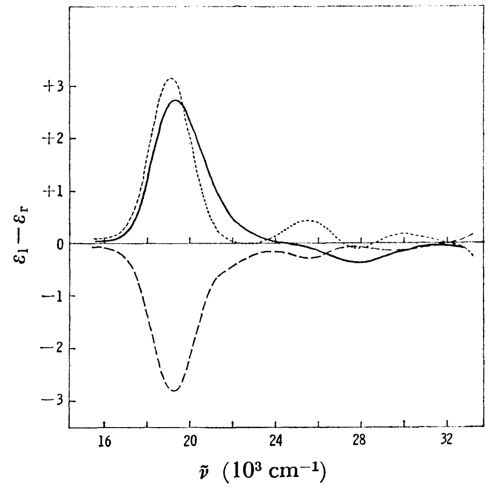

Fig. 3. CD curves for the carbonato complexes formed by the reactions of Eqs. (3) (----), (4) (———), and (5) (——).

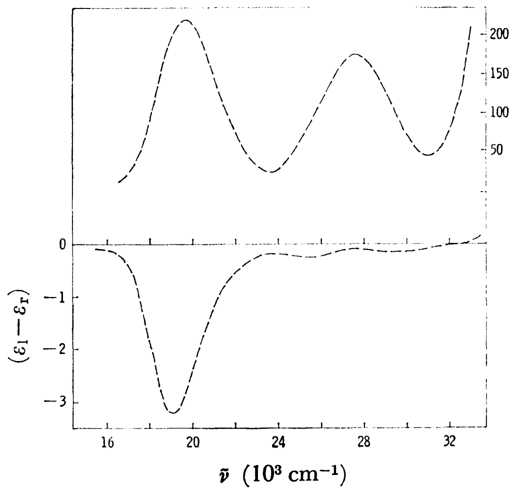

Fig. 4. Visible absorption and CD spectra of Δ-β-$[CoCO_3((3S,8S)\text{-dimetrien})]ClO_4 \cdot 2H_2O$.

The proton magnetic resonance (PMR) measurements would be useful for deciding whether (I) has C_2 axis or not. The PMR spectrum of (I) obtained in D_2O is given in Fig. 2(a), which exhibits two overlapped doublet in the 1.2—1.4 ppm region, assignable to the C-methyl groups of the ligand. The PMR spectrum corresponds, therefore, to that for the *cis*-β geometry and not for the *cis*-α form. Consequently, the absolute configuration of (I) can be determined to be the Λ-β(*S*,*S*), which has been confirmed by X-ray crystallographic study.[11]

Sargeson and Searle provided an alternative method for preparing carbonatocobalt(III) complexes with trien.[10] The *cis*-α and *cis*-β-dichloro complexes were aquated completely and then treated with hydrogencarbonate ion with retention of the configurations. A similar treatment was carried out for the Λ-*cis*-α, Δ-*cis*-β and *trans* isomers of $CoCl_2((3S,8S)\text{-dimetrien})^+$ ion (Eqs. (3)—(5); L indicates the (3*S*,8*S*)dimetrien).

$$\Lambda\text{-}cis\text{-}\alpha\text{-}CoCl_2(L)^+ \xrightarrow{H_3O^+}$$

$$\Lambda\text{-}cis\text{-}\alpha\text{-}CoCl(H_2O)(L)^{2+} \xrightarrow{HCO_3^-} \Lambda\text{-}\alpha\text{-}CoCO_3(L)^+ \quad (3)$$

$$\Delta\text{-}cis\text{-}\beta\text{-}CoCl_2(L)^+ \xrightarrow{H_3O^+}$$

$$\Delta\text{-}cis\text{-}\beta\text{-}CoCl(H_2O)(L)^{2+} \xrightarrow{HCO_3^-} \Delta\text{-}\beta\text{-}CoCO_3(L)^+ \quad (4)$$

$$trans\text{-}CoCl_2(L)^+ \xrightarrow{H_3O^+}$$

$$\text{(red complex)} \xrightarrow{HCO_3^-} \Lambda\text{-}\beta\text{-}CoCO_3(L)^+ \quad (5)$$

The carbonato complexes produced *in situ* according to Eqs. (3) and (4) have a positive and negative CD band, respectively, in the first absorption band region (Fig. 3). If we assume the complete retention of the configurations these CD curves can be ascribed to the Λ-α and Δ-β isomer of $[CoCO_3((3S,8S)\text{-dimetrien})]^+$ ion, respectively. The carbonato complex derived from the *trans* dichloro complex (Eq. (5)) showed the CD curve depicted in Fig. 3, which is identical with that of complex (I) (or Λ-β isomer) shown in Fig. 1. Although both complexes, which result from reactions (3) and (5), have a CD pattern attributable to the Λ configuration, details of the curves apparently differ from each other.

Attempts to isolate the crystalline product of the Λ-α isomer, formed *in situ*, were unsuccessful because of high solubility of the complex. However, the Δ-β and Λ-β isomers could be easily obtained as perchlorate according to reactions (4) and (5). The Δ-β isomer exhibited the PMR spectrum which had two doublets due to the methyl groups in the 1.2—1.4 ppm region (Fig. 2(b)). The visible absorption and CD spectra of this complex are given in Fig. 4. The CD curve of the crystalline product of Δ-β isomer in Fig. 4 is slightly different from that in Fig. 3, probably due to a small contamination of the other complex in the latter case. The Λ-β isomer obtained under acidic condition (Eq. (5)) showed identical CD and PMR spectra for the Λ-β(*S*,*S*) isomer obtained in the basic medium (complex (I)) (Figs. 1 and 2(a)).

The molecular structure of the Λ-β-$CoCO_3$ ((3*S*,8*S*)-dimetrien)$^+$ ion determined by the X-ray diffraction

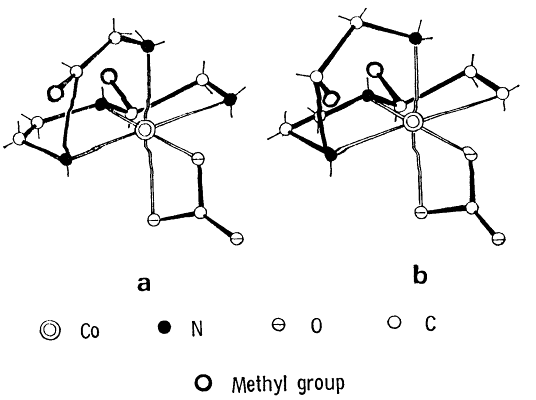

Fig. 5. Possible structures for Λ-β-[$\mathrm{CoCO_3}$((3S,8S)-dimetrien)]$^+$ ion.

study is illustrated in Fig. 5(a), in which the methyl group on the chelate ring (A) which is not coplanar with the central chelate ring has an unusual axial orientation.[11] An alternative structure of the Λ-β configuration, both the methyl groups being equatorial, is also shown in Fig. 5(b). Chelate ring (A) in the latter structure takes the δ conformation, the methyl group being able to take an equatorial orientation. Chelate ring (A) in the former structure has alternatively the Λ conformation. It seems that in solution both conformers (a) and (b) undergo rapid interchange with each other, and are in an equilibrium governed by the free energy difference. The existence of two conformers similar to those in Fig. 5 has been demonstrated in the case of β_2-[Co(gly)(trien)]$^+$ ion.[12]

The existence of (3S,8S)-dimetrien complex with the Λ-*cis*-β(S,S) configuration was not taken into consideration in previous papers.[2,3] The assumption that the stereoisomers possible for the cobalt(III) complexes with methyl-substituted trien derivatives are restricted to those having the equatorial methyl groups has been found to be incorrect. It is of interest to note that the Λ-β(S,S)-[$\mathrm{CoCO_3}$((3S,8S)-dimetrien)]$\mathrm{ClO_4}$ is the sole product which can be isolated under basic preparative conditions. This suggests that the Λ-*cis*-β(S,S) geometry is more stable than the other *cis* forms Λ-*cis*-α(R,R) and Δ-*cis*-β(R,S).

No Λ-*cis*-β(S,S) isomer has been obtained for the dichloro and dinitro complexes with (3S,8S)-dimetrien.[2,3] The reactions carried out following Eqs. (1) and (2) should yield the corresponding dichloro or dinitro complex with Λ-*cis*-β(S,S) geometry, at least in the case of ordinary trien complexes.[10] The *trans*-(S,S) isomer, the actual products of reactions (1) and (2), and the Λ-*cis*-β(S,S) isomer are in common as regards the absolute configuration of the secondary N atoms. These isomers can be in an equilibrium in the acidic medium with retention of the secondary N configurations as indicated for the dichloro complexes in Eq. (6). When the perchlorate ion is present in a mixture of these isomers, the precipitation of only the less soluble salt of the *trans* isomer is induced, the Λ-*cis*-β isomer being highly soluble or hard to crystallize. A similar situation would occur for the *trans* and Λ-*cis*-β isomers of the dinitro complex.

$$\begin{tikzcd} \Lambda\text{-}cis\text{-}\beta(S,S)\text{-}[\mathrm{CoCl_2(L)}]^+ \arrow[r, shift left] & trans(S,S)\text{-}[\mathrm{CoCl_2(L)}]^+ \arrow[l, shift left] \arrow[d, "\mathrm{ClO_4^-}"] \\ & trans(S,S)\text{-}[\mathrm{CoCl_2(L)}]\mathrm{ClO_4} \end{tikzcd} \tag{6}$$

*The dichlorocobalt(III) complex of (4R,5S)-4,5-*dimethyl-3,6-diazaoctane-1,8-diamine gave rise to the *cis*-β(RS,SR) isomer as the chloride form, while the *trans*(R,S) isomer was obtained as the perchlorate from a similar reaction mixture.[5] This suggests that either of two equilibrated isomers can be separately crystallized in pure state by use of different counter ions. However, an attempt to get crystalline product of Λ-*cis*-β-[$\mathrm{CoCl_2}$((3S,8S)-dimetrien)]$^+$ by use of chloride or other anions was not successful and resulted in obtaining the trans isomer.

It was found unexpectedly that the chloride of Λ-*cis*-β-$\mathrm{Co(NO_2)_2}$((3S,8S)-dimetrien)$^+$ ion crystallizes out in the course of the usual air-oxidation procedure, except that methanol was used as the solvent. The novel dinitro complex contains one half mole of methanol of crystallization per mole of the complex. The PMR and CD spectra of this isomer are shown in Figs. 6(a) and 7, respectively. The PMR spectrum indicates two kinds of doublet assignable to the C-methyl groups of the ligand in the 1.2—1.4 ppm region and can be attributed to the *cis*-β topology. The sharp signal at 3.40 ppm is assigned to the methyl group of methanol of crystallization. For the sake of comparison the PMR spectra of the Δ-*cis*-β, Λ-*cis*-α, and *trans* isomers are shown in Figs. 6(b), (c), and (d), which are appropriate to the specified geometries of the isomers. The CD curve of the present isomer shows a dominant positive and a minor negative peak in the first absorption band region, which establishes the Λ configuration.[3]

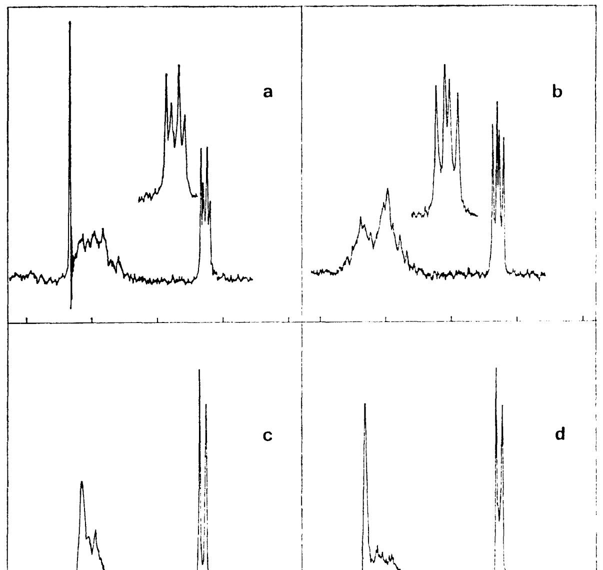

Fig. 6. PMR spectra of [$\mathrm{Co(NO_2)_2}$((3S,8S)-dimetrien)]$^+$ isomers: (a) Λ-*cis*-β, (b) Δ-*cis*-β, (c) Λ-*cis*-α, and (d) *trans* (in $\mathrm{D_2O}$).

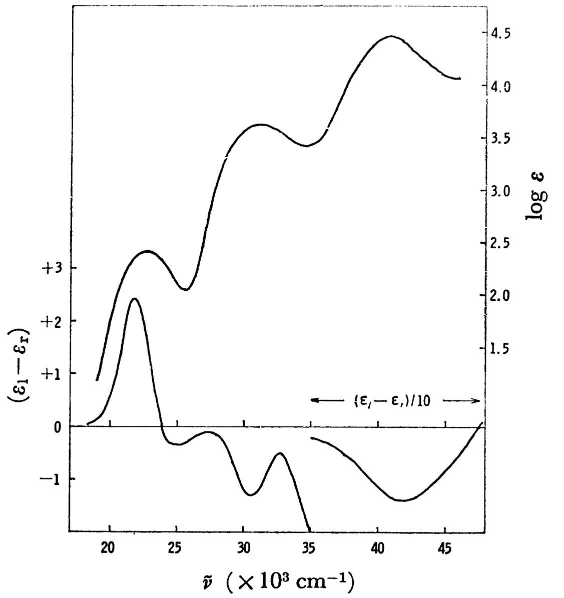

Fig. 7. Absorption and CD spectra of Λ-*cis*-β-$[Co(NO_2)_2$-$((3S,8S)$-dimetrien)]Cl·0.5 H_2O·0.5 CH_3OH.

A greyish violet solution was obtained on treating the Λ-*cis*-β-$[Co(NO_2)_2((3S,8S)$-dimetrien)]Cl with warm concentrated hydrochloric acid, no crystalline material being formed by concentration to near dryness. Addition of perchlorate ion to this solution resulted in the nearly quantitative formation of green crystals of the *trans*-(S,S)-$[CoCl_2((3S,8S)$-dimetrien)]ClO_4. The intermediate of the reaction should be highly soluble Λ-*cis*-β(S,S) dichloro complex which isomerizes into the *trans*(S,S) isomer in the same manner as in Eq. (6). It is therefore clarified that the Λ-*cis*-β dinitro complex adopts the (S,S) configuration with respect to the secondary N centers, since there is no possibility of inversion at the secondary N atoms under the conditions mentioned above.

The formation ratio of three isomers of $[CoCl_2((3S,8S)$-dimetrien)]$^+$ ion is *trans* : Δ-*cis*-β : Λ-*cis*-α= 15 : 5 : 1, when isolated as the perchlorate.[2] No exact estimation of the yields has been made, since it is difficult to isolate completely the materials in solution especially for highly soluble compounds such as the Δ-*cis*-β isomer. Furthermore, isomerization from the Λ-*cis*-β to the *trans* form should take place during the course of isolation, which affect the yield of the *trans* form. Thus, we can estimate the relative stability between the Δ-*cis*-β and Λ-*cis*-α, since these isomers would not undergo conversion or be obtained from the others in the acidic medium.

The strain energy minimization calculations applied to the isomers of $[Co(NO_2)_2((3S,8S)$-dimetrien)]$^+$ ion indicate that three isomers are in the order Δ-*cis*-β> *trans*>Λ-*cis*-α (according to the calculated enthalpy terms).[9] As far as the order of the Δ-*cis*-β and Λ-*cis*-α is concerned, the result of the calculation is in line with experimental results of the dichloro isomers. On the other hand, there is a distinct discrepancy between the calculated and experimental results with respect to the order of the *trans* isomer. We consider that the *trans* configuration is intrinsically unstable relative to the Δ-*cis*-β configuration due to the unfavorable bond angle distortions involved, as indicated by the strain energy minimization study.[9] Most part of the *trans* dichlorocomplex should be generated by the isomerization of the Λ-*cis*-β.

A preliminary study on the strain energy minimization calculation revealed that the Λ-*cis*-β form has an equivalent or more favorable stability as compared with the Δ-*cis*-β form.[13] It would be certain that higher yield of the *trans* isomer does not reflect its thermodynamic preference. For some metal chelate compounds the stereoisomers with an axially-oriented substituent with appreciable stability might be possible.

References

1) In IUPAC nomenclature rule, this ligand should be written as $(2S,7S)$-2,7-dimethyl-1,8-diamino-3,6-diazaoctane. In this paper, the ligand was termed as $(3S,8S)$-3,8-dimethyl-1,4,7,10-tetraazadecane in line with our previous reports: Refs. 2, 3.

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

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