

Preparation of {N-(2-Aminoethyl)-1,3-propanediamine}(diethylenetriamine)-cobalt(III) Complex, and Separation and Optical Resolution of the Isomers

Minoru ISHII

Department of Chemistry, College of Science, Rikkyo (St. Paul's) University,
Nishi-ikebukuro, Toshima-ku, Tokyo 171

(Received February 24, 1984)

The mixed ligand complex {N-(2-aminoethyl)-1,3-propanediamine}(diethylenetriamine)cobalt(III) was prepared. Of the five possible geometrical isomers, two were isolated by column chromatography; their formation ratio was *ca.* 6:4. Both isomers were completely resolved by chromatography. Their configurations were assigned to the meridional type on the basis of electronic, infrared, and circular dichroism spectroscopy, and the X-ray analysis data.

The linear triamine, N-(2-aminoethyl)-1,3-propanediamine (NH₂CH₂CH₂CH₂NHCH₂CH₂NH₂; abbreviated as *aepn*), can act as a terdentate ligand. It coordinates to the central metal ion in two topological ways. The mixed complex, [Co(*aepn*)(dien)]³⁺ (dien; diethylenetriamine), exists in five geometrical isomers: Three *facial* (*fac*) isomers and two *meridional* (*mer*) isomers (Fig. 1). The difference between the two *mer*-geometries arises from the orientation of the N (secondary)-H bond in the dien ligand. Further, there are the optically active antipodes arising from an alternative configuration (*R/S*) of the secondary nitrogen atom in the *aepn* (Fig. 2). Thus, this isomerism can be expected to hold for the *mer*-isomers, and it should be recognized as a new type.

As a few examples of complexes which can be expected to show similar stereochemistry and isomerism, [Co(dien)₂]³⁺,¹⁾ [Co(dema)(dien)]³⁺, [Co(dema)₂]³⁺ (dema; N-methylbis(2-aminoethyl)amine),²⁾ and [Co(dpt)₂]³⁺ (dpt; bis(3-aminopropyl)amine)³⁾ have been prepared and their spectroscopic data reported. Among these complexes, all three of the possible iso-

mers of [Co(dien)₂]³⁺ were isolated,¹⁾ and the molecular structures were determined by the X-ray analysis of the *sym-fac*-[Co(dien)₂]Br₃,⁴⁾ (–)₅₈₉ *unsym-fac*-[Co(dien)₂]-[Co(CN)₆]·2H₂O⁵⁾ and (+)₅₈₉ *mer*-[Co(dien)₂]Br₃·1.6H₂O⁶⁾ crystals.

Various types of optically active complexes also have been reported recently and studied for their stereochemical geometries. With respect to the polyamine cobalt(III) complexes, a considerable number of determinations of absolute configurations were accomplished by an X-ray analysis technique. On the basis of these results, attempts to relate the spectroscopic data with the geometrical structures were carried out. Hence, it has become feasible to discuss quantitative details, such as the relationship between the absolute configuration and the circular dichroism (CD) spectrum, and the estimation of the contributions in the CD spectrum. This discussion is, however, limited to special types. Most of the empirical and quasi-empirical rules are useful for the complexes containing a five-membered chelate or planar six-membered chelate rings, but no

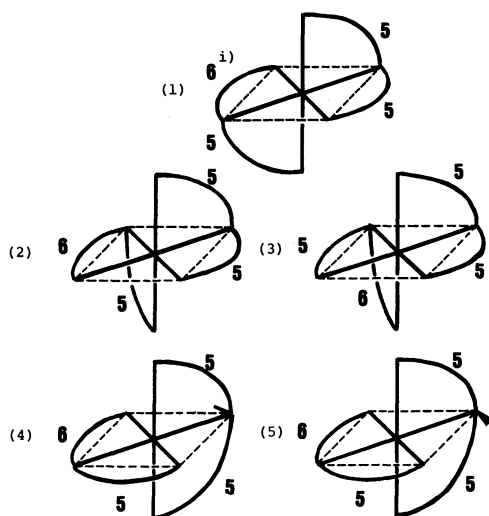


Fig. 1. Geometrical isomers of [Co(*aepn*)(dien)]³⁺. (1): *sym-fac* type, (2),(3): *unsym-fac* type, (4),(5): *mer* type.

i) The numbers 5, 6 mean the number of chelate ring members.

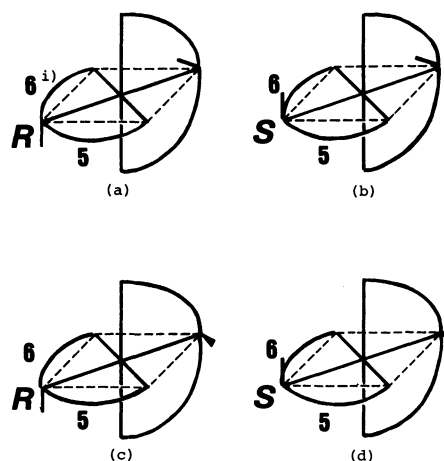


Fig. 2. Two types of *mer*-[Co(*aepn*)(dien)]³⁺ and their antipodes.

mer-I type: (a) *trans*- δ -NH(*R*),¹¹⁾ (b) *trans*- λ -NH(*S*),
mer-II type: (c) *trans*- λ -NH(*R*), (d) *trans*- δ -NH(*S*).

i) The numbers 5, 6 mean the number of chelate ring members.

ii) See Appendix of Ref. 12.

rule is useful for the nonplanar six-membered chelate and larger chelate ring systems. In the [Co(aepn)(dien)]³⁺ complex, three five-membered chelate rings and a six-membered one may coexist and be fused. From this viewpoint, it seemed that it would be interesting to investigate this complex. Moreover, the very fact that this is a new type of isomerism for the *mer*-isomers is worth noting.

In this paper, the preparation of [Co(aepn)(dien)]³⁺, and its d-d absorption, CD and infrared spectra will be presented.

Experimental

Ligands and Reagents. The aepn and dien ligands were obtained from the Aldrich Chemical Co., Inc., and the Tokyo Kasei Co., Inc., respectively, and were used without further purification. The *mer*-[CoCl₃(dien)] complex was prepared according to the method described in the literature.⁷ An ion-exchange resin (SP-Sephadex C-25) was obtained from Pharmacia Fine Chemicals Co., Inc. All the other reagents were obtained commercially.

Measurements. The elution curves were recorded with a Hitachi Perkin Elmer 139 spectrophotometer. The visible and near-ultraviolet absorption spectra were measured with a Hitachi EPS 3T spectrophotometer using 10-mm quartz cells. The CD spectra were obtained on a JASCO J-500 automatic spectropolarimeter using attached 10-mm quartz cells. The infrared spectra were measured with a JASCO A 202 infrared spectrophotometer by using Nujol mulls. All the spectral measurements were carried out at room temperature.

Analytical. The content of cobalt was colorimetrically determined by the nitroso-R method, while the contents of the other elements, C, H, N, and Cl, were measured at the Organic Analysis Center of the Institute of Physical and Chemical Research.

Preparation of the Complex, and Separation and Resolution of the Isomer. To 2.7 g of finely ground *mer*-[CoCl₃(dien)]⁷ suspended in 5 cm³ of dimethyl sulfoxide (DMSO), 1.5 g of aepn was added in small portions, after which the mixture was stirred for 3 h at room temperature. The resulting orange solution was diluted with a small amount of water, and then the unreacted material was filtered off rapidly. The filtrate was poured into a SP-Sephadex C-25 column (H⁺ form, ϕ 4 cm \times ca. 30 cm) in several portions. After washing with 1.0 dm³ of water and 1.0 dm³ of 0.01 mol dm⁻³ hydrochloric acid, the elution was carried out with 0.10 mol dm⁻³ hydrochloric acid. The eluate was collected and evaporated to dryness with an evaporator (35 °C) to

remove the hydrochloric acid. The residue was dissolved in a small amount of water. Upon the addition of NaClO₄, the resulting solution gave 3.7 g of the desired product in a 64% yield for perchlorate. This product was then dissolved in a small amount of water, and the solution was poured into a column containing the SP-Sephadex C-25 resin (H⁺ form, ϕ 2.0 cm \times ca. 100 cm) and washed with a large amount of water. When the elution was carried out with an acidic solution (pH \approx 2, 0.20 mol dm⁻³ Na₂SO₄ + H₂SO₄), two orange-colored bands descended (the elution order: I, II).⁹ The two eluates of these bands were independently collected and once more charged on a column of SP-Sephadex C-25 resin (H⁺ form, ϕ 2.0 cm \times ca. 100 cm). By elution with a 0.20 mol dm⁻³ sodium bis[(+)-589 tartrato]diantimonate(III) solution, the two orange bands were separated. The four layers thus obtained (I-(1), I-(2), II-(1), and II-(2)) were optically active. The four eluents corresponding to these layers were independently collected and poured into a column of SP-Sephadex C-25 resin (H⁺ form, ϕ 4.0 cm \times ca. 30 cm). After having been washed with 2.0 dm³ of water and 1.0 dm³ of 0.01 mol dm⁻³ hydrochloric acid, elution with 0.10 mol dm⁻³ hydrochloric acid was carried out. The eluted solutions were evaporated to dryness at a low temperature (35 °C) and *in vacuo*. After the removal of the hydrochloric acid by evaporation, the residue was dissolved in a small amount of water. To this orange solution, NaClO₄ was added, after which the mixture was kept in a refrigerator. The orange precipitate was recrystallized from warm water. The analytical data of the four isomers thus obtained (I-(1), I-(2), II-(1), and II-(2)) are listed in Table 1.

Results and Discussion

The elution curves obtained at each step are shown in Fig. 3. Only two single bands are found in the first elution as shown in Fig. 3 (a) (the area ratio I:II is ca. 6:4); no indication of further separation can be recognized. On the preparation of complexes containing diverse ligands, it is generally known that a series of complexes which differ in the composition of the ligands is obtained as by-products. However, in the present reaction, there is little expectation that any [Co(dien)₂]³⁺⁹ and [Co(aepn)₂]³⁺¹⁰ can be obtained. In order to examine the behavior of these impurities in SP-Sephadex chromatography, these complexes were added beforehand to [Co(aepn)(dien)]³⁺, and then the mixed samples (Fig. 4 (a), (b)) and a sample containing [Co(dien)₂]³⁺ (Fig. 4 (c)) were eluted independently in a manner similar to the above. It was found that the behavior of *mer*-[Co(dien)₂]³⁺ and the mixture of

TABLE 1. ELEMENTAL ANALYSIS OF ISOMERS

Isomer	Formula	Found (Calcd) (%)				
		Co	C	H	N	Cl
I-(1)	CoC ₉ H ₂₈ N ₆ Cl ₃ O ₄ ·H ₂ O	12.78	23.48	6.30	17.73	22.30
		(12.60)	(23.11)	(6.47)	(17.97)	(22.74)
I-(2)	CoC ₉ H ₂₈ N ₆ Cl ₃ O ₄ ·H ₂ O	12.35	22.39	5.97	17.34	22.55
		(12.60)	(23.11)	(6.47)	(17.97)	(22.74)
II-(1)	CoC ₉ H ₂₈ N ₆ Cl ₃ O ₁₂ ·1/2H ₂ O	9.77	18.53	4.87	14.42	18.27
		(10.04)	(18.43)	(4.98)	(14.33)	(18.12)
II-(2)	CoC ₉ H ₂₈ N ₆ Cl ₃ O ₈ ·1/2H ₂ O	11.69	21.01	5.49	15.77	19.58
		(11.28)	(20.68)	(5.59)	(16.08)	(20.35)

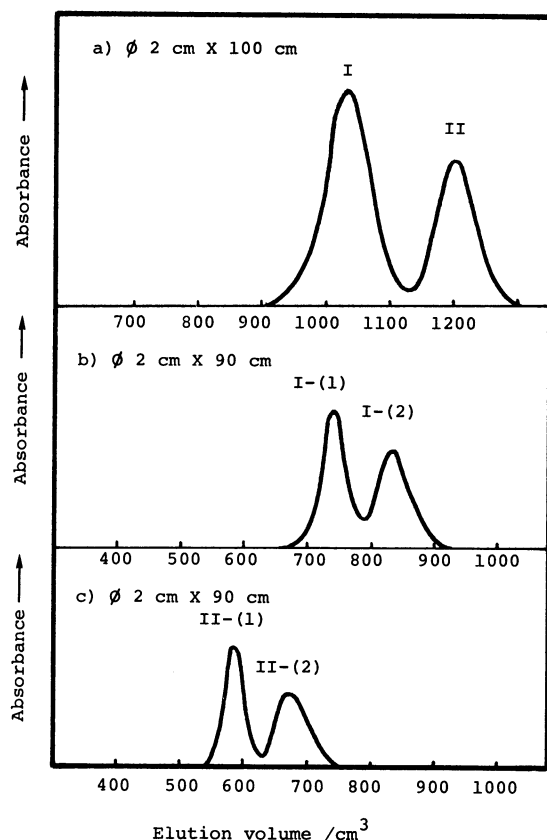


Fig. 3. Elution curves of the isomers of $[\text{Co(aepn)(dien)}]^{3+}$ at 475 nm. Eluents are as follows : a) $0.20 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ acidic solution ($\text{pH} \approx 2$). b), c) 0.20 mol dm^{-3} sodium bis[(+)₅₈₉-tartrato]diantimonate(III) solution.

isomers of $[\text{Co(aepn)}_2]^{3+}$ was somewhat analogous to that of the I and II isomers in chromatogram. However, careful and repeated elution of the I and II isomers of $[\text{Co(aepn)(dien)}]^{3+}$ did not provide any evidence indicating any further separation of other species. In the following elution, two bands with the area ratio of *ca.* 1:1 descended (Fig. 3 (b), (c)). From these facts, it was concluded that little or no $[\text{Co(dien)}_2]^{3+}$ and $[\text{Co(aepn)}_2]^{3+}$ were obtained by this synthetic process; hence, the process was effective for the preparation of $[\text{Co(aepn)(dien)}]^{3+}$.

The absorption and CD spectra of the isolated isomers in the visible and near-ultraviolet region ($18000\text{--}46000 \text{ cm}^{-1}$) are shown in Figs. 5 and 6 respectively, while their spectroscopic data are listed in Table 2. Among the absorption spectra, the positions and intensities of all the bands were approximately the same. In the three isomers (*mer*-, *unsym-fac*-, and *sym-fac*-) of $[\text{Co(dien)}_2]^{3+}$,¹⁾ differences in the maxima of the absorption bands were observed. These facts indicate that the four isomers (I-(1), I-(2), II-(1), and II-(2)) of $[\text{Co(aepn)(dien)}]^{3+}$ have a structural resemblance. Compared with the known complexes of the $[\text{Co(triamine)}_2]^{3+}$ type, the maximum of the first absorption band is at a lower energy side than those of the three isomers of $[\text{Co(dien)}_2]^{3+}$ ¹⁾ and at a higher energy side than those of

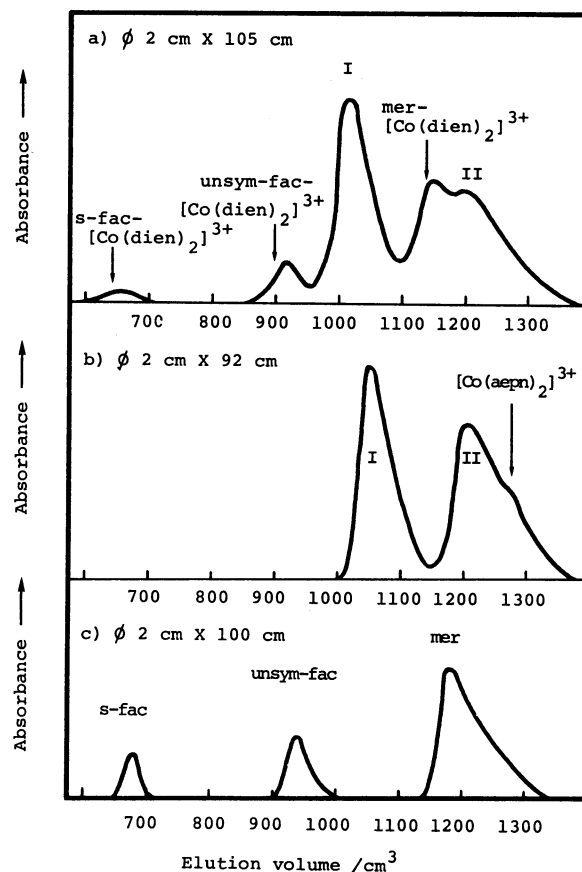


Fig. 4. Behavior of relevant complexes in column chromatography. a): $[\text{Co(aepn)(dien)}]^{3+} + [\text{Co(dien)}_2]^{3+}$, b): $[\text{Co(aepn)(dien)}]^{3+} + [\text{Co(aepn)}_2]^{3+}$, c): $[\text{Co(dien)}_2]^{3+}$. The eluent is $0.20 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ acidic solution ($\text{pH} \approx 2$).

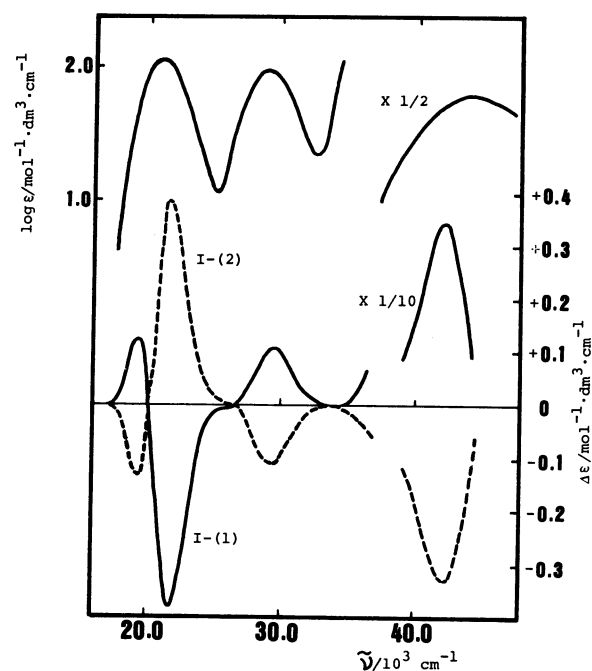


Fig. 5. Absorption and CD spectra of isomer I of $[\text{Co(aepn)(dien)}]^{3+}$.

[Co(aepn)₂]³⁺¹⁰ and *mer*-[Co(dpt)₂]³⁺³⁾ These differences in absorption bands were concluded to be due to aepn which was located at a lower position than dien and at a higher position than dpt in the spectrochemical series. In a series of complexes of the [Co(en)_x(tn)_y(tmd)_z]³⁺ type ($x=0-3$, $y=0-3$, $z=0-3$, $x+y+z=3$: tn=1,3-propanediamine, tmd=1,4-butanediamine), it was observed by Kojima *et al.*¹¹⁾ that the maximum of the absorption bands shifted to the lower energy side as the number of ring members increased. A similar shift is observed for the complexes of the [Co(triamine)₂]³⁺ type as the number of ring members increases from 5 to 6.

In the CD spectra as well as in the absorption spectra, a similarity in the band positions is also found for the four isomers. The pattern and magnitude of two pairs of the spectra, (I-(1) and I-(2), and II-(1) and II-(2)), are mirror images of each other. These findings indicate that they are two pairs of enantiomers with a structural resemblance; this fact agrees with the results obtained from chromatography.

The present author and his associates have already determined the molecular and absolute structures of the I-(1) isomer to be *mer-trans-δ-NH(R)* (corresponding to the *mer-I* type in Fig. 2 (a)) by the X-ray crystal analysis of the iodide monohydrate crystal.¹²⁾ Therefore, the structure of the antipode I-(2) can naturally be assigned to *mer-trans-λ-NH(S)* and, further, that of other pair (II-(1) and II-(2)), to the *mer-II* type isomers (Fig. 2 (c), (d)). The magnitudes of the CD spectra are rather weaker than those of the tris-(chelate)cobalt(III) complexes in the d-d transition region. The values of $\Delta\epsilon$ are of the same order of magnitude as those of the optically active forms of *mer*-[Co(dien)₂]³⁺,¹⁾ *mer*-[Co(dema)(dien)]³⁺,²⁾ and *mer*-[Co(dpt)₂]³⁺,³⁾ except that the major peak in the first absorption band region is somewhat intense. This finding is consistent with the assignment of the configuration presented above.

The infrared spectra of the I and II isomers are shown in Fig. 7. The similarity of these spectra also indicates that the structures of the two isomers

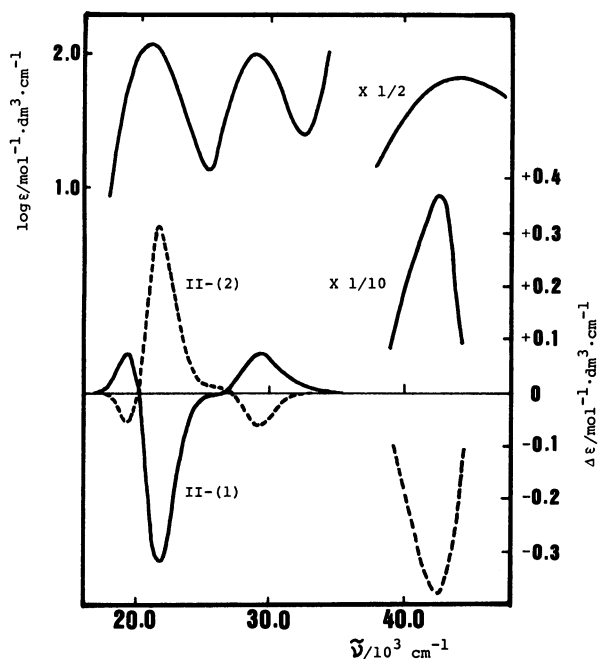


Fig. 6. Absorption and CD spectra of isomer II of [Co(aepn)(dien)]³⁺.

TABLE 2. ABSORPTION AND CD SPECTRA

Isomer	Absorption spectra		CD spectra	
	$\bar{\nu}_{\max}$ cm ⁻¹	log ϵ mol ⁻¹ dm ³ cm ⁻¹	$\bar{\nu}_{\max}$ cm ⁻¹	$\Delta\epsilon$ mol ⁻¹ dm ³ cm ⁻¹
I-(1)	21150	2.05	19450	+0.128
			21700	-0.384
	29100	1.99	29500	+0.107
I-(2)	44200	4.30	42400	+3.42
	21150	2.05	19450	-0.140
			21700	+0.386
II-(1)	29100	1.99	29500	-0.110
	44200	4.30	42200	-3.30
	21160	2.06	19450	+0.078
II-(2)			21750	-0.322
	28950	2.00	29100	+0.074
	44200	4.30	42400	+3.76
II-(2)	21160	2.06	19450	-0.056
			21750	+0.310
	28950	2.00	29100	-0.060
	44200	4.30	42400	-3.76

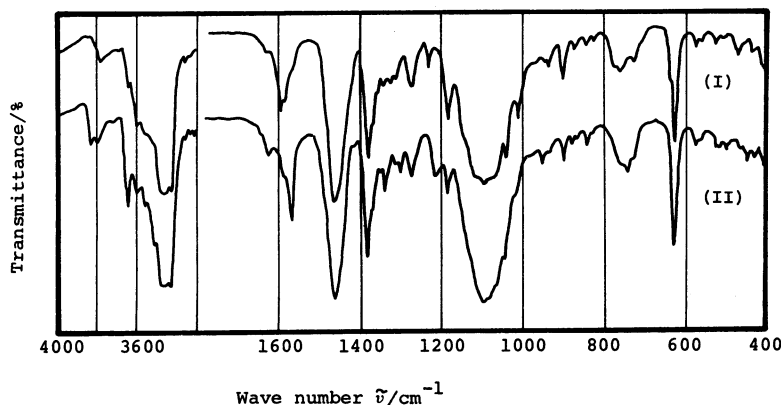


Fig. 7. Infrared spectra of *mer*-[Co(aepn)(dien)]³⁺.

resemble each other. In $[\text{Co}(\text{dien})_2]^{3+}$, Yoshikawa and Yamasaki¹⁾ identified the absorption bands at 1610–1550 cm^{-1} as antisymmetric NH_2 bending vibrations and observed a larger splitting for the *mer*-isomer. In the case of $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$, similar splitting was observed (I; 1585, 1595, 1625 cm^{-1} , II; 1570, 1585(sh), 1625 cm^{-1}). This observation confirmed that I and II are *mer*-type isomers.

Yoshikawa and Yamasaki investigated in detail the isomeric ratio of $[\text{Co}(\text{dien})_2]^{3+}$ ¹⁾ and $[\text{Co}(\text{dema})(\text{dien})]^{3+}$ ²⁾ using several synthetic pathways, and reported that the use of *mer*- $[\text{CoCl}_3(\text{dien})]$ as a starting material gave the *mer*-isomer in an overwhelming yield. This agrees with the results obtained in the present paper. Thus, in the *mer*- $[\text{CoCl}_3(\text{dien})] \rightarrow [\text{Co}(\text{aepn})(\text{dien})]^{3+}$ process, clearly no rearrangement of the configuration occurred. Therefore, the remaining three *fac*-isomers were not obtained through this synthetic pathway. The *fac*- $[\text{CoCl}_3(\text{dien})]$ complex seems to be one of the most suitable starting materials for the *fac*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$; unfortunately, this complex is not yet well known. The present author's attempts to obtain this complex were unsuccessful. Some synthetic attempts to obtain these *fac*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ were, therefore, carried out with the use of typical compounds as raw materials.

1) The oxidation of a mixture containing equivalent amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dien, and aepn with an air stream in the presence of active charcoal.

2) The stirring of a mixture containing equivalent amounts of $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, dien, and aepn. Both methods were carried out in aqueous solutions and gave large amounts of the by-products, $[\text{Co}(\text{dien})_2]^{3+}$ and $[\text{Co}(\text{aepn})_2]^{3+}$, and a small amount of $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$. The $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ thus obtained was chromatographically identified as consisting of *mer*-isomers. The *fac*-isomers were never isolated or detected, however. For both synthetic pathways, further attempts were carried out in the nonaqueous solvent DMSO. The reaction, however, did not proceed, and $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ was not obtained. Therefore, no *fac*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ has yet been isolated, though there may be a possibility of formation *via* other pathways. However, in the case of the $[\text{Co}(\text{triamine})_2]^{3+}$ complexes, it is known that the *mer*-isomer is obtained as the chief product. In particular, it has been observed that any attempts to prepare $[\text{Co}(\text{dpt})_2]^{3+}$ gave only the *mer*-isomer.³⁾ These facts suggest that the probability of obtaining the *fac*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ isomers is low.

The CD spectrum of the I-(1) isomer has a small positive peak on the lower energy side of the first absorption band region and a main negative peak on the higher energy side. As has been mentioned before, Okiyama *et al.* determined the molecular structure of a similar *mer*-type complex, *mer*- $[\text{Co}(\text{dien})_2]^{3+}$, by the X-ray analysis of the (+)₅₈₉ *mer*- $[\text{Co}(\text{dien})_2]\text{Br}_3 \cdot 1.6\text{H}_2\text{O}$ crystal; the absolute configuration of this antipode, which showed a main negative peak in the first absorption band region (19500 cm^{-1} $\Delta\epsilon = +0.096 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$, 21900 cm^{-1} $\Delta\epsilon = -0.181 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), was assigned to *trans*- λ -NH. In the present work, an

obvious inversion was observed for the CD pattern between *mer*-*trans*- δ -NH- $[\text{Co}(\text{dien})_2]^{3+}$ and *mer*-*trans*- δ -NH(*R*)- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ (or *mer*-*trans*- λ -NH- $[\text{Co}(\text{dien})_2]^{3+}$ and *mer*-*trans*- λ -NH(*S*)- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$). At first sight, *mer*- $[\text{Co}(\text{dien})_2]^{3+}$ appears to have pseudo-planes of symmetry and two-fold axes of rotation in the octahedral situation. However, the possibility of a second source of asymmetry arises in this situation. Since the conformations of the two fused five-membered chelate rings must be δ and λ , the chiral contribution from the conformational effects may be cancelled out. The net chirality in the optically active geometry probably comes from the stereochemical relationship between the two N(secondary)-H bonds of two dien ligands. In contrast to this simple model, the chirality of *mer*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ may be complicated by the presence of the six-membered chelate ring of the aepn ligand; that is, the contributions coming from the asymmetric secondary nitrogen of aepn and from the remaining conformational effect must be applied. As has been mentioned above, the isomerism of *mer*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ is a new type. For example, in the case of the $[\text{Co}(\text{triamine})_2]^{3+}$ complex, neither theoretical attempts nor empirical attempts to estimate these contributions were carried out. However, it will be possible to find, in the complexes containing quadridentate tetramine ligands, convenient models which possess this geometrical feature in common with the *mer*- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$. Among these models, *trans*-(*R,R*)- $[\text{Co}(3,2,3\text{-tet})\text{XY}]^{n+}$ ($n=1, 2, 3$; X, Y=unidentate ligands: 3,2,3-tet=4,7-diazadecane-1,10-diamine; Fig. 8) could be one of the complexes which would supply useful clues. Since the 3,2,3-tet moiety of this complex coincides with those of the aepn of *mer*-*trans*- δ -NH(*R*)- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ (Fig. 2 (a), *mer*-I) and *mer*-*trans*- λ -NH(*R*)- $[\text{Co}(\text{aepn})(\text{dien})]^{3+}$ (Fig. 2 (c), *mer*-II), there are extensive similarities between the geometries of these species. Bosnich and Harrowfield¹³⁾ have studied in detail the spectra of *trans*-(*R,R*)- $[\text{Co}(3,2,3\text{-tet})\text{XY}]^{n+}$. In the case of X=Y= NH_3 , a typical CoN_6 species, they found that *trans*-(*R,R*)- $[\text{Co}(3,2,3\text{-tet})(\text{NH}_3)_2]^{3+}$ had a main negative peak in the first absorption band region. From the structure shown in Fig. 8, it is clear that the chirality of the 3,2,3-tet complex arises exclusively from the contributions of the configurations of the asymmetric nitrogen atoms and the conformations of the chelate rings. Thus, the main negative peak can be expected to reflect these contributions exactly. The chirality of

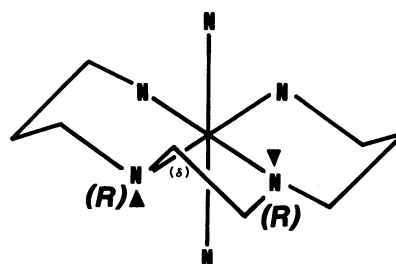


Fig. 8. Conformation of *trans*-(*R,R*)- $[\text{Co}(3,2,3\text{-tet})(\text{NH}_3)_2]^{3+}$.

mer-[Co(aepn)(dien)]³⁺ came from the effects of the relationships between the two *trans*-NH bonds, the configuration of the asymmetric atom, and the conformation of the chelate rings, as has previously been described. In the first absorption band region, the main negative peak observed for *mer-trans*- δ -NH(*R*)-[Co(aepn)(dien)]³⁺ suggests that the last two contributions may be superior to the first. It is clear that the inversion of the CD pattern in this region is attributable to differences between the magnitudes of these contributions. This finding can help us establish the relationships between the sign of the CD main peak in the first absorption band region and the situation of aepn. By the use of these relationships, the following structures of the remaining enantiomers can be assigned: II-(1); *trans*- λ -NH(*R*), and II-(2); *trans*- δ -NH(*S*).

In *mer*-[Co(dpt)₂]³⁺, Yamada *et al.*³⁾ obtained a CD spectrum with an extraordinarily small value of $\Delta\epsilon$ and predicted a decrease in the contribution from the two N-H bonds as a result of a flattening of the four six-membered rings. For *mer*-[Co(aepn)(dien)]³⁺ also, such a decrease can be expected.

The author gratefully acknowledges the valuable discussions and encouragement to Professor M. Nakahara of Rikkyo (St. Paul's) University during the course of this work.

References

- 1) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972).
- 2) M. Kojima, M. Iwagami, Y. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 3216 (1977).
- 3) S. Yamada, M. Umehara, M. Ishii, and M. Nakahara, *Nippon Kagaku Kaishi*, **1983**, 1733.
- 4) M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 470 (1972).
- 5) M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).
- 6) K. Okiyama, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **35**, 2389 (1979).
- 7) D. A. House, *Inorg. Nucl. Chem. Lett.*, **3**, 67 (1967).
- 8) By the use of a 0.20 mol dm⁻³ Na₂SO₄ solution (pH \approx 7) as an eluent, two bands were also eluted from the column of the Na⁺ form. However, they isomerized to each other while being purified. When the elution was carried out with a 0.20 mol dm⁻³ Na₂SO₄+H₂SO₄ acidic solution (pH \approx 2), a mixture of the isomers was separated into two bands which behaved chromatographically like the I and II isomers. In an earlier paper (Ref. 12), the present author and his associates reported a separation into four layers. It seems clear that this earlier report overlooked this isomerization and so should be amended here.
- 9) The [Co(dien)₂]³⁺ was prepared according to Method C described in Ref. 1 of this paper.
- 10) A paper to be submitted to *Bull. Chem. Soc. Jpn.*, will describe the preparation and isolation of the isomers in detail. Under these conditions, the [Co(aepn)₂]³⁺ showed no separation. The absorption spectroscopic data of the mixture are as follows: 20900 cm⁻¹ (log ϵ =1.95 mol⁻¹ dm³ cm⁻¹), 29000 cm⁻¹ (log ϵ =2.08 mol⁻¹ dm³ cm⁻¹).
- 11) M. Kojima, H. Yamada, H. Ogino, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 2325 (1977).
- 12) M. Ishii, S. Sato, Y. Saito, and M. Nakahara, *Chem. Lett.*, **1981**, 1613; *Bull. Chem. Soc. Jpn.*, **57**, 3094 (1984).
- 13) B. Bosnich and J. M. Harrowfield, *Inorg. Chem.*, **14**, 828 (1975).