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Stereochemical Studies of Metal Chelates. VI. The Separation and Stereochemistry of Isomers of Dichloro((3*S*, 8*S*)-dimethyltriethylenetetramine)cobalt(III) Perchlorate

Masahiko Saburi and Sadao Yoshikawa
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

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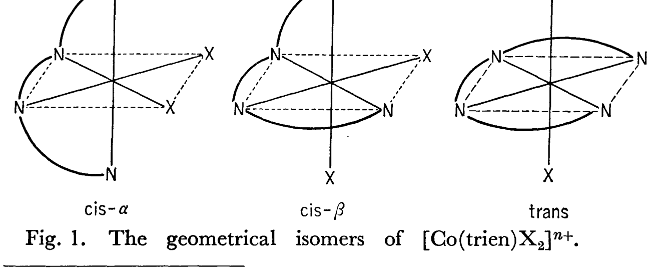
The *cis*-α and *cis*-β isomers of dichlorocobalt(III) complexes with (3*S*, 8*S*)-dimethyltriethylenetetramine were isolated. These isomers were stereospecifically formed in the Λ and Δ absolute configurations respectively. The *cis*-β isomerh as the Δ-β(*RS*) geometry, in which the configurations with respect to the coordinated secondary nitrogen centersof tetramine differ from one another. The difference between the Δ-β(*RS*) and Δ-β(*RR*) (and Λ-β(*SS*)) forms was noticed in the circular dichroism curves in the first absorption band region.

In a study of the diacidocobalt(III) complexes of triethylenetetramine (trien),[1] Basolo first pointed out the possibility of three geometrical isomers, *i.e.*, *cis*-α, *cis*-β, and *trans* (*c.f.* Fig. 1). These were isolated and resolved into optically-active antipodes by Sargeson and Searle for the first time.[2,3] The exact geometries of trien in the α and β configurations have recently been shown by X-ray diffraction studies.[4,5] Furthermore, it was suggested that the second *cis*-β form exists as a product of the Hg^{2+}-promoted acid hydrolysis reaction of the optically-active *trans*-$[Co(trien)Cl_2]^+$ ion.[6]



cis-α cis-β trans

Fig. 1. The geometrical isomers of $[Co(trien)X_2]^{n+}$.

The difference between the two *cis*-β geometries arises from the combination of the configuration of the coordinated secondary nitrogen centers. The asymmetric character of the coordinated secondary nitrogen atom has been well established for some cobalt(III) com-

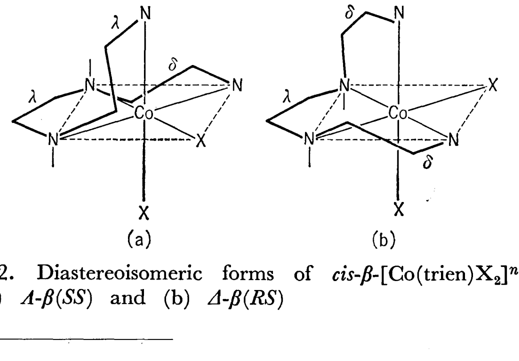


Fig. 2. Diastereoisomeric forms of *cis*-β-$[Co(trien)X_2]^{n+}$ (a) Λ-β(*SS*) and (b) Δ-β(*RS*)

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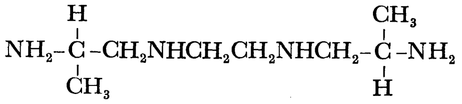
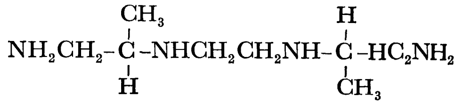
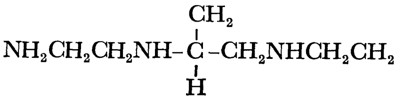
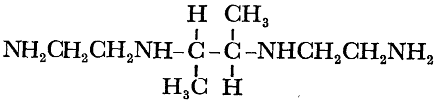
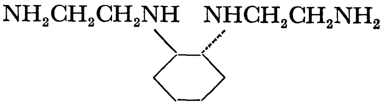
1) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).
2) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).
3) A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).
4) M. Dwyer and I. E. Maxwell, *ibid.*, **9**, 1450 (1970).
5) H. C. Freeman and I. E. Maxwell, *ibid.*, **8**, 1293 (1969).
6) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

plexes.[7–12] The structures of the two isomers of *cis*-β geometry are shown in Fig. 2. They are illustrated for the enantiomer, in which the central chelate ring takes the λ[13] conformation. The absolute configurations of the coordinated secondary nitrogen centers are the same for one isomer, designated as Λ[13]-*cis*-β(*SS*)[14] in Fig. 2 and its enantiomorph (Δ-*cis*-β(*RR*)), and different for the other, Δ-*cis*-β(*RS*)[14] in Fig. 2 and its enantiomorph (Λ-*cis*-β(*SR*)[14]). The former geometry was, in fact, observed for some *cis*-β isomers of trien complexes.[5,15–17] On the other hand, the trien cobalt(III) complex with the latter geometry has not yet been isolated except for some β_2-amino acidato complexes.[18]

A detail discussion of the chelate ring conformation of the β-configuration was published recently.[19] It is interesting to note that the conformations of the outer-side chelate rings are the same (δ and δ) for the Δ-*cis*-β(*RS*) geometry, while they are different (δ and λ) for the Λ-*cis*-β(*SS*) geometry, as is indicated in Fig. 2. In a recent study of the minimization of the conformational potential energy, it was suggested[20] that the most stable structures for the Δ-β_2-(*RS*) and Λ-β_2(*SR*) isomers of the $[Co(trien)(S\text{-}pro)]^{2+}$ ion are those in which the side arms of trien have the same conformation.

It has been well established by X-ray diffraction[21,22] and proton magnetic resonance[23] studies that the methyl group of propylenediamine adopts preferentially the equatorial position with respect to the diamine chelate ring. (2*S*,9*S*)-Dimethyltriethylenetetramine ((2*S*,9*S*)-dimetrien) and (3*S*,8*S*)-dimethyltriethylenetetramine ((3*S*,8*S*)-dimetrien) are optically-active derivatives of trien. The abbreviations and structures of trien derivatives used in the present study are summarized in Table 1. The absolute configuration of the asymmetric carbon atoms is the same *S* configuration for these tetramines, since all the asymmetric centers are derived from the *S*-alanine used as a starting material. If the substituted methyl groups prefer the equatorial orientation, the outer-side chelate rings should have the δ conformation. Accordingly, it was supposed that the *cis*-β isomer containing (2*S*,9*S*)- and (3*S*,8*S*)-dimetrien belongs to the Δ-*cis*-β(*RS*) geometry (shown in Fig. 2), since both the outer-side chelate rings for this structure are expected to have the δ conformation, as has been mentioned previously.

TABLE 1. ABBREVIATION AND STRUCTURE OF LIGANDS

Abbreviation	Structure
(2*S*,9*S*)-dimetrien	 $NH_2\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}CH_2NHCH_2CH_2NHCH_2\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}NH_2$
(3*S*,8*S*)-dimetrien	 $NH_2CH_2\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}NHCH_2CH_2NH\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}HC_2NH_2$
5(*R*)-metrien	 $NH_2CH_2CH_2NH\text{-}\overset{CH_2}{\underset{H}{C}}\text{-}CH_2NHCH_2CH_2NH_2$
(5*S*,6*S*)-dimetrien	 $NH_2CH_2CH_2NH\text{-}\overset{H}{\underset{H_3C}{C}}\text{-}\overset{CH_3}{\underset{H}{C}}\text{-}NHCH_2CH_2NH_2$
(*R*)-ECE	

Asperger and Liu[24] isolated three geometrical isomers of dichlorocobalt(III) complexes coordinated with (2*S*,9*S*)-dimetrien, *i.e.*, *cis*-α, *cis*-β, and *trans*. It was noticed by these authors[24] that the *cis*-α and *cis*-β isomers have stereospecifically the Λ- and Δ-absolute configurations respectively. Although the Δ-*cis*-β isomer was isolated, the detailed structure of this complex has not yet been clarified. It was supposed that the *cis*-α and *cis*-β isomers of dichlorocobalt(III) complexes with (3*S*,8*S*)-dimetrien, if obtained, should have the Λ and Δ-configurations respectively, as well as the (2*S*,9*S*)-dimetrien complexes. This is based on the expectation that, for both ligands, the outer-side chelate rings are fixed in the δ conformation due to the substituted methyl groups, though their positions are different in the two ligands. We have succeeded in the isolation of Λ-*cis*-α and Δ-*cis*-β-$[Co((3S,8S)\text{-}dimetrien)Cl_2]ClO_4$ and will report our results in the present paper.

Experimental

(2S,9S)-Dimethyltriethylenetetramine Tetrahydrochloride. This was prepared according to the method described by Asperger and Liu.[24]

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[7] B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).

[8] D. A. Buckngham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966).

[9] J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnnull, *Chem. Commun.*, **1967**, 324.

[10] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).

[11] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968).

[12] M. Saburi, Y. Tsujito, and S. Yoshikawa, *ibid.*, **9**, 1476 (1970).

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

[14] The nomenclature used is as follows: *R* and *S* designate the asymmetry about the "angular" and "planar" asymmetric N atoms of trien in that order and follow the rules suggested by R. S. Chan, C. K. Ingold, and V. Prelog (*Angew. Chem. Intern. Edn.*, **5**, 385 (1966), *cf.* ref. (6).

[15] D. A. Buckngham, H. C. Freeman, L. G. Marzilli, I. E. Maxwell, and A. M. Sargeson, *Chem. Commun.* **1969** 583.

[16] H. C. Freeman, L. G. Marzilli, and I. E. Maxwell, *Inorg. Chem.* **9**, 2408 (1970).

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

[18] C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, **4**, 1 (1970).

[19] D. A. Buckngham, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Inorg. Chem.*, **9**, 1921 (1970).

[20] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Am. Chem. Soc.*, **92**, 3617 (1970).

[21] Y. Saito and H. Iwasaki, This Bulletin, **35**, 1131 (1962).

[22] H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).

[23] S. Yano, H. Ito, Y. Koike, J. Fugita, and K. Saito, *ibid.*, **42**, 3184 (1969).

[24] R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).

(3S,8S)-Dimethyltriethylenetetramine Tetrahydrochloride. A tetraamide (11.5 g) obtained by the reaction of *S*-alanine amide with oxalyl chloride (described earlier[25]) was stirred into a suspension of lithium aluminum hydride (13.3 g) in anhydrous tetrahydrofuran (300 m*l*), after which the mixture was stirred and heated under reflux for 24 hr. After cooling to room temperature, 25 m*l* of water diluted with 50 m*l* of tetrahydrofuran was vigorously stirred, drop by drop, into the reaction mixture, after which the mixture was stirred for a further 30 min. The resultant slurry was filtered off and washed with tetrahydrofuran (100 m*l*). The residue was extracted with boiling tetrahydrofuran (200 m*l*) under reflux for 2 hr, filtered off, and washed as above. The filtrates and washing were combined, and the tetrahydrofuran was removed under reduced pressure. To the remaining liquid we added 20 m*l* of concentrated hydrochloric acid, and then ethanol was gradually added while hot until the mixture became turbid. After the solution has been cooled to room temperature overnight, the white crystals which separated were collected, washed with ethanol and ether, and dried under vacuum. Yield, 7.0 g.

Trans-*Dichloro((3S,8S)-dimethyltriethylenetetramine)cobalt(III) Perchlorate.* The preparation of this compound was described previously.[26]

Λ-cis-α-*Dichloro((3S,8S)-dimethyltriethylenetetramine)cobalt(III) Perchlorate.* The filtrate from which the *trans*-isomer has been removed as above was again cooled to 5°C, and the small amount of green crystals (*trans*-isomer) which precipitated was filtered off. To the filtrate we added 2 more m*l* of 60% perchloric acid, and the solution was stored at 5°C for 2 hr after scratching the side of the vessel with a glass rod. The violet crystals which separated was collected, washed with methanol and acetone, and air-dried. Yield, 0.1 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.81; H, 5.50; N, 13.88. Found: C, 23.20; H, 5.84; N, 13.51.

Δ-cis-β-*Dichloro((3S,8S)-dimethyltriethylenetetramine)cobalt(III) Perchlorate.* The filtrate from the separation of the Λ-*cis*-α-isomer was left to stand at room temperature for one or two days. The reddish-purple crystals which separated were filtered off, washed with ethanol and acetone, and air-dried. Yield, 0.3 g. A second crop could be obtained by letting the filtrate stand for one or two more days. Yields, 0.2 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.81; H, 5.50; N, 13.88. Found: C, 23.72; H, 5.63; N, 13.84.

Λ-cis-α-*Dinitro((2S,9S)-dimethyltriethylenetetramine)cobalt(III) Chloride.* To a solution containing (2S,9S)-dimetrien·4HCl (3.40 g) and $LiOH \cdot H_2O$ (1.25 g) in 50 m*l* of water, we added $CoCl_2 \cdot 6H_2O$ (2.38 g) and then the solution was cooled in an ice bath. After $NaNO_2$ (1.47 g) had been added, the resultant solution was aerated with carbon dioxide-free air in an ice bath for 1 hr and then for 4 more hr at room temperature. The precipitated impurity was filtered off and washed with a small volume of water. The filtrate and washings were combined and evaporated on a steam bath to a volume of 15 m*l* and then cooled in an ice bath overnight. The yellow-brown crystals which separated were filtered off and washed with a small volume of cold water and ethanol. Yield, 1.5 g. The combined filtrate and washings were further evaporated on a steam bath to about 7 m*l* and then cooled as above. The crystals were filtered off and washed with cold water and ethanol. Yield, 1.0 g. The crude products, which were contaminated with a black impurity, were dissolved in a minimum volume of warm water, filtered, and cooled to room temperature. After the solution had stood overnight, the yellow-brown crystals were filtered off, washed with a small volume of cold water and ethanol, and air-dried. *Anal.* Calcd for $[Co(C_8H_{22}N_4)(NO_2)_2]Cl$: C, 26.64; H, 6.15; N, 23.30. Found: C, 26.52; H, 6.20; N, 23.41.

Λ-*cis*-α-*Dichloro((2S,9S)-dimethyltriethylenetetramine)cobalt(III) Chloride Monohydrate.* Λ-*cis*-α-[Co((2*S*,9*S*)-dimetrien)-$(NO_2)_2$]Cl (1.0 g) was dissolved in 30 m*l* of hydrochloric acid (1:1), and the resultant solution was evaporated on a steam bath almost to dryness. The residue was treated with 10 m*l* of methanol with gentle boiling, and the crystallized product was filtered off, washed with cold methanol and acetone, and air-dried. Yield, 0.7 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]Cl \cdot H_2O$: C, 26.88; H, 6.76; N, 15.67. Found: C, 26.60; H, 6.60; N, 15.97.

Δ-*cis*-β-*Dichloro((2S,9S)-dimethyltriethylenetetramine)cobalt(III) Perchlorate.* A mixture of Λ-*cis*-α-[Co((2*S*,9*S*)-dimetrien)]-$Cl_2 \cdot H_2O$ (0.51 g) and Li_2CO_3 (0.15 g) in 5 m*l* of water was heated on a steam bath for 30 min, cooled to room temperature, and filtered to remove the excess Li_2CO_3. To a solution of Δ-β-[Co((2*S*,9*S*)-dimetrien)CO_3]$^+$ prepared *in situ.* as above, we added 5 N HCl (2 m*l*); the resultant solution was evaporated under a current of air on the surface at room temperarure. When the volume of solution was reduced to 2 m*l*, 60% perchloric acid (1 m*l*) was added. The green crystals of *trans*-[Co((2*S*,9*S*)-dimetrien)Cl_2]ClO_4 which separated were removed whenever necessary, and the filtrate was allowed to stand at room temperature. The reddish-purple crystals which separated were collected, washed with methanol, and air-dried.

Measurements. The visible absorption spectra were measured with a Shimadzu MPS-50L spectrophotometer. The circular dichroism spectra were measured with a JASCO J-20 automatic spectropolarimeter. The spectra of the *cis*-α isomers and of the *cis*-β isomers were measured in 5 N HCl and concentrated HCl solutions to avoid aquation of the complexes.

Results and Discussion

Yoshikawa, Sekihara, and Goto isolated a green *trans* isomer of the dichlorocobalt(III) complex with (3*S*,8*S*)-dimetrien.[25] In spite of the poor agreement between the calculated and found values, especially for

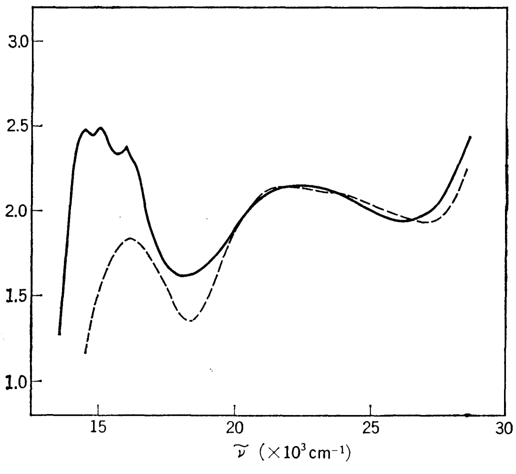

Fig. 3. Absorption Spectra of *trans*-[Co((3*S*,8*S*)-dimetrien)-Cl_2]$_2$$CoCl_4$ in concentrated hydrochloric acid (———) and *trans*-[Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4 in methanol (---------).

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

[26] M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *ibid.*, **9**, 1488 (1970).

the hydrogen proportion (Found 5.5%; Calcd 6.5%), the constitution of this compound was considered to be $[Co(C_8H_{22}N_4)Cl_2]Cl \cdot HCl \cdot 1.5\ H_2O$. However, it has now been found that the exact constitution of this complex is $[Co(C_8H_{22}N_4)Cl_2]_2(CoCl_4)$. The calculated and found values for this constitution are as follows; Calcd: C, 23.8; H, 5.5; N, 13.9; Cl, 35.1. Found: C, 24.0; H, 5.5; N, 13.9; Cl, 35.2.

The absorption spectrum of the above *trans* complex, measured in concentrated hydrochloric acid, is shown in Fig. 3, where the ε value is evaluated per mole of the Co(III) complex. The complicated strong absorption bands found in the region of 14000—17000 cm^{-1} in a concentrated HCl solution are characteristic of the tetrachlorocobaltate(II) anion.[27] The diffusion reflectance spectrum shows similar peaks in this region, indicating that the $CoCl_4^{2-}$ ion is present in the solid state as the counter ion of this dichlorocobalt(III) complex. This complex anion was also found as the counter ion of *trans*-dichlorocobalt(III) complexes containing *N*-alkyl ethylenediamines.[28] The $CoCl_4^{2-}$ ion appears to be decomposed immediately after the complex is dissolved in methanol, and so it was overlooked in the former study.[25]

We perceived some difficulties in the course of isolating the pure crystalline product of Λ-*cis*-α-[Co((2*S*,9*S*)-dimetrien)Cl_2]Cl by the method of Asperger and Liu,[24] which can be regarded as an ordinary procedure for preparing the dichlorocobalt(III) complex. This was probably the result of the coexistence of the $CoCl_4^{2-}$ ion, which disturbs the crystallization of the desired products.

It was effective to use anions other than the chloride ion in order to isolate the pure crystalline products of the *cis*-α and *cis*-β isomers of the dichloro complex with (3*S*,8*S*)-dimetrien. We succeeded in isolating the *cis*-α and *cis*-β isomers by the use of perchlorate ion along with the *trans* isomer.

On the addition of 60% perchloric acid to a concentrated solution which seemed to contain three possible isomers of the [Co((3*S*,8*S*)-dimetrien)Cl_2]$^+$ ion, green crystals of the *trans*-[Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4 immediately crystallized out.[26] The absorption spectrum of this isomer (given in Fig. 3) resembles that of the *trans*-[Co((3*S*,8*S*)-dimetrien)Cl_2]$_2$($CoCl_4$) except for the region of the absorption due to the $CoCl_4^{2-}$ complex anion. The CD spectra of the complexes of such a type have been discussed previously.[25,29]

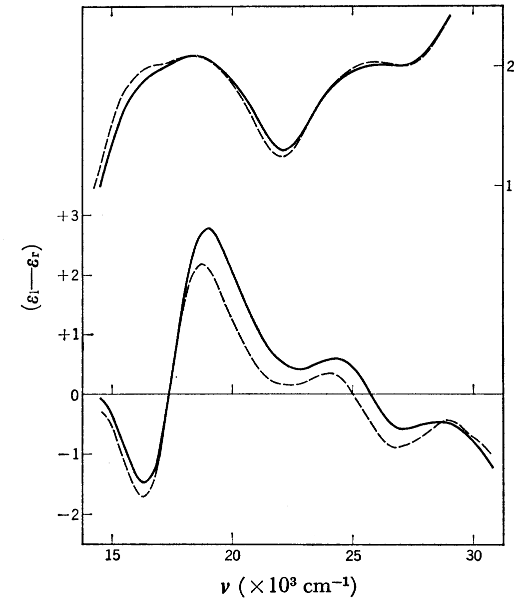

Fig. 4. Absorption and CD spectra of Λ-α isomers; (3*S*,8*S*)-dimetrien (——) and (2*S*,9*S*)-dimetrien (------)

Table 2. Spectral data

Complex	Absoption spectra		CD spectra	
	λ_{max} (cm^{-1})	log ε_{max}	λ_{max} (cm^{-1})	$\Delta\varepsilon_{max}$
Λ-*cis*-α-[Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4	18450	2.09	16340	−1.49
			18940	+2.78
	26040	2.02	24270	+0.59
			27100	−0.57
Λ-*cis*-α-[Co((2*S*,9*S*)-dimetrien)Cl_2]Cl·H_2O	18350	2.09	16290	−1.71
			18690	+2.19
	25970	2.04	24100	+0.35
			26810	−0.89
Δ-*cis*-β-[Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4	18420	2.11	18690	−1.18
	25190	2.10	24330	−0.60
Δ-*cis*-β-[Co((2*S*,9*S*)-dimetrien)Cl_2]ClO_4	18800	2.21	19050	−1.55
	25320	2.18	24630	−0.40
Λ-*cis*-β-[Co((5*R*)-metrien)Cl_2]Cl·$0.5H_2O$	18690	2.12	(14750	−0.04)
			17090	+0.94
	25640	2.10	24270	+0.34
Δ-*cis*-β-[Co((5*S*,6*S*)-dimetrien)Cl_2]Cl·H_2O	18800	2.14	17090	−1.05
	25580	2.10	23980	−0.38
Λ-*cis*-β-[Co((*R*)-ECE)-Cl_2]Cl·H_2O	18590	2.14	(14490	−0.04)
			16860	+1.37
	25640	2.12	24390	+0.33

After the *trans* isomer has been completely removed, a small amount of blue-violet crystals was separated from the filtrate by the addition of more perchloric acid. The visible absorption and CD spectra of this complex are shown in Fig. 4. The spectral data are summarized in Table 2. The absorption spectrum shows a shoulder at a lower wave-number side of the first absorption band. The same feature in the first absorption band was also observed for the *cis*-α-[Co(trien)Cl_2]$^+$ ion, but it was not detected for the *cis*-β isomer of the trien complex. This suggests that the blue-violet isomer has the *cis*-α configuration. Further, the CD spectrum shown in Fig. 4 apparently resembles that of $(+)_D$-*cis*-α [Co(trien)Cl_2]ClO_4 shown by Sargeson and Searle,[2] which was assigned the Λ configuration. Therefore, it was determined that the blue-violet isomer of [Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4 takes, stereospecifically, the Λ-*cis*-α configuration.

The dichlorocobalt(III) complex of (2*S*,9*S*)-dimetrien, which has been shown to adopt preferentially the Λ-*cis*-α configuration, was also prepared. As has been mentioned previously, it was slightly difficult to

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27) L. I. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954).

28) E. W. Gillow and G. M. Harris, *Inorg. Chem.*, **7**, 394 (1968).

29) D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Commun.*, **1967**, 433.

obtain the pure crystalline product of this complex by the method of Asperger and Liu.[24] Hence, we prepared it through a reaction of the corresponding dinitro complex with hydrochloric acid. The product thus obtained showed visible and CD spectra identical with those of the complex obtained by the method of Asperger and Liu,[24] shown in Fig. 4. Apparently, the first absorption band has a shoulder on the lower wave number side. This spectral feature may be regarded as a characteristics of the *cis*-α isomer of the dichlorocobalt(III) complex with tetramines. The CD curve is also similar to those of the (+)$_D$-*cis*-α-[Co(trien)Cl_2]ClO_4 and of the blue-violet isomer of the (3*S*,8*S*)-dimetrien complex.

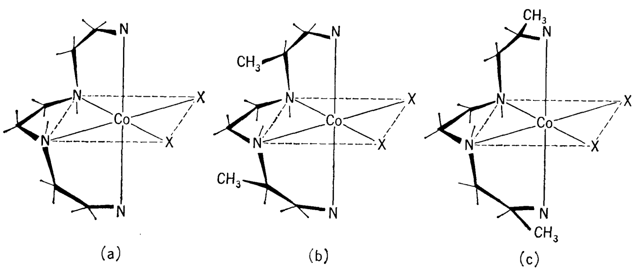

Fig. 5. Structures of Λ-α configurations; (a) trien, (b) (3*S*,8*S*)-dimetrien, and (c) (2*S*,9*S*)-dimetrien.

According to a recent X-ray analysis study,[4] the structure of the Λ-*cis*-α trien complex has been determined to be as shown in Fig. 5(a), where both the outer-side chelate rings adopt the δ conformation. Since the preferred conformation of the outer chelate rings of the (3*S*,8*S*)- and (2*S*,9*S*)-dimetrien is the δ-gauche form, as has been mentioned previously, it is reasonable that the *cis*-α isomers of these complexes give rise to the Λ configuration. Their probable structures are illustrated in Fig. 5, (b) and (c) respectively. For these configurations, the methyl groups are all situated in the equatorial orientations. The Δ isomer, in which the methyl groups should adopt the axial orientations, is energetically unstable as compared with the Λ isomer. This is a reason why the former isomer could not be obtained in this study.

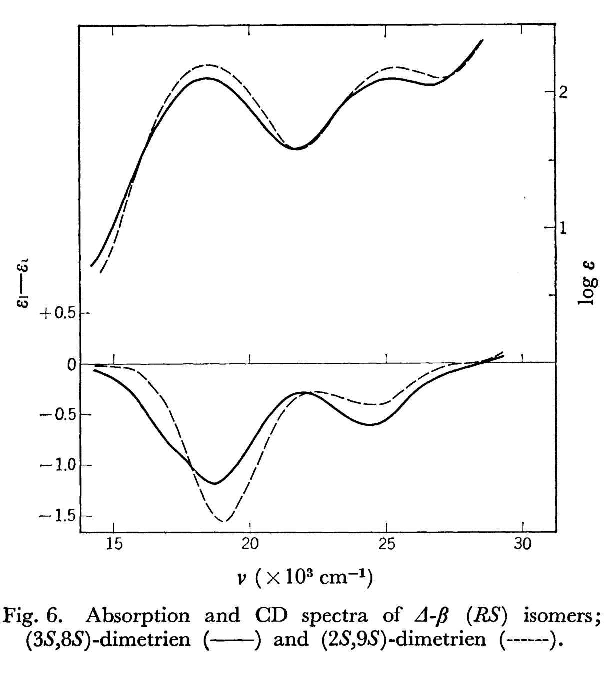

Fig. 6. Absorption and CD spectra of Δ-β (*RS*) isomers; (3*S*,8*S*)-dimetrien (——) and (2*S*,9*S*)-dimetrien (------).

The third isomer of [Co((3*S*,8*S*)-dimetrien)Cl_2]ClO_4 was obtained as reddish-pink precipitates, which are separated out by letting the filtrate from which the *cis*-α isomer has been removed stand for two or three days. The visible absorption and CD spectra of this compound are shown in Fig. 6. No shoulder of the first absorption band was detected for the present complex, suggesting that it takes the *cis*-β configuration. The CD curve of this isomer shows only one negative peak in the first absorption band region. The Δ-*cis*-β-[Co((2*S*,9*S*)-dimetrien)Cl_2]$^+$ ion, which was first obtained by Asperger and Liu,[24] was prepared by a different method through the Λ-*cis*-α isomer in the present study. This complex shows the absorption and CD curves given in Fig. 6. They are apparently similar to the corresponding curves of the reddish-pink isomer of the (3*S*,8*S*)-dimetrien complex. Thus, it was determined that the reddish-pink isomer takes, stereospecifically, the same absolute configuration as the *cis*-β isomer of the (2*S*,9*S*)-dimetrien complex, *i.e.*, the Δ-*cis*-β configuration.

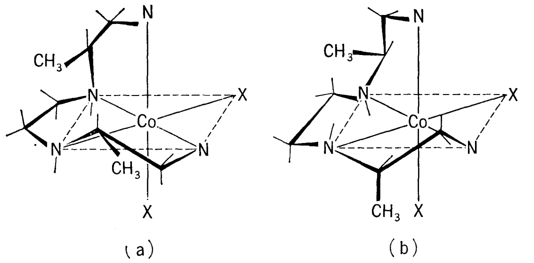

Fig. 7. Structures of Δ-β isomers of (3*S*,8*S*)-dimetrien; (a) Δ-β(*RS*) and (b) Δ-β(*RR*).

The probable structures for the Δ-*cis*-β isomer of (3*S*,8*S*)-dimetrien are illustrated in Fig. 7(a) and (b). For the Δ-*cis*-β(*RS*)[30] geometry (a), both the methyl groups are equatorially oriented, and the outer chelate rings take the δ conformation. On the other hand, one of the methyl groups, which is present in the "in-plane" chelate ring, having the λ conformation, takes the axial orientation for the Δ-*cis*-β(*RR*) geometry, though the other is in the equatorial position. Because of the difference in methyl orientation, the former geometry is more probable than the latter. The difference in axial and equatorial methyl groups was estimated to be 2.0 kcal/mole for the propylenediamine chelate ring.[31] It is reasonable to consider that the above estimation is applicable to the (2*S*,9*S*)-dimetrien complex. It was demonstrated by the X-ray diffraction method for the dinitro complex that the Δ-*cis*-β

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[30] The *RS* representation of the absolute configuration of the coordinated nitrogen centers is complicated in the 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. Therefore, the absolute configuration of the coordmated secondary nitrogen centers is represented by *R* and *S*, neglecting, for simplicity, the substituted methyl groups in this paper.

[31] A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

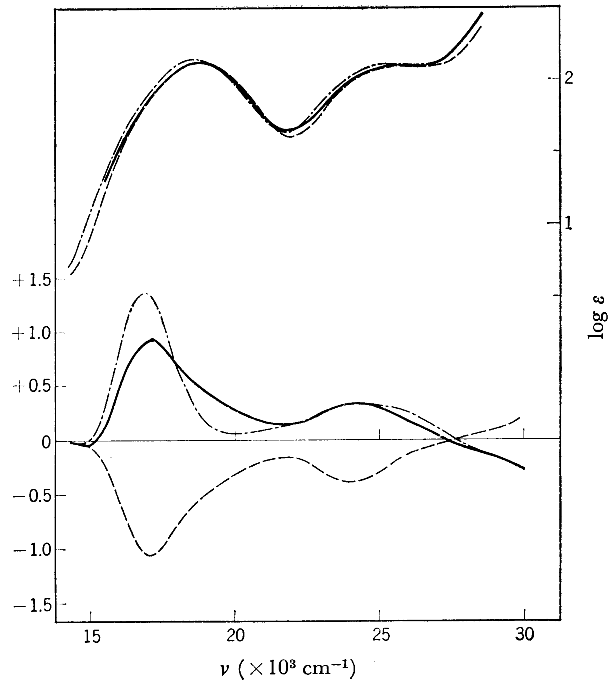

Fig. 8. Absorption and CD spectra for *Λ*-*β*(*SS*) and *Δ*-*β*(*RR*) geometries; (5*R*)-metrien (*Λ*) (——), (5*S*,6*S*)-dimetrien (*Δ*) (------), and (*R*)-ECE (*Λ*) (-·-·-·).

isomer of (3*S*,8*S*)-dimetrien possesses the *Δ*-*cis*-*β*(*RS*) geometry, as has been expected.[32]

It seems likely that CD curves are affected by the structural differences, *i.e.*, the absolute configuration of the coordinated secondary nitrogen center and the conformation of each chelate ring. The CD curves of the *Λ*-*cis*-*β*(*SS*) or *Δ*-*cis*-*β*(*RR*)-dichloro complexes of trien derivatives with equatorially-oriented substituents at the central diamine linkage were examined. The structures of these complexes had previously been established as indicated.[33] Their CD and absorption curves are shown in Fig. 8.

There was no definite difference in the absorption spectra of the two types of *cis*-*β* isomer. The *Δ*-*β*(*RS*) isomer exhibited its first absorption maxima at about 18500 cm^{-1}, while the *Λ*-*β*(*SS*) and *Δ*-*β*(*RR*) isomers exhibited theirs at about 18600—18800 cm^{-1}. This suggests that the difference in ligand field due to the structural changes is negligibly small for both the geometries.

On the contrary, an obvious difference in their CD curves could be noted between the *Δ*-*β*(*RS*) and *Δ*-*β*-(*RR*) (or *Λ*-*β*(*SS*)) forms in the first absorption band region. The *Δ*-*β*(*RS*) isomers of (3*S*,8*S*)- and (2*S*,9*S*)-dimetrien complexes showed dominant negative CD maxima at about 19000 cm^{-1}. The *Δ*-*β*(*RR*) isomer of (5*S*,6*S*)-dimetrien showed a negative CD peak at 17000 cm^{-1}. The *Λ*-*β*(*SS*) isomers of (5*R*)-metrien and (*R*)-ECE also exhibited the corresponding positive CD peaks at about 17000 cm^{-1}. It was clearly observed that the dominant CD peak for the *Δ*-*β*(*RS*) forms is shifted by 2000 cm^{-1} to the higher wavenumber side than those for the *Δ*-*β*(*RR*) and *Λ*-*β*(*SS*) forms. The observed shift of the CD maxima in the first absorption band region may be useful for distinguishing the geometries of *cis*-*β* dichlorocobalt(III) complexes with any trien derivatives.

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

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