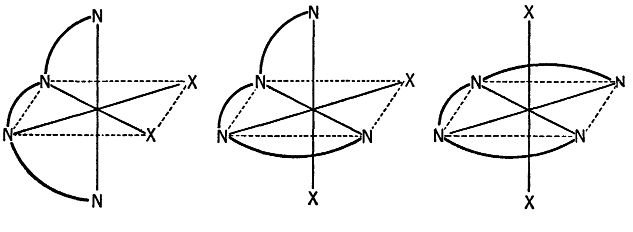
Stereochemical Studies of Metal Chelates. VII.1) The Preparation, Stereochemistry, and Circular Dichloism of Dinitrocobalt(III) Complexes with (3*S*, 8*S*)-Dimethyltriethylenetetramine and Related Tetramines

Masahiko Saburi, Tsutomu Sawai, and Sadao Yoshikawa
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received September 10, 1971)

Dinitrocobalt(III) complexes with (3*S*,8*S*)-dimethyltriethylenetetramine((3*S*,8*S*)-dimetrien) and related ligands were prepared and separated into the geometrical isomers. The *cis*-α and *cis*-β isomers of the (3*S*,8*S*)-dimetrien complex gave rise to the Λ and Δ isomers respectively. A similar stereospecificity could be observed for the other dissymmetric ligands employed in this study. The circular dichroism (CD) spectra of the *cis*-β isomers showed three kinds of patterns, which were related to the structural features of the complexes.

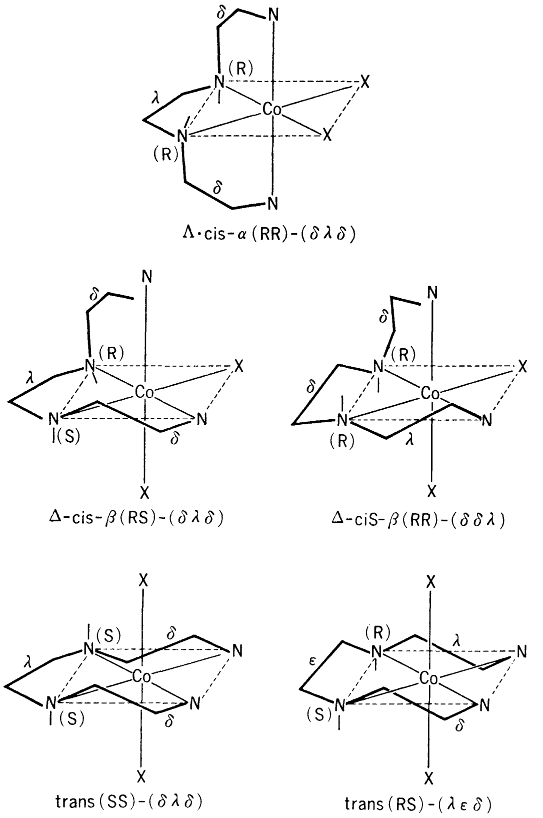
There are three topological ways for coordinating triethylenetetramine (trien) to a cobalt(III) ion, *cis*-α, *cis*-β, and *trans*, as is shown in Fig. 1. The actual stereochemistry of the trien complex is, however, more complicated because of the asymmetric feature of the secondary amino groups coordinated. Taking into account this source of asymmetry, the possible isomers of the trien complex are those shown in Fig. 2, where one of the enantiomeric pair is represented for each dissymmetric isomer. Only the *meso trans* isomer is intrinsically optically-inactive. In Fig. 2, the absolute configurations of the coordinated secondary amino groups and those of the central metal ion are denoted by *R* or *S*,2) and by Λ or Δ,3) respectively.



cis-α *cis*-β *trans*

Fig. 1. Topological isomers of trien complex. *cis*-α, *cis*-β, and *trans*.

Although only one enantiomeric pair is probable for the *cis*-α isomer (Λ-α(*RR*) and Δ-α(*SS*)), two kinds of diastereoisomers can be expected for the *cis*-β and *trans* isomers, because of the difference in the combination of the absolute configurations of the coordinated secondary N atoms. These configurations are the same for one of the β isomers (Λ-β(*SS*) and Δ-β(*RR*)) and the dissymmetric *trans* isomer (*trans*(*SS*) and (*RR*)), whereas they are antimeric for the other β isomer (Δ-β(*RS*) and Λ-β(*SR*)) and the *meso trans* form.



Λ-cis-α(RR)-(δλδ)

Δ-cis-β(RS)-(δλδ)

Δ-ciS-β(RR)-(δδλ)

trans(SS)-(δλδ)

trans(RS)-(λεδ)

Fig. 2. Probable isomers of octahedral trien complexes. Λ-*cis*-α(*RR*)(δλδ), Δ-*cis*-β(*RS*)(δλδ), Δ-*cis*-β(*RS*)(δλδ), *trans*-(*SS*)(δλδ), *meso-trans*(*RS*)(δελ).

The conformations of the three chelate rings are closely related to the stereochemistry of the trien complex. The conformation of each chelate ring is represented by δ or λ,5) as is shown in Fig. 2. The conformations of both of the outer chelate rings are the same in the *cis*-α form, as has been proved in a recent X-ray diffraction study.6) On the other hand, they are antimeric in the usual *cis*-β isomers,7–9) where

---

1) Part VI. M. Saburi and S. Yoshikawa, This Bulletin, **45**, 806 (1972).

2) The asymmetric configuration is described as *R* or *S* according to the sequence rule of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Emgl.*, **5**, 385 (1966).

3) The absolute configuration about a central metal ion is described as Λ or Δ according to the tentative rule of *Inorg. Chem.*, **9**, 1 (1970).

4) The order of two kinds of sec-N atoms in the *cis*-β isomers follows the order proposed by D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

5) The conformation of diamine chelate ring is represented as δ or λ. See ref. (3).

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

7) H. C. Freeman and I. E. Maxwell, *ibid.*, **8**, 1293 (1969).

8) H. C. Freeman and I. E. Maxwell, *ibid.*, **9**, 649 (1970).

9) H. C. Freeman, L. G. Marzilli, and I. E. Maxwell, *ibid.*, **9**, 2408 (1970).

the coordinated asymmetric secondary N atoms of trien take the same configurations (see *Λ-cis-β(SS)* in Fig. 2).

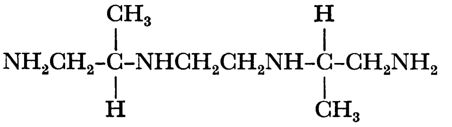
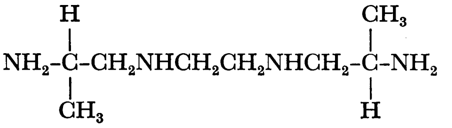
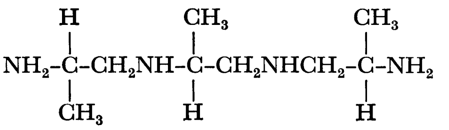
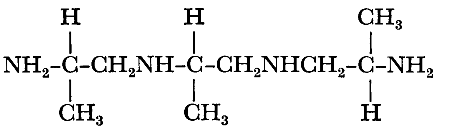
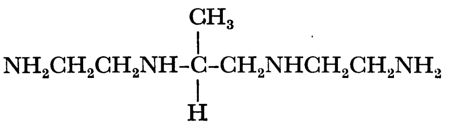
However, a detailed examination of the Dreiding stereomodels shows[10] that these chelate rings probably take the same conformations in the *Δ-β(RS)* and its enantiomer. It appears, therefore, that the *cis-β* isomer of such a steric form (*Δ-β(RS)* and/or *Λ-β(SR)*) can be obtained by the use of trien analogues modified in such a way that the outer-side chelate rings are restricted to the same conformation by some steric effect(s) of the substituents.

For (3*S*,8*S*)-dimethyltriethylenetetramine ((3*S*,8*S*)-dimetrien) and (2*S*,9*S*)-dimethyltriethylenetetramine ((2*S*,9*S*)-dimetrien), the absolute configurations of the asymmetric carbon centers of both side arms have the same *S* configuration. The structures and abbreviations for these tetramines, along with the other ligands employed in the present study, are summarized in Table 1. Both the side chelate rings are fixed in the same (*δ*) conformation for these ligands, ((3*S*,8*S*)- and (2*S*,9*S*)-dimetrien); therefore, diacidocobalt(III) complexes with these tetramines give rise to the *Δ-cis-β(RS)* isomer (in which both the outer chelate rings have the *δ* conformation).

Recently, the *Δ-cis-β* isomers of dichlorocobalt(III) complexes with (3*S*,8*S*)-[1] and (2*S*,9*S*)-dimetrien[11] were isolated. The structures of these isomers could be determined to be the *Δ-cis-β(RS)* form on the basis of their circular dichroism (CD) spectra. It was shown that the CD curve of the *Δ-β(RS)* forms are different from those of the *Δ-β(RR)* forms (or *Λ-β(SS)*) in the case of dichloro complexes.

It is interesting to investigate the difference(s) in the CD spectra between the *Δ-β(RR)* and *Δ-β(RS)* forms (or their antipodes) for cobalt(III) complexes other than the dichloro complex. In order to examine this problem, we prepared and separated the isomers of dinitrocobalt(III) complexes coordinated with (3*S*,8*S*)-dimetrien, (2*S*,9*S*)-dimetrien, and related trien derivatives. The CD spectra of these complexes will be measured and discussed in the present paper.

TABLE 1. ABBREVIATION AND STRUCTURE OF LIGANDS

Structure	Abbreviation
 $NH_2CH_2\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}NHCH_2CH_2NH\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2NH_2$	(3*S*, 8*S*)-dimetrien
 $NH_2\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2NHCH_2CH_2NHCH_2\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}NH_2$	(2*S*, 9*S*)-dimetrien
 $NH_2\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2NH\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}CH_2NHCH_2\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}NH_2$	(5*R*)-Me$_3$trien
 $NH_2\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2NH\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}CH_2NHCH_2\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}NH_2$	(5*S*)-Me$_3$trien
 $NH_2CH_2CH_2NH\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}CH_2NHCH_2CH_2NH_2$	(5*R*)-metrien

Experimental

(3S,8S)-Dimethyltriethylenetetramine Tetrahydrochloride (3S,8S)-dimetrien·4HCl). The method of preparing this ligang has been described previously.[1]

Λ-cis-α-Dinitro ((3S,8S)-dimethyltriethylenetetramine)cobalt(III) Perchlorate(Λ-cis-α-[Co((3S,8S)-dimetrien)(NO$_2$)$_2$]ClO$_4$). To a solution of (3*S*,8*S*)-dimetrien·4HCl (2.55 g) and LiOH·H_2O (0.94 g) in 30 m*l* of water, $CoCl_2\cdot 6H_2O$ (1.80 g) and $NaNO_2$ (1.10 g) were added successively; then the solution was aerated with carbon dioxide-free air for 10 hr at room temperature. The resultant solution was gradually evaporated on a water bath at 50°C until the volume was reduced to about 10 m*l*; it was then filtered, and 20 m*l* of ethanol were added. The white precipitates were removed quickly, 10 more m*l* of ethanol were added, and the mixture was kept in an ice bath for 1 hr. After the white precipitates has been removed once more, the filtrate was allowed to stand in an ice bath for 3 hr. The yellow precipitates which thus separated were filtered off and washed with a small volume of ethanol. The filtrate and washings were united and cooled in a refrigerator overnight. A further crop of yellow precipitates was then collected and washed with ethanol. The filtrate and washings were stored in order to separate the *cis-β* isomer.

The crude, hygroscopic yellow precipitates were dissolved in a small volume of warm water and then filtered. The pure perchlorate salt could be obtained by adding excess solid $LiClO_4\cdot 3H_2O$ to the filtrate. It was recrystallized from warm water. Found: C, 22.65; H, 5.23; N, 19.62%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.62; H, 5.22; N, 19.79%.

Δ-cis-β-Dinitro((3S,8S)-dimethyltriethylenetetramine) cobalt (III) Perchlorate (Δ-cis-β-[Co((3S,8S)-dimetrien)(NO$_2$)$_2$]ClO$_4$). To the combined filtrate and washings from the separation of the *Λ-cis-α* isomer, we added an excess amount of solid $LiClO_4\cdot 3H_2O$; the yellow-brown crystals which thus separated were collected and washed with ethanol and ether. The product thus obtained was contaminated with the *Λ-cis-α* isomer, and so it was fractionally recrystallized from a warm aqueous solution. After removing the less soluble *Λ-cis-α* isomer, the *Δ-cis-β* isomer could be obtained as yellowish-brown crystals. It was recrystallized from warm water. Found: C, 22.86; H, 5.23; N, 19.31%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.62, H, 5.22; N, 19.79%.

(2S,9S)-Dimethyltriethylenetetramine Tetrahydrochloride (2S,9S)-dimetrien·4HCl). This ligand was prepared by the method of Asperger and Liu.[11]

Λ-cis-α-Dinitro((2S,9S)-dimethyltriethylenetetramine) cobalt (III) Chloride (Λ-cis-α-[Co((2S,9S)-dimetrien)(NO$_2$)$_2$]Cl). The method of preparing this complex has been previosuly described.[1]

Δ-cis-β-Dinitro((2S,9S)-dimethyltriethylenetetramine) cobalt (III) Perchlorate (Δ-cis-β-[Co((2S,9S)-dimetrien)(NO$_2$)$_2$ClO$_4$). To a solution of *Δ-β*[Co(2*S*,9*S*)-dimetrien)CO$_3$]$^+$ prepared *in situ.* as has been described previously[1] (1.5×10^{-3} mol

---

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

[11] R. G. Asperger and C. F. Liu, *ibid.*, **4**, 1395 (1965).

scale), we added 5 N $HClO_4$ to pH 1, and then the solution was warmed at 80°C for 2 min. 5 N $HClO_4$ was further added in order to adjust the pH of the solution to 1, after which solid $NaNO_2$ (0.8 g) was added and dissolved. After the mixture had stood at room temperature for 15 min, an excess of solid $LiClO_4 \cdot 3H_2O$ was added to the brown solution. The yellow-brown crystals which separated out immediately were collected after standing 1 hr in an ice bath and washed with a small volume of cold water, ethanol, and ether. The product was slightly contaminated with the Λ-*cis*-α-isomer, and so it was fractionally recrystallized from a warm aqueous solution. The fractions showing a negative Cotton effect in the first absorption band region (~450 mμ) were combined and recrystallized repeatedly from warm water until they showed a constant CD curve. Found: C, 22.55; H, 5.38; N, 19.37%. Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]ClO_4$: C, 22.62; H, 5.22; N, 19.79%.

(R)-$(-)_D$- and (S)-$(+)_D$-*Propylenediamine.* These substances were obtained by resolving commercially-available racemic propylenediamine according to the method of Dwyer *et al.*[12]

N,N′-*Bis(carbobenzoxy-*(S)*-alanyl)-*(R)*-propylenediamine.* 17.8 g (0.075 mol) of carbobenzoxy-(*S*)-alanine hydrazide, obtained by a usual method,[13] was dissolved in a mixture of acetic acid (90 m*l*), 5 N HCl (38 m*l*), and water (375 m*l*). The solution was cooled to below −5°C in an ice-salt bath, and then a cold aqueous solution of $NaNO_2$ (5.5 g, 0.08 mol) was added in one portion. The carbobenzoxy-(*S*)-alanyl azide thus formed was extracted with 500 m*l* of cold ether. The ether layer was separated, washed with water (100 m*l*) a 3% sodium bicarbonate solution (100 m*l*), and water (100 m*l*) successively, and then dried briefly over anhydrous sodium sulfate. Sodium sulfate was removed and to the ether solution we added 2.22 g (0.03 mol) of (*R*)-$(-)_D$-propylenediamine; the mixture was subsequently stirred for 24 hr in an ice bath and then for 12 hr at room temperature. The resultant white precipitates were filtered off and washed with ether. For elemental analysis, small portion of the product was recrystallized from hot ethanol. mp 199.4—200.0°C (corr.). Found: C, 61.14; H, 6.25; N, 12.19%. Calcd for $C_{25}H_{32}N_4O_6$: C, 61.97; H, 6.66; N, 11.56%.

N,N′-*Bis(*(S)*-alanyl)-*(R)*-propylenediamine Diacetate.* 4.85 g (0.01 mol) of *N,N′*-bis(carbobenzoxy-(*S*)-alanyl)-(*R*)-propylenediamine was hydrogenated for 4 hr in 100 ml of methanol containing 1.5 g of acetic acid and 1 g of paradium black, using a Parr low-pressure apparatus. After the removal of the catalyst, the solution was concentrated to dryness under reduced pressure, giving white prceipitates of *N,N′*-bis((*S*)-alanyl)-(*R*)-propylenediamine diacetate. For the subsequent reaction, the product was used without further purification.

(2S,5R,9S) - *Trimethyltriethylenetetramine Tetrahydrochloride* ((5R)-*Me*$_3$*trien·4HCl*). 9.48 g (0.282 mol) of *N,N′*-bis((*S*)-alanyl)-(*R*)-propylenediamine diacetate was added to a suspension of 7.6 g of lithium aluminum hydride in 200 m*l* of anhydrous tetrahydrofuran. The mixture was stirred and heated under reflux for 24 hr. After the mixture had then been cooled to room temperature, 14.4 m*l* of water diluted with 50 m*l* of tetrahydrofuran was added, drop by drop; the resultant slurry was filtered off and washed with a small volume of tetrahydrofuran. The residue was extracted with boiling tetrahydrofuran (200 m*l*) under reflux (2 hr) and then filtered again. After repeating the extraction once more, the combined filterates and extracts were concentrated under reduced pressure, leaving an oily residue. This residue was dissolved in ethanol (100 m*l*), and exess dry HCl gas was bubbled through, yielding white precipitates. These were filtered off and recrystallized from 5 N HCl and ethanol. Found: C, 31.98; H, 8.41; N, 16.38%. Calcd for $C_9H_{24}N_4 \cdot 4HCl$: C, 32.35; H, 8.45; N, 16.77%.

Λ-cis-α-*Dinitro (*(2S,5R,9S)*-trimethyltriethylenetetramine) cobalt(III) Chloride (*Λ-cis-α-*[Co((*5R)*-Me*$_3$*trien)(NO*$_2$*)*$_2$*]Cl).* To a solution of 1.02 g of (5*R*)-Me$_3$ trien·4HCl and 0.36 g of $LiOH \cdot H_2O$ in 25 m*l* of water $CoCl_2 \cdot 6H_2O$ (0.64 g) and $NaNO_2$(0.42 g) were added and dissolved successively; the resultant solution was aerated for 6 hr at room temperature. The yellow precipitates which were thus separated were collected and washed with cold water and ethanol. A second crop could be obtained by concentrating the filtrate on a water bath (50°). The crude products were recrystallized from water and ethanol. Found: C, 29.03; H, 6.33; N, 22.14%. Calcd for $[Co(C_9H_{24}N_4)(NO_2)_2]Cl$: C, 28.85; H, 6.46; N, 22.43%.

Δ-cis-β-*Dinitro (*(2S,5R,9S)*-trimethyltriethylenetetramine)cobalt(III) Perchlorate (*Δ-cis-β-*[Co((*5R)*-Me*$_3$*trien)(NO*$_2$*)*$_2$*]ClO*$_4$*).* To the filtrate from the isolation of the Λ-*cis*-α isomer as above, a large excess of solid $LiClO_4 \cdot 3H_2O$ was added. After the mixture had stood overnight, yellow-brown precipitates were collected, washed with water and ethanol, and dried *in vacuo.* They were then recrystallized from warm water. Found: C, 23.31; H, 5.80; N, 18.01%. Calcd for $[Co(C_9H_{24}N_4)(NO_2)_2]ClO_4 \cdot H_2O$: C, 23.67; H. 5.74; N, 18.40%.

N,N′-*Bis(carbobenzoxy-*(S)*-alanyl)-*(S)*-propylenediamine.* This compound was prepared by a procedure similar to that used for *N,N′*-bis(carbobenzoxy-(*S*)-alanyl)-(*R*)-propylenediamine, but using (*S*)-$(+)_D$-propylenediamine instead of (*R*)-$(-)_D$-propylenediamine. For the elemental analysis, a small portion of the product was recrystallized from ethanol. mp 233.5—234.5°C (corr.). Found: C, 61.92; H, 6.76; N, 12.14%. Calcd for $C_{25}H_{32}N_4O_6$: C, 61.97; H, 6.66; N, 11.56%.

N,N′-*Bis(*(S)*-alanyl)-*(S)*-propylenediamine Diacetate.* *N,N′*-Bis(carbobenzoxy-(*S*)-anlayl)-(*S*)-propylenediamine was hydrogenated in the same way as the corresponding (*R*)-propylenediamine derivative. The product was used in the following reaction without further purification.

(2S,5S,9S)-*Trimethyltriethylenetetramine (*(5S)*-Me*$_3$*trien).* *N,N′*-Bis((*S*)-alanyl)-(*S*)-propylenediamine diacetate (10.1 g, 0.03 mol) was treated with lithium aluminum hydride (9.1 g) in anhydrous tetrahydrofuran (200 m*l*) in a manner similar to that used in preparing (5*R*)-Me$_3$trien. The oily residue thus obtained was dried over KOH pellets and distilled under reduced pressure. bp 108—109°C (2 mmHg). Since the hydrochloride of this tetramine was hygroscopic, it was converted to the picrate salt for analysis. Found: C, 35.00; H, 3.73; N, 19.45%. Calcd for $C_9H_{24}N_4 \cdot 4C_6H_3N_3O_7 \cdot 2H_2O$: C, 34.75; H, 3.53; N, 19.65%.

Δ-cis-β-*Dinitro(*(2S,5S,9S)*-trimethyltriethylenetetramine)cobalt(III) Iodide Monohydrate (*Δ-cis-β-*[Co((*5S)*-Me*$_3$*trien)(NO*$_2$*)*$_2$*]I·H*$_2$*O).* To a solution of (5*S*)-Me$_3$trien (0.565 g) in 20 m*l* of water containing 3 m*l* of 1 N HCl, we added $CoCl_2 \cdot 6H_2O$ (0.714 g) and $NaNO_2$ (0.435 g); the resultant solution was aerated with carbon dioxide-free air for 10 hr at room temperature. The solution was concentrated on a water bath to about 5 m*l*, and then 10 m*l* of ethanol were added. The white precipitates which thus separated (NaCl) were removed by filtration, and more ethanol was added. After removing the white precipitates if necessary, 5.64 g

---

[12] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 920 (1959).

[13] J. P. Greenstein and M. Winitz, "Chemistry of Amino Acid," p. 951. Vol. 2, John Wiley & Sons, Inc., New York, N. Y. (1961).

of $LiI \cdot 3H_2O$ were added. When the mixture was left standing at room temperature, slightly hygroscopic yellow precipitates began to separate; they were collected and recrystallized from methanol and ethanol. A further crop was obtained from the filtrate by adding ethanol and isopropanol. Found: C, 22.41; H, 5.35; N, 16.78%. Calcd for $[Co(C_9H_{24}N_4)(NO_2)_2]I \cdot H_2O$: C, 22.33; H, 5.41; N, 17.36%.

Measurements. The visible absorption spectra were measured with a Shimadzu MPS-50L spectrophotometer. The circular dichroism spectra were measured with a JASCO J-10 automatic spectropolarimeter.

Results and Discussion

The dinitrocobalt(III) complexes coordinated with (3*S*,8*S*)-dimetrien, (2*S*,9*S*)-dimetrien, and other tetramines were prepared by the usual air-oxidation procedures. The isomers were separated by fractional crystallization. In a previous study,[1] the stereospecificity incorporated with the (3*S*,8*S*)- and (2*S*,9*S*)-dimetrien was clarified for the dichlorocobalt(III) complexes; it was revealed that only the *Λ* and *Δ* isomers could be isolated for the *cis*-α and *cis*-β isomers respectively. Thus, in the case of dinitro complexes, the *cis*-α and *cis*-β isomers with these tetramines would also take, stereospecifically, the *Λ* and *Δ* absolute configurations respectively. Hence, the structures of the fractionally-separated products were examined by measuring the CD and ORD curves.

The chloride salts of the dinitrocobalt(III) complexes of (3*S*,8*S*)-dimetrien were highly soluble in an aqueous solution. The first and second fractions obtained by adding ethanol showed ORD curves similar to that of the *Λ*-*cis*-α-$[Co(trien)(NO_2)_2]^+$ ion[14] and were regarded as consisting of the *Λ*-*cis*-α isomer of $[Co((3S,8S)\text{-dimetrien})(NO_2)_2]Cl$. However, these fractions were slightly hygroscopic and were considered to involve other isomer(s) as well. Thus, the chloride salt was converted into the perchlorate salt, the solubility of which was relatively low in water. The pure perchlorate salt of this isomer shows the absorption and CD spectra given in Fig. 3. The spectral data are summarized in Table 2.

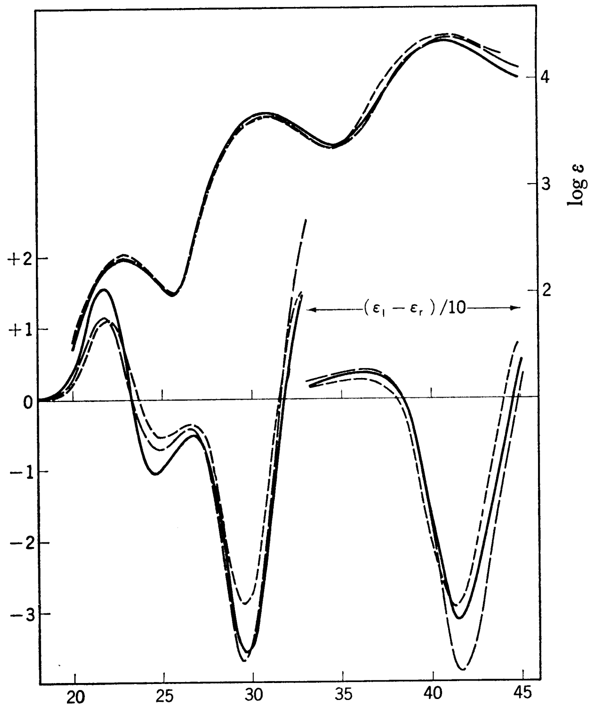


Fig. 3. Electronic absorption and CD spectra of the *Λ*-*cis*-α isomers. (3*S*,8*S*)-dimetrien (——), (2*S*,9*S*)-dimetrien (- - -) and 5(*R*)-Me_3trien (— — —).

On the basis of the similarity in the CD spectra between the present complex and the *Λ*-*cis*-α isomer of the trien complex,[14] the former was identified as

TABLE 2. SPECTRAL DATA

Complex	λ_{max}(cm^{-1})	log ε_{max}	λ(cm^{-1})	$\Delta\varepsilon_{max}$
Λ-α-$[Co((3S, 8S)\text{-dimetrien})(NO_2)_2]^+$	22880	2.31	21830	+1.60
			24570	−1.03
	30860	3.68	29670	−3.57
			36500	+4.3
	40650	4.35	41490	−31.3
Λ-α-$[Co((2S, 9S)\text{-dimetrien})(NO_2)_2]^+$	22880	2.32	21740	+1.18
			24880	−0.71
	30960	3.65	29500	−3.68
			35970	+4.2
	40980	4.38	41670	−38.6
Λ-α-$[Co((5R)\text{-}Me_3trien)(NO_2)_2]^+$	22850	2.33	22080	+1.15
			25000	−0.53
	30960	3.64	29590	−2.94
			35710	+2.8
	40900	4.40	41320	−29.5
Δ-β(*RS*)-$[Co((3S, 8S)\text{-dimetrien})(NO_2)_2]^+$	22570	2.40	21880	−2.66
			25000	+0.43
	30860	3.49	31060	+1.72
			36500	+1.1
	40650	4.34	42020	−12.1
Δ-β(*RS*)-$[Co((2S, 9S)\text{-dimetrien})(NO_2)_2]^+$	22730	2.36	22120	−2.68
			25380	+0.42
	30960	3.61	31550	+2.01
			37450	+1.5
	40980	4.38	42550	−8.9
Δ-β(*RS*)-$[Co((5R)\text{-}Me_3trien)(NO_2)_2]^+$	22570	2.44	22030	−3.40
			25000	+0.85
	31150	3.62	31250	+3.14
			37590	+2.5
	40900	4.45	42190	−14.5
Λ-β(*SS*)-$[Co(trien)(NO_2)_2]^+$	22680	2.38	22120	+2.20
			25380	−0.23
	31150	3.63	29850	−1.08
			33110	+0.73
	40980	4.45	42370	−12.3
Λ-β(*SS*)-$[Co((5R)\text{-metrien})(NO_2)_2]^+$	22730	2.40	22170	+2.50
			25320	−0.32
	31250	3.66	29940	−0.82
			32890	+1.08
	40820	4.48	42020	−12.6
Δ-β(*RS*)-$[Co((5S)\text{-}Me_3trien)(NO_2)_2]^+$	22450	2.50	22220	−2.56
	30700	3.73	29590	+1.04
			33000	−0.56
			37040	+0.8
	40800	4.54	41320	−5.7

---

[14] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

Λ-*cis*-α(*RR*)[15]-[Co((3*S*,8*S*)-dimetrien)$(NO_2)_2$]ClO_4. An X-ray analysis of this complex[16] revealed that the complex ion takes the Λ-*cis*-α structure illustrated in Fig. 4.

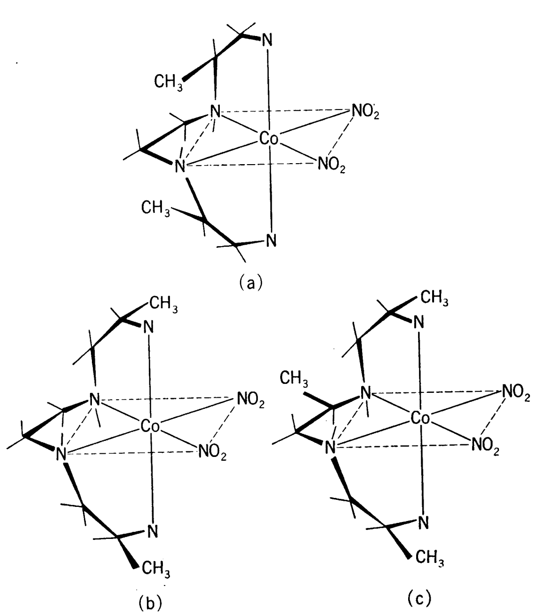


Fig. 4. Probable structures of the Λ-*cis*-α isomers. (a) (3*S*,8*S*)-dimetrien, (b) (2*S*,9*S*)-dimetrien, and (c) (5*R*)-Me_3trien.

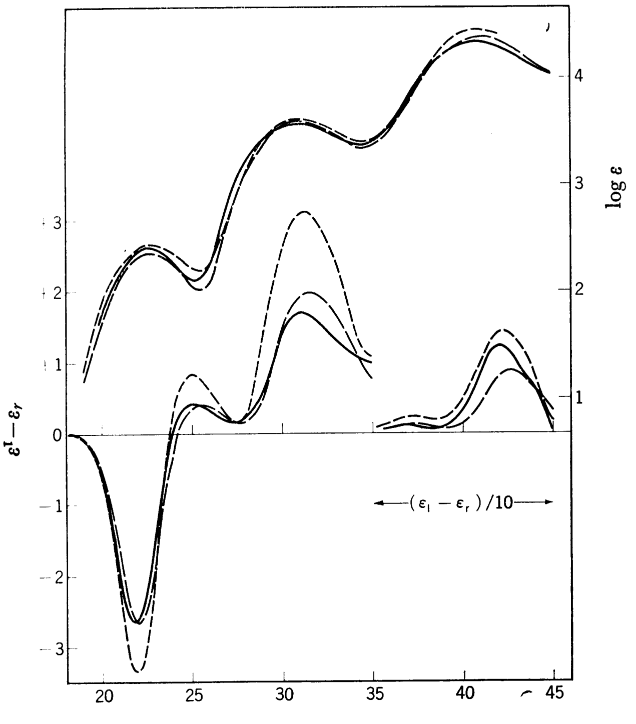
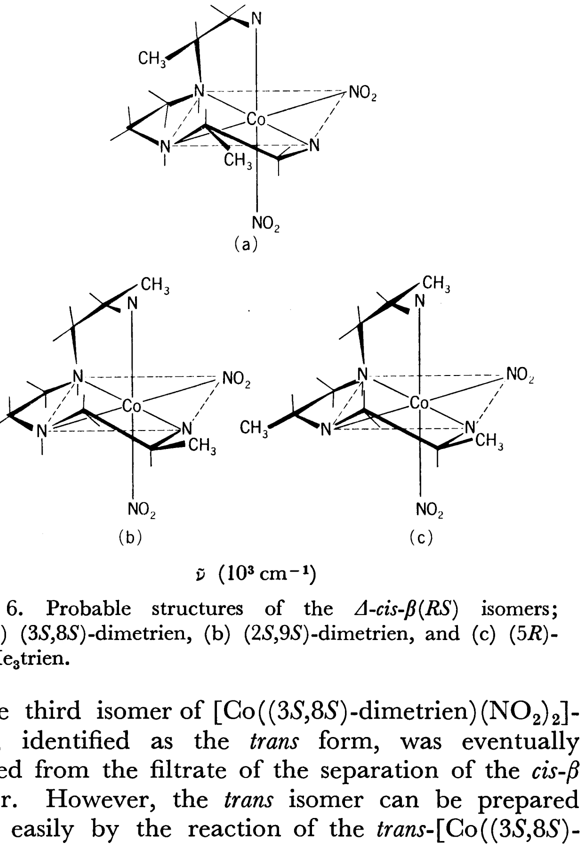


Fig. 5. Electronic absorption and CD spectra of the Δ-*cis*-β(*RS*) isomers. (3*S*,8*S*)-dimetrien (——), (2*S*,9*S*)-dimetrien (- - -) and (5*R*)-Me_3trien (— — —).

The second isomer of [Co((3*S*,8*S*)-dimetrien)$(NO_2)_2$]ClO_4 could be obtained from the mother liquor by adding excess $LiClO_4$. The exact structure of the present isomer has been determined by a X-ray crystallographic study,[17] which showed that the complex ion takes the Δ-*cis*-β(*RS*) geometry, as is illustrated in Fig. 5. The electronic absorption and the CD spectra for this complex are shown in Fig. 6. A detailed comparison of the CD of the Δ-β(*RS*) geometry with that for the diastereoisomeric β geometry (Λ-β-(*SS*) and Δ-β(*RR*)) will be presented later.



$\tilde{\nu}$ (10^3 cm^{-1})

Fig. 6. Probable structures of the Δ-*cis*-β(*RS*) isomers; (a) (3*S*,8*S*)-dimetrien, (b) (2*S*,9*S*)-dimetrien, and (c) (5*R*)-Me_3trien.

The third isomer of [Co((3*S*,8*S*)-dimetrien)$(NO_2)_2$]ClO_4, identified as the *trans* form, was eventually isolated from the filtrate of the separation of the *cis*-β isomer. However, the *trans* isomer can be prepared more easily by the reaction of the *trans*-[Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4 with $NaNO_2$ in hot methanol. The absorption and CD spectra of this isomer have been reported previously.[18]

The Λ-*cis*-α isomer of the dinitrocobalt(III) complex coordinated with (2*S*,9*S*)-dimetrien was readily obtained from an aerated solution as the chloride form because of its low solubility. The absorption and CD spectra of this complex are given in Fig. 3; they are similar to those of the corresponding (3*S*,8*S*)-dimetrien complex. This means that the present complex also has the Λ-*cis*-α(*RR*) geometry shown in Fig. 4, where the substituted methyl groups are situated in equatorial positions.

On the other hand, it was difficult to obtain the Δ-*cis*-β isomer of the (2*S*,9*S*)-dimetrien complex from the mother liquor of the Λ-*cis*-α isomer. Hence, the

---

[15] The *RS* representation of the absolute configuration of the asymmetric secondary N atoms is complicated in substituted triens by the presence of methyl groups. For example, (3*S*,8*S*)-dimetrien and trien complexes have the opposite configurations in the Λ-α form; (*SS*) for the former and (*RR*) for the latter. In this paper the absolute configuration of the coordinated secondary N centers is represented by *R* and *S*, neglecting the substituted methyl groups.

[16] M. Ito, F. Marumo, and Y. Saito, to be published.

[17] M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr.*, **B26**, 1408 (1970).

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

Δ-β isomer was prepared by the reaction of $NaNO_2$ with Δ-*cis*-β-[Co((2*S*,9*S*)-dimetrien)$(H_2O)_2]^{3+}$ ion, which is prepared *in situ* through the carbonato complex. The carbonato complex, prepared *in situ* by the reaction of the Λ-*cis*-α-[Co((2*S*,9*S*)-dimetrien)-$Cl_2]^+$ ion with excess Li_2CO_3, was found to show a dominant negative Cotton effect in the first absorption band region, suggesting that the resultant carbonato complex takes the Δ configuration predominantly.

The dinitro complex obtained above showed a negative CD band in the first absorption band region. The absorption and CD spectra of this complex are shown in Fig. 5. The CD spectrum markedly resembles that of the Δ-*cis*-β(*RS*) isomer of the (3*S*,8*S*)-dimetrien complex. Therefore, the *cis*-β siomer of the (2*S*,9*S*)-dimetrien complex can be said to adopt preferentially the Δ-β(*RS*) geometry, as is shown in Fig 6.

We supposed that a (2*S*,9*S*)-dimetrien analogue with a methyl group introduced into the central ethylenediamine linkage would give rise to the Δ-*cis*-β-(*RS*) isomer more preferentially than the original (2*S*,9*S*)-dimetrien. This was based on the observation[10] that trien derivatives with any equatorially-oriented substituent(s) at the central chelate ring yield, stereoselectively, *cis*-β isomers, though they have the Λ-β(*SS*) and/or Δ-β(*RR*) geometry. Therefore, it is necessary that the methyl group introduced into the (2*S*,9*S*)-dimetrien skeleton take the equatorial orientation with respect to the central diammine linkage. (2*S*,5*R*,9*S*)-Triemethyltriethylenetetramine ((5*R*)-Me_3trien) satisfies the above requirement. For this tetramine, the central chelate ring would be fixed in the λ conformation because of the steric effect of the methyl group, which has the *R* absolute configuration.

By the use of the (5*R*)-Me_3trien, the Λ-*cis*-α and Δ-*cis*-β isomers of dinitrocobalt(III) complex were isolated. The former was obtained as the chloride form by concentrating the aerated solution, while the latter was also obtained as the perchlorate salt by adding $LiClO_4$ to the mother liquor. The absorption and CD spectra of these complexes are shown in Figs. 3 and 5 respectively.

The CD spectra of the Λ-*cis*-α and Δ-*cis*-β isomers are clearly similar to those of the (3*S*,8*S*)- and (2*S*,9*S*)-dimetrien complexes, though the intensity of each CD band of the present cis-β isomer is slightly higher than those of the others. This means that the *cis*-α and *cis*-β isomers of the (5*R*)-Me_3trien complex have the Λ-*cis*-α(*RR*) and Δ-*cis*-β(*RS*) geometries respectively. The probable structures of these isomers are also shown in Figs. 4 and 6.

The steric effects incorporated with the equatorial methyl group introduced into the central diamine linkage were clearly observed for the (5*R*)-Me_3trien, since the *cis*-β isomer could be isolated from the mother liquor more readily than in the case of the (2*S*,9*S*)-dimetrien complex; morevoer, it was recognized that the yield of the *cis*-β isomer is larger than that of the *cis*-α isomer. However, the presence of the *cis*-α isomer suggests that the steric effect of the equatorial methyl group in the central chelate ring, which provides preferentially the *cis*-β isomer, is not so sufficient in the case of (5*R*)-Me_3trien as in the previous case.[10]

(2*S*,5*S*,9*S*)-Trimethyltriethylenetetramine ((5*S*)-Me_3-trien) is an epimer of (5*R*)-Me_3trien, and the asymmetric carbon atom at the central chelate ring has the *S* configuration. In this ligand the absolute configurations of all the asymmetric carbon centers are *S*; therefore, all three chelate rings should take the δ conformations if the methyl groups tend to take the equatorial orientations. However, it is impossible for complexes of trien derivatives to take a structure in which all three chelate rings have the same configuration at the same time, as is shown in Fig. 2.

It seems likely for the coordination of (5*S*)-Me_3-trien that one of the chelate rings takes the λ conformation and that the methyl group comes to lie in the axial orientation in this chelate with the λ conformation. Otherwise, a new very strained form may be brought about, in which at least one of the chelate rings no longer has the gauche conformation.

Only one isomer has been isolated for the dinitrocobalt(III) complex coordinated with (5*S*)-Me_3trien. The electronic absorption and CD spectrum of this complex are shown in Fig. 7. The CD curve is obviously different from that of the Λ-*cis*-α (or its enantiomer); it rather resembles those of the Δ-*cis*-β(*RS*) isomers. This suggests that the present complex has a *cis*-β geometry and the Δ absolute configuration.

The (5*S*)-Me_3trien complex may belong to either of two diastereoisomeric forms (Δ-β(*RR*) and Δ-β(*RS*)), though some deformations from the ordinary structures may be involved. The structure of this complex is difficult to identify in detail by only examining the

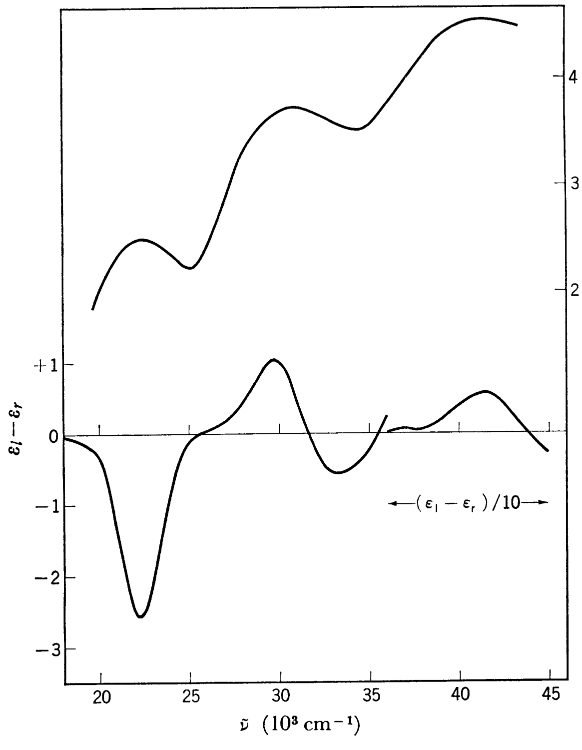
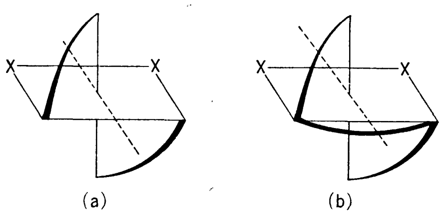


Fig. 7. Electronic absorption and CD spectra of the (5*S*)-Me_3trien complex.

CD spectrum, as will be described later. However, the influence of the difference in the absolute configuration of the methyl group introduced into the central diamine linkage was demonstrated in the different behavior between (5*R*)- and (5*S*)-Me$_3$trien as (2*S*,9*S*)-dimetrien analogues.

It has been indicated[19,20] that, in a *cis*-bis(diamine) complex, such as the *cis*-Co(en)$_2$X$_2$$^{n+}$ ion, with C$_2$ symmetry, the octahedral $A_{1g} \rightarrow T_{1g}$ transition breaks down into one component with A symmetry and two components with B symmetry. The three transitions have been distinguished, by means of their symmetry and trigonal (D$_3$) parentages, as A(E$_a$), B(E$_a$), and B(A$_2$) transition.[19] The CD curve of the $(-)_D$-[Co(en)$_2$(NO$_2$)$_2$]$^+$ ion, which has the Λ-absolute configuration, shows a dominant positive band and a minor negative band at 21700 and 25000 cm^{-1} respectively. The former band was assigned to the (A(E$_a$)+B(E$_a$)) transitions, and the latter, to the B(A$_2$) transition.[19]

The CD spectra of the Λ-*cis*-α isomers shown in Fig. 3 have a dominat positive band and a minor negative band at about 21800 and 25000 cm^{-1} respectively; they are markedly similar to those of $(-)_D$-*cis*-[Co(en)$_2$(NO$_2$)$_2$]$^+$ ion. Therefore, the CD bands at 21800 and 25000 cm^{-1} for the Λ-*cis*-α isomers can be assigned to the (A(E$_a$)+B(E$_a$)) transitions and the B(A$_2$) transition respectively. This is reasonable, since both of the bis(en) and the α-trien complexes are related by a common two-fold rotation axis (C$_2$), as is shown in Fig. 8.



(a) (b)

Fig. 8. The common two-fold rotation axis for *cis*-bis(en) and *cis*-α-trien complexes.

The CD spectra of the Δ-*cis*-β(*RS*) isomers show a dominant negative band and a minor positive band at about 22000 cm^{-1} and 25000 cm^{-1}, respectively. The positions of the band maxima of the major and the minor CD peaks correspond closely between the Λ-*cis*-α and Δ-*cis*-β(*RS*) isomers. This suggests that the *cis*-β isomer, which no longer has any symmetry elements, can be approximated by the same C_2 symmetry as the *cis*-α isomer. On this supposition, we assign the dominant negative band and the minor positive CD band of the Δ-β(*RS*) isomers to the (A(E$_a$)+B(E$_a$)) and the B(A$_2$) transitions respectively.

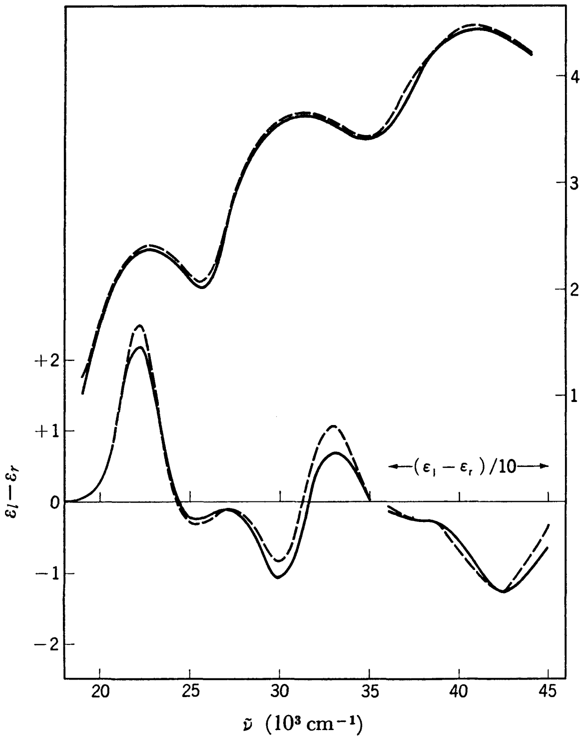


Fig. 9. Electronic absorption and CD spectra of the Λ-*cis*-β(*SS*) isomers. trien (——) and (5*R*)-metrien (- - -).

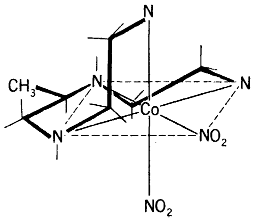


Fig. 10. Probable structure of the Λ-*cis*-β(*SS*)-[Co(5*R*)-metrien)(NO$_2$)$_2$]$^+$ ion.

The CD spectra of the Λ-*cis*-β(*SS*) isomers are given in Fig. 9. The exact structure of the dinitrocobalt(III) complex with (5*S*)-methyltriethylenetetramine ((5*S*)-metrien), which is enantiomeric to the (5*R*)-metrien used in this study, has been determined by a recent X-ray analysis study,[21] which has revealed that the complex ion takes the Δ-*cis*-β(*RR*) geometry, as expected. Thus, the (5*R*)-metrien complex should have the Λ-*cis*-β(*SS*) configuration, which is illustrated in Fig. 10. The CD curves in Fig. 9 have a major positive band and a minor negative band at about 22100 cm^{-1} and 25300 cm^{-1} respectively. The patterns of the CD curve of the present isomers are rather similar to those of the Δ-β(*RS*) isomers. Therefore, the two CD bands can be assigned in the same way as for the Δ-β(*RS*) isomers. This is in contrast to the cases of the dichloro complexes, where a notable shift is observed between these geometries in the CD maxima in the first absorption band region.

However, there is a notable difference in the CD curves of the Δ-β(*RS*) and of the Λ-β(*SS*) isomers in the NO$_2$ specific absorption band region (26000—35000 cm^{-1}). The Λ-β(*SS*) isomers show two CD peaks with opposite signs in this region, a negative

---

[19] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

[20] H. Yamatera, This Bulletin, **31**, 95 (1958).

[21] K. Tanaka, M. Ito, F. Marumo, and Y. Saito, unpublished result.

band at the lower-wavenumer side (near 30000 cm^{-1}) and a positive band at the higher-wavenumber side (near 33000 cm^{-1}), whereas the Δ-β(*RS*) isomers show only one positive band, near 31000 cm^{-1}, in this region. Since the bands of nitro-cobalt(III) complexes in this region consist not only of the ligand field transition (T_{2g} in the O_h symmetry), but also of the charge transfer transitions (between Co^{3+} and NO_2^-), it was impossible to assign the CD band in this region. However, the observed difference in the CD curves must be attributed to the differences in the structures of the diastereoisomeric complexes, that is, to the configuration of the secondary N centers and the conformations of the three chelate rings.

The CD curve of the (5*S*)-Me_3trien complex shows two CD bands with opposite signs in the specific absorption band region, a positive band at about 30000 cm^{-1} and a negative band at about 33000 cm^{-1}. This appears to indicate that the (5*S*)-Me_3trien has the Δ-*cis*-β(*RR*) geometry. At present, this complex is considered to have the Δ-*cis*-β-(*RS*) geometry; this assignment is based on a study of trien derivatives with an axially-oriented methyl group in the central diamine linkage.[22] The new type of Δ-*cis*-β(*RS*) isomer, which shows two CD bands with opposite signs in the specific absorption band region, has a fairly distorted structure because of the axial methyl group. It is noticiable that the (5*S*)-Me_3trien complex and its homologs show only one CD band in the first absorption band region, as is indicated in Fig. 7.

Thus, it is revealed that the CD curves of *cis*-β dinitrocobalt(III) complexes with trien derivatives can be classified into the following series; (1) the λ-β(*SS*) and Δ-β(*RR*) isomers have two CD bands in the first absorption band region and two CD bands in the specific absorption band region; (2) the Δ-β(*RS*) isomers have two CD bands in the first absorption band region and one CD band in the specific absorption band region, and (3) the distorted Δ-β(*RS*) isomers have one CD band in the first absorption band region and two CD bands in the specific absorption band region. The detailed structure for the distorted Δ-β(*RS*) isomer will be discussed in a subsequent paper.[22]

---

[22] H. Matsushita, M. Goto, M. Saburi, and S. Yoshikawa, unpublished result.