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Stereochemical Studies of Metal Chelates. IX.[1] The Preparation and Stereochemistry of Cobalt(III) Complexes Coordinated with the *meso*-Form of 3,6-Diaza-2,7-dimethyl-1,8-diaminooctane

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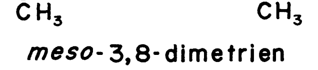
The *meso*-form of 3,6-diaza-2,7-dimethyl-1,8-diaminooctane (*meso*-3,8-dimetrien), one of the triethylenetetramine derivatives, was prepared. Dinitro- and dichlorocobalt(III) complexes with this ligand were also prepared and characterized. The *Λ-cis-β*(*SS*) and/or the *Δ-cis-β*(*RR*) configuration were assigned to these complexes. The *trans*-dichlorocobalt(III) complex of *meso*-3,8-dimetrien derived from the *cis-β*-dichloro complex was determined to have the *meso-trans* configuration (the absolute configurations of the coordinated secondary nitrogen atoms were antimeric to each other, namely, *R* and *S*), on the basis of proton magnetic resonance measurements.

We have investigated the stereoisomerism of cobalt(III) complexes coordinated with triethylenetetramine (=trien) derivatives substituted with methyl groups at various carbon atoms of trien. Almost all of them were optically active enantiomorphs and showed a remarkable stereospecificity when coordinated.[2-5] The studies of complexes with substituted triens have occasionally served to elucidate the stereochemistry of the unsubstituted trien complex. The structures of the probable isomers so far proposed[3-7] are shown in Fig. 1. The structural features for these isomers have been discussed in detail in previous papers.[4,5] The presence of all the isomers except for the *meso-trans* form (*trans*-(*RS*)[8] form) has been proven for diacidocobalt(III) complexes with trien and/or its derivatives.[3-5]

Studies of trien derivatives[3-5] have pointed out the importance of the conformational rigidity attending to the chelate ring with the *C*-substituted methyl group, which tends to take the equatorial orientation with regard to the chelate ring. The 3,6-diaza-2(*S*),7(*S*)-dimethyl-1,8-diaminooctane (=(3*S*,8*S*)-dimetrien), for example, yielded the *Δ-cis-β*(*RS*) isomer,[4,5] among others. The isolation of the *Δ-cis-β*(*RS*) isomer was attributed to the effect of the methyl groups of the ligand used. It was difficult to obtain the *Δ-cis-β*(*RS*) and its enantiomeric forms in the case of trien complexes.[6] This suggests that any isomeric forms not isolated for unsubstituted trien might be obtained by employing trien derivatives substituted with methyl group(s) at the suitable position(s) and of the appropriate configuration(s).

As has been mentioned above, the *meso-trans* form is the only isomer not hitherto detected for complexes of trien or its derivatives. The most conspicuous characteristic of the *meso-trans* form is the fact that the two outer chelate rings have opposed conformations (δ and λ). This isomeric form might be obtained if methyl groups are introduced into a trien derivatives so that the two side chelate rings adopt the configurations opposed to each other. With this in view, we prepared the *meso*-form of 3,6-diaza-2,7-dimethyl-1,8-diaminooctane (*meso*-3,8-dimetrien), which is the epimer of (3*S*,



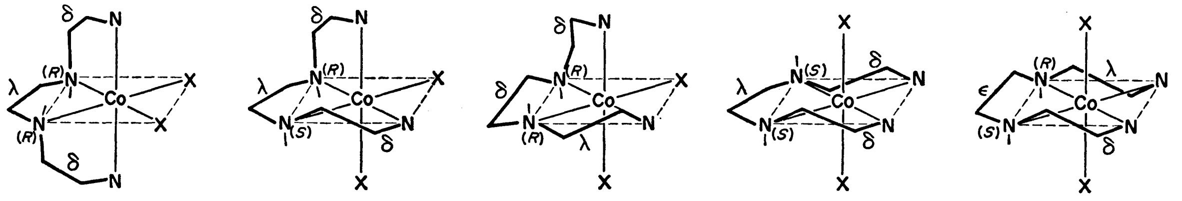
$\mathrm{NH_2CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}NHCH_2CH_2NH{-}\underset{CH_3}{\overset{H}{C}}{-}CH_2NH_2}$

3(*S*),8(*S*)-dimetrien

$\mathrm{NH_2CH_2{-}\underset{CH_3}{\overset{H}{C}}{-}NHCH_2CH_2NH{-}\underset{CH_3}{\overset{H}{C}}{-}CH_2NH_2}$

meso-3,8-dimetrien

Fig. 2. Structures of Ligands.



Λ-cis-α(*RR*)(δλδ) *Δ-cis-β*(*RS*)(δλδ) *Δ-cis-β*(*RR*)(δδλ) *trons* (*SS*)(δλδ) *trons* (*RS*)(λεδ)

Fig. 1. Possible isomers of octahedral trien complexes; *Λ-cis-α-*(*RR*)(δλδ), *Δ-cis-β*(*RS*)(δλδ), *Δ-cis-β-*(*RR*)(δδλ), *trans* (*SS*)(δλδ), and *meso-trans*(*RS*)(δελ).

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[1] Part VIII. M. Saburi, C. Hattori, and S. Yoshikawa, *Inorg. Chim. Acta*, in press.

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

[3] M. Goto, M. Saburi, and S. Yoshikawa, *ibid.*, **8**, 358 (1969).

[4] M. Saburi and S. Yoshikawa, This Bulletin, **45**, 806 (1972).

[5] M. Saburi, T. Sawai, and S. Yoshikawa, *ibid.*, **45**, 1086 (1972).

[6] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

[7] A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).

[8] *R* and *S* refer to the absolute configuration of the coordinated secondary nitrogen atoms, following the rules by R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Edn.*, **5**, 385 (1966).

8*S*)-dimetrien, as is indicated in Fig. 2. Some cobalt(III) complexes with *meso*-3,8-dimetrien were prepared and characterized. It was decided that the *trans*-dichloro complex with this ligand had the *meso-trans* configuration.

Experimental

Racemic alanine amide was prepared by the usual method.[9] Oxalyl chloride was prepared by the method of Staudinger.[10]

Tetramide Mixture. Racemic alanine amide (46.0 g) and sodium carbonate (25.0 g) were dissolved in 200 m*l* of water, and the solution was cooled in an ice bath. Oxalyl chloride (27.6 g) dissolved in 150 m*l* of benzene was added dropwise with vigorous stirring using a blender. After the addition was completed, stirring was continued for 10 min; the resultant white precipitates were filtered off, washed with water, methanol, and ether, and dried under vacuum. Yield, 37.8 g.

Separation of meso- *and* racemic-*Tetramide.* 5.0 g of the tetramide mixture were dissolved in 100 m*l* of boiling acetic acid, and then the solution was cooled to room temperature. After 4 hr, the white crystals which separated were collected by decantation. The crystals were washed with methanol and air-dried. This fraction was almost pure *meso*-tetramide. Yield, 1.5 g. The decanted solution was stood at room temperature overnight; the crystals which appeared were filtered off, and then washed and dried, as in the case of the first fraction. Yield, 1.0 g. The second fraction was *meso*-tetramide containing a small portion of the racemic form; recrystallization from acetic acid gave the pure product.

racemic-Tetramide was recovered from the filtrate of the second crop by the evaporation of the solvent. The product was contaminated with a small amount of the *meso*-isomer.

Found for *meso*-tetramide: C, 41.66; H, 6.02; N, 23.94%. Found for *racemic*-tetramide: C, 41.74; H, 6.15; N, 23.37%. Calcd for $C_8H_{14}N_4O_4$: C, 41.74; H, 6.13; N, 24.34%.

Preparation of meso-*3,6-Diaza-2,7-dimethyl-1,8-diaminooctane (*meso-*3,8-dimetrien).* To 150 m*l* of anhydrous tetrahydrofuran were added 8.0 g of lithium aluminum hydride in small portions, followed by 6.9 g of well-pulverized *meso*-tetramide in small portions. The mixture was stirred and heated under reflux for 24 hr and then cooled to room temperature. 15.5 m*l* of water diluted with 30 m*l* of tetrahydrofuran was added dropwise to the mixture with vigorous stirring. The resultant slurry was stirred for 30 min, filtered off, and washed with tetrahydrofuran (100 m*l*). The residue was extracted by boiling with tetrahydrofuran (100 m*l*) for 1 hr and then filtered again. After this procedure had been repeated, the extracts and filtrates were combined and concentrated under reduced pressure. The oily residue was dissolved in 100 m*l* of ethanol, and the solution was saturated with dry hydrogen chloride gas. The white precipitates were collected and dissolved in warm water. Ethanol was added, while hot, until the solution became turbid, and then the solution was cooled to room temperature. The white crystals of the hydrochloride salt of the desired tetramine were collected, washed with ethanol and ether and dried under vacuum. Yield, 3.5 g. Found: C, 28.49; H, 8.48; N, 15.83%. Calcd for $C_8H_{22}N_4\cdot 4HCl\cdot H_2O$: C, 28.41; H, 8.35; N, 16.57%.

Preparation of racemic-*3,6-Diaza-2,7-dimethyl-1,8-diaminooctane (*rac-*3,8-dimetrien).* This was prepared by the same procedures as were used for the *meso* form, but employing *racemic*-tetramide in place of *meso*-tetramide. The desired product was isolated as the hydrochroride. Found: C, 29.57; H, 7.88; N, 17.74%. Calcd for $C_8H_{22}N_4\cdot 4HCl$: C, 30.02; H, 8.18; N, 17.50%.

cis-*β-Dinitro(*meso-*3,6-diaza-2,7-dimethyl-1,8-diaminooctane)-cobalt(III) Chloride Sesquihydrate (*cis-*β-[Co(*meso-*3,8-dimetrien)-$(NO_2)_2$]Cl·1.5H_2O).* To a solution of *meso*-3,8-dimetrien·4HCl (3.40 g) and $LiOH\cdot H_2O$ (1.25 g) in 40 m*l* of water, $CoCl_2\cdot 6H_2O$ (2.38 g) and $NaNO_2$ (1.47 g) were added successively. The resultant solution was aerated with carbon dioxide-free air for 5 hr. The yellow-brown crystals which thus appeared were filtered off and washed with a small volume of cold water. Yield, 1.15 g. The second crop could be obtained by concentrating the combined filtrate and washings to a volume of 15 m*l*, followed by cooling in a refrigerator overnight. This crop was collected and washed with cold water and ethanol. Yield, 1.20 g. A further product was recovered from the filtrate. Total yield, 3.00 g. All the products were recrystallized from warm water. Found: C, 24.93; H, 6.56; N, 21.66%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]Cl\cdot 1.5H_2O$: C, 24.78; H, 6.50; N, 21.68%.

Resolution of cis-*β-[Co(*meso-*3,8-dimetrien)$(NO_2)_2$]Cl·1.5H_2O.* A 2 g sample of *cis-β*-[Co(*meso*-3,8-dimetrien)$(NO_2)_2$]Cl·1.5H_2O was dessolved in 15 m*l* of warm water. To the solution was added an aqueous solution of ammonium α-bromocamphor-π-sulfonate (1.60 g). Yellow precipitates began to separate immediately. After the mixture had stood at room temperature overnight, the precipitates were filtered off and washed with ethanol. Yield, 2.90 g. These crystals were dissolved in boiling methanol (150 m*l*), and the resultant solution was cooled and allowed to stand overnight. The crystals which separated were collected, washed with ethanol and ether, and air-dried. Yield, 1.25 g. $[\alpha]_D^{20}+147°$ ($c=0.2$, H_2O). The product was the pure diastereomer salt of the Λ isomer. Found: C, 33.21; H, 6.05; N, 12.53%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2](C_9H_{14}BrO_4S)\cdot CH_3OH$: C, 32.98; H, 6.15; N, 12.82%.

The α-bromocamphor-π-sulfonate salt of the Λ-isomer obtained as above was ground with excess $NaClO_4$ and a small volume of water in a mortar. The yellow crystals thus obtained were collected and recrystallized from warm water. $[\alpha]_D^{20}+180°$ ($c=1.0$, H_2O). Found: C, 22.41; H, 5.33; N, 19.94%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.62; H, 5.38; N, 19.79%.

The Δ isomer which remains in the filtrate could not be isolated as the optically pure form.

cis-*β-Dichloro(*meso-*3,6-diaza-2,7-dimethyl-1,8-diaminooctane)-cobalt(III) Chloride Hemihydrate (*cis-*β-[Co(*meso-*3,8-dimetrien)-Cl_2]·0.5H_2O).* 1.70 g of *meso*-3,8-dimetrien·4HCl and 0.625 g of $LiOH\cdot H_2O$ were dissolved in 20 m*l* of water, and then 1.19 g of $CoCl_2\cdot 6H_2O$ was added. The resultant solution was aerated with carbon dioxide-free air for 7 hr. To the solution were added 10 m*l* of concentrated HCl, and the resultant solution was then evaporated on a water bath below 50°C. When a small portion of purple crystals began to separate, heating was stopped and ethanol (20 m*l*) was added. After the mixture had stood in a refrigerator overnight, the purple crystals which separated were filtered off, washed with methanol, acetone, and ether, and dried under vacuum. The product was recrystallized from dilute HCl. Found: C, 27.51; H, 6.92; N, 15.86%. Calcd for $[Co(C_8H_{22}N_4)Cl_2]Cl\cdot 0.5H_2O$: C, 27.56; H, 6.65; N, 16.07%.

trans-*Dichloro(*meso-*3,6-diaza-2,7-dimethyl-1,8-diaminooctane)-cobalt(III) Perchlorate (*trans-*[Co(*meso-*3,8-Dimetrien)Cl_2]ClO_4).* A 0.2 g sample of *cis-β*-[Co(*meso*-3,8-dimetrien)Cl_2]Cl·0.5H_2O was added to 100 m*l* of anhydrous methanol, and the mixture

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[9] P.S. Yang and M.R. Rising, *J. Amer. Chem. Soc.*, **53**, 3183 (1931).

[10] H. Staudinger, *Ber.*, **41**, 3563 (1908).

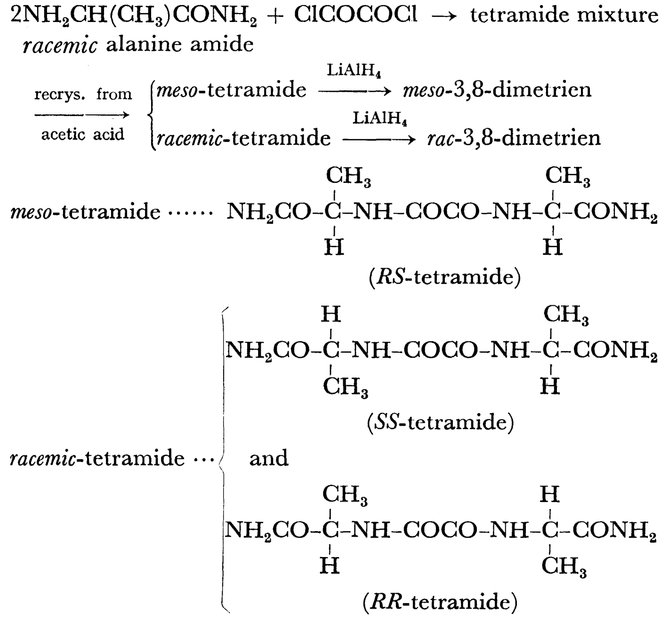
was heated under reflux for 6 hr. The resultant red-brown solution was filtered and concentrated in a rotary evaporator almost to dryness. To the residue were added 3 m*l* of methanol and a excess amount of solid $LiClO_4$, and the mixture was scratched with a glass rod. The crystals which appeared were collected and washed with ethanol and ether. The product thus obtained was the desired complex contaminated with perchlorate salt of the unchanged *cis-β* isomer. This crude product was treated with 20 m*l* of methanol with gentle heating, after which the sparingly soluble *cis-β* form was removed by filtration. The pure *trans* isomer was obtained from the filtrate after concentration in a rotary evaporator. The product was filtered off, and washed with ethanol and ether. The product was recrystallized from concentrated HCl. Found: C, 23.46; H, 5.63; N, 13.84%. Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.81; H, 5.50; N, 13.88%.

trans-*Dichloro(*racemic*-3,6-diaza-2,7-dimethyl-1,8-diaminooctane)cobalt(III) Perchlorate (*trans*-[Co(*rac*-3,8-dimetrien)Cl$_2$]ClO$_4$).* A 1.60 g sample of *rac*-3,8-dimetrien·4HCl and 0.625 g sample of $LiOH \cdot H_2O$ were dissolved in 25 m*l* of water, and then 1.19 g of $CoCl_2 \cdot 6H_2O$ were added. The solution was aerated with carbon dioxide free air for 7 hr, and then 10 m*l* of concentrated HCl were added. The resultant solution was concentrated on a water bath below 50°C. When a small quantity of dark green crystals began to form, heating was stopped and the mixture was cooled in a refrigerator overnight. The dark green crystals which thus separated were filtered off, washed with methanol, acetone, and ether, and dried under vacuum. The dark green crystals were dissolved in hot methanol (100 m*l*), and the solution was refluxed for 2 hr. To the resultant green solution were added an excess amount of solid $LiClO_4$, and the methanol was removed under reduced pressure. The green crystals which separated were the desired complex. The products were collected, washed with methanol and acetone, and air-dried. Found: C, 24.27; H, 5.67; N, 13.82%. Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.81; H, 5.50; N, 13.88%.

Measurements. The visible and ultraviolet absorption spectra were obtained with a Shimadzu MPS-50L spectrophotometer. The circular dichroism spectrum was measured with a JASCO J-20 automatic spectropolarimeter. The absorption spectrum for the *cis-β* dichloro isomer was obtained in a concentrated HCl solution in order to avoid the aquation of the complex. The absorption spectra for the *trans*-dichloro isomers were obtained in a methanol solution, while the absorption and CD spectra for the dinitro complex were obtained in an aqueous solution. The proton magnetic resonance spectra for the *trans*-dichloro complexes were obtained with a JNM C-60 spectrometer in a hexadeuterodimethyl sulfoxide solution immediately after dissolution. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as the internal standard reference. The infrared spectra were obtained with a JASCO DS-301 spectrophotometer by means of the KBr disk method.

Results and Discussion

(3*S*,8*S*)-Dimetrien has been prepared by the lithium aluminum hydride reduction of a tetramide obtained by the reaction of *S*-alanine amide (2 mol) with oxalyl chloride (1 mol) (designated hereafter as *SS*-tetramide).[4] If the *meso*-tetramide (or *RS*-tetramide), which contains an *S*-alanine moiety on one branch and an *R*-alanine moiety on the other, is available, the desired trien derivative, *meso*-3,8-dimetrien, may be readily prepared by the same procedure.



$$2NH_2CH(CH_3)CONH_2 + ClCOCOCl \rightarrow \text{tetramide mixture}$$
racemic alanine amide

$$\xrightarrow[\text{acetic acid}]{\text{recrys. from}} \begin{cases} \textit{meso}\text{-tetramide} \xrightarrow{LiAlH_4} \textit{meso}\text{-3,8-dimetrien} \\ \textit{racemic}\text{-tetramide} \xrightarrow{LiAlH_4} \textit{rac}\text{-3,8-dimetrien} \end{cases}$$

$$\textit{meso}\text{-tetramide}\cdots\cdots\ NH_2CO\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}NH\text{-}COCO\text{-}NH\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}CONH_2 \quad (RS\text{-tetramide})$$

$$\textit{racemic}\text{-tetramide}\cdots \begin{cases} NH_2CO\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}NH\text{-}COCO\text{-}NH\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}CONH_2 \quad (SS\text{-tetramide}) \\ \text{and} \\ NH_2CO\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}NH\text{-}COCO\text{-}NH\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}CONH_2 \quad (RR\text{-tetramide}) \end{cases}$$

Scheme

However, the reaction of racemic alanine amide (2 mol) with oxalyl chloride (1 mol) must give a "tetramide mixture" composed of *SS*-, *RR*-, and *RS*-tetramide (See Scheme). The *SS*- and *RR*-tetramide are enantiomeric to each other, and an equimolar mixture of them may be designated as *racemic*-tetramide. The *RS*-tetramide is, on the other hand, diastereoisomeric with the racemic form. The above "tetramide mixture" must contain the *racemic*- and *meso*-tetramide in equal amounts.

The separation of the tetramide mixture into the *meso* and the *racemic* forms can be achieved by fractional crystallization from hot acetic acid. The more soluble and the less soluble parts fractionated as above showed infrared spectra evidently different to each other. Further, both fractions were distinguished in thin-layer chromatography, using cellulose powder (MN 300, Macherey, Nagel & Co.) as the absorbent and a pyridine-water mixture (82:12) as the developing solvent. The R_f value for the less soluble fraction was nearly zero, while that for the more soluble fraction was 0.83. The *SS* tetramide, which was expected to have the same R_f value as the *racemic*-tetramide, showed a chromatogram identical with that of the more soluble fraction. Therefore, the more soluble and the less soluble fraction were identified as the *racemic*- and the *meso*-tetramide respectively.

The *meso*-3,8-dimetrien was obtained by the lithium aluminum hydride reduction of the *meso*-tetramide. In a similar way, the *rac*-3,8-dimetrien was prepared for the sake of comparison. The distinction of these ligands will be clarified by the differences in their complexes, such as *trans*-dichlorocobalt(III) complexes.

Among the possible isomers of trien complexes shown in Fig. 1, there are two isomers which adopt opposed conformations with respect to both of the outer chelate rings, *i.e.*, *Δ-cis-β*(*RR*) (and its antipodes) and *meso-trans* (*trans*(*RS*)) form. It was expected that the com-

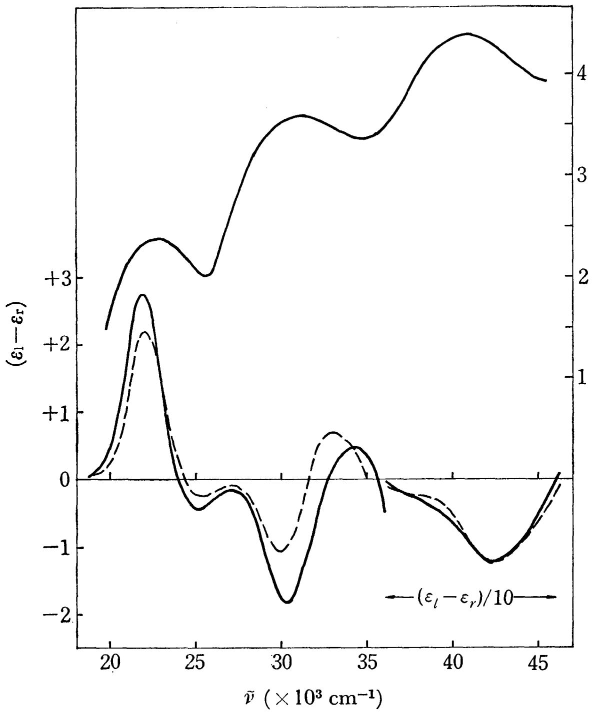


Fig. 3. Absorption and CD curves of *Λ-cis-β*-Co(*meso*-3,8-dimetrien)$(NO_2)_2^+$ ion (——) and CD curve of *Λ-cis-β*(*SS*)-Co(trien)$(NO_2)_2^+$ ion (----).

plexes with *meso*-3,8-dimetrien might give rise to these two geometries stereoselectively, since the present ligand prefers the λ conformation for one arm (the *R* absolute configuration site) and the δ conformation for the other (the *S* configuration site). However, the *meso-trans* geometry must be less stable than the *cis-β* form. In the former structure, the central chelate ring adopts an eclipsed envelope conformation, while all the three chelate rings take gauche conformations in the latter case. Therefore, the most preferred structure for *meso*-3,8-dimetrien complexes may be the *cis-β* configuration (*Δ-β*(*RR*) and *Λ-β*(*SS*)).

The dinitrocobalt(III) complex of *meso*-3,8-dimetrien showed the absorption spectrum given in Fig. 3. The second absorption band was found at 31,250 cm⁻¹, indicating the *cis* configuration of the complex. The absorption maxima for the *cis* isomers of the $Co(N)_4(NO_2)_2^+$ type were found at about 31,000 cm⁻¹, while those of the *trans* isomers were found in the vicinity of 29,000 cm⁻¹.[11] Such a tendency of absorption spectra was also observed in the case of dinitro complexes with some trien derivatives.[12]

The Co(*meso*-3,8-dimetrien)$(NO_2)_2^+$ ion was resolved into the optically active form using ammonium α-bromocamphor-π-sulfonate as the resolving agent. The (+)$_D$-enantiomorph isolated from the less soluble diastereoisomer salt showed the CD curve given in Fig. 3. This curve has a dominant positive CD peak ($\Delta\varepsilon=+2.75$), along with a minor negative peak ($\Delta\varepsilon=-0.46$), in the first absorption band region, indicating the *Λ* absolute configuration.[5] Further, this CD curve markedly resembles that of the *Λ-cis-β*-(*SS*)-Co(trien)$(NO_2)_2^+$ ion, as shown in Fig. 3. The dinitro complex of some trien derivatives which have configurations other than the *Λ-β*(*SS*) or *Δ-β*(*RR*) geometry (*i.e.*, the *Λ-α*-(*RR*) and *Δ-β*(*RS*) forms) showed CD patterns different from this (*Λ-β*(*SS*)) geometry.[5] Hence, it was established that the dinitrocobalt(III) complex of *meso*-3,8-dimetrien have the *Λ-β*(*SS*)[13] and *Δ-β*(*RR*) configurations, as expected previously.

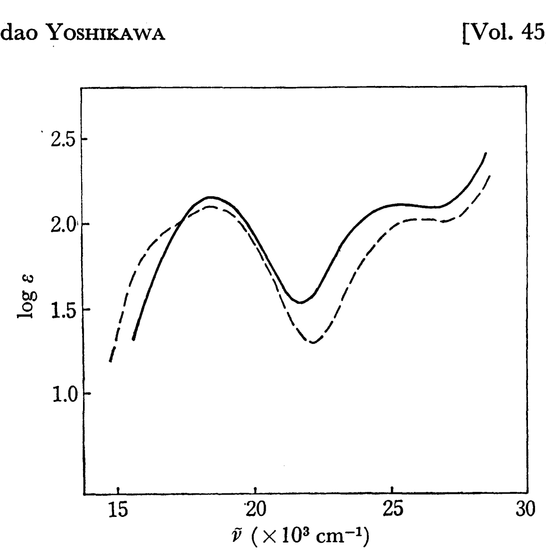


Fig. 4. Absorption curves of *cis-β*-Co(*meso*-3,8-dimetrien)Cl_2^+ ion (——) and *Λ-cis-α*-Co(3*S*, 8*S*)-dimetrien)Cl_2^+ion (----).

The dichlorocobalt(III) complex of *meso*-3,8-dimetrien prepared by the usual method was purple and showed the visible absorption curve given in Fig. 4. It has been recognized that the *cis-α* isomers of dichloro complexes with trien or its derivatives have a shoulder on the shorter wave number side of the first absorption band. The absorption curve of the *Λ-cis-α*-Co((3*S*,8*S*)-dimetrien)Cl_2^+ ion is shown for the sake of comparison in Fig. 4. For the *cis-β* configuration, such a shoulder has not been detected in the corresponding region in spite of the geometry of the *cis-β* isomers (*Λ-β*(*SS*) and

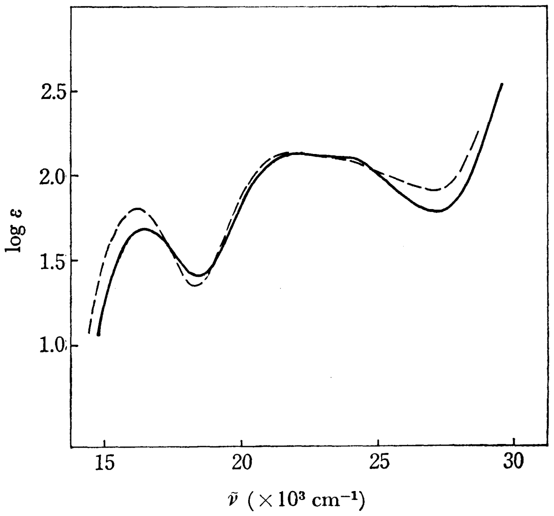


Fig. 5. Absorption curves of *trans*-Co(*meso*-3,8-dimetrien)Cl_2^+ ion (——) and *trans*-Co(*rac*-3,8-dimetrien)Cl_2^+ ion (----).

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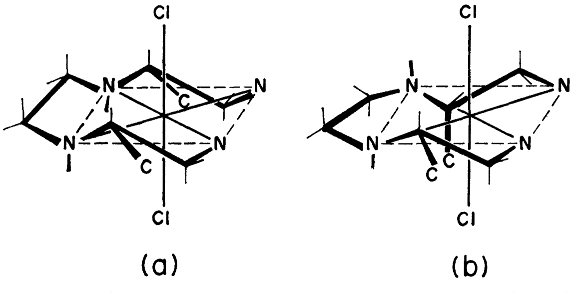
[11] F. Basolo, *J. Amer. Chem. Soc.*, **72**, 4393 (1950).

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

[13] The absolute configuration of the coordinated secondary nitrogen center is represented by *R* and *S*, neglecting the substituted methyl groups. See ref. (4) and (5).

Δ-β(*RS*) or their enantiomorphs).[4] No shoulder was observed in the first absorption band of the *meso*-3,8-dimetrien complex either (Fig. 4). Therefore, the present complex should have the *cis-β* configuration. Further, this complex ion probably takes the Λ-β(*SS*) and/or Δ-β(*RR*) configurations in the same manner as the corresponding dinitro complex.

When this *cis-β* dichloro complex suspended in methanol was heated under reflux, a red-brown solution was obtained, from which the *trans*-dichloro isomer of *meso*-3,8-dimetrien was isolated. The absorption spectra of this *trans* isomer and of the *trans*-Co(*rac*-3,8-dimetrien)-Cl$_2^+$ ion are shown in Fig. 5. These curves are apparently different from each other, reflecting the difference in the structures of the ligands. The absorption curve of the *rac*-3,8-dimetrien complex was identical with that of the (3*S*,8*S*)-dimetrien complex,[4] as expected.



(a) (b)

Fig. 6. Possible structures of *trans*-Co(*meso*-3,8-dimetrien)Cl$_2^+$ ion; (a) *meso-trans* and (b) *racemic-trans* (*SS* enantiomer).

There are two possible structures for the *trans* complexes of *meso*-3,8-dimetrien; they are illustrated in Fig. 6. In the *meso-trans* configuration, both of the methyl groups are situated equatorially. On the other hand, one of the methyl groups has the axial, and the other has the equatorial orientation for the *racemic-trans* configuration. (One of the enantiomers, the *trans*(*SS*) isomer, is represented in Fig. 6).

The PMR measurements may be useful in determining the actual structure of the *trans*-Co(*meso*-3,8-dimetrien)-Cl$_2^+$ ion. If the complex takes the *meso-trans* configuration, the PMR signals for the methyl groups should be observed as only one doublet. On the contrary, the methyl signals would be, in principle, observed as two doublets of equal intensity for the *racemic-trans* form.

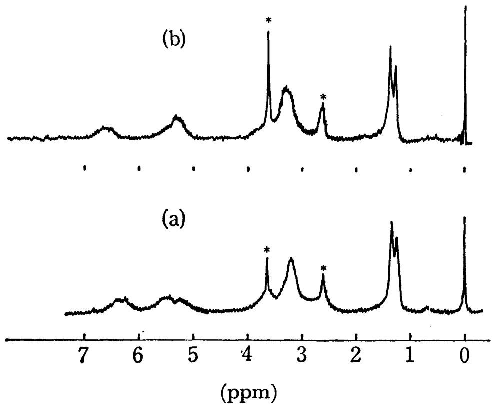


Fig. 7. PMR spectra of *trans-Co*(*meso*-3,8-dimetrien)Cl$_2^+$ ion (a) and *trans*-Co(*rac*-3,8-dimetrien)Cl$_2^+$ ion (b) in DMSO-d_6 (* are due to DMSO-d_6).

The PMR spectrum of the *trans*-dichloro complex of *meso*-3,8-dimetrien is shown in Fig. 7. The methyl signals were observed as a single soublet at about 1.3 ppm, indicating that the present complex has the *meso-trans* geometry. The PMR spectrum of the *rac*-3,8-dimetrien complex is given for the sake of comparison. The present complex also showed a single doublet for the methyl signals. However, the difference between the *meso*- and *rac*-3,8-dimetrien complexes was revealed clearly in the region of the N-bonded proton signals, which were found in the region of 5—7 ppm as broad peaks.

It was concluded, therefore, that the *trans*-dichloro complex of *meso*-3,8-dimetrien has the *meso-trans* configuration. Thus, it was clarified that the steric effects of methyl groups introduced into the trien backbone with appropriate configurations make it possible to obtain specific geometrical isomer(s) which would not be obtained in the case of non-substituted trien complexes.