Crystal Structure of $(-)^{CD}_{474}$ *mer*-{*N*-(2-Aminoethyl)-1,3-propanediamine}(diethylenetriamine)cobalt(III) Iodide Monohydrate, $(-)^{CD}_{474}$ *mer*-[Co(aepn)(dien)]$I_3 \cdot H_2O$

Minoru Ishii,* Shoichi Sato,† Yoshihiko Saito,†† and Masayoshi Nakahara
Department of Chemistry, College of Science, Rikkyo (St. Paul's) University, Nishi-ikebukuro, Toshima-ku, Tokyo 171
†*The Institute for Solid State Physics, The University of Tokyo, Roppongi 7, Minato-ku, Tokyo 106*
††*Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223*
(Received February 24, 1984)

The crystal structure of $(-)^{CD}_{474}$ *mer*-[Co{*N*-(2-aminoethyl)-1,3-propanediamine}(diethylenetriamine)]$I_3 \cdot H_2O$ has been determined by means of X-ray diffraction. The crystal is monoclinic, with a space group of $P2_1$, a=9.662 (2), b=14.602(2), c=8.201(3), β=112.87(4)°, and Z=2. The structure was solved by the Patterson-Fourier method and refined by the full-matrix least-squares method, which yielded an R value of 0.060 for the 2441 observed reflections. Each ligand molecule acts as a terdentate with meridional configurations. The absolute configuration of the coordinated asymmetric nitrogen atom in *N*-(2-aminoethyl)-1,3-propanediamine was determined to be *R*. The six-membered chelate ring in *N*-(2-aminoethyl)-1,3-propanediamine adopts a chair conformation, and the conformation of the five-membered chelate ring is δ. The conformations of the two five-membered chelate rings formed by diethylenetriamine are δ and λ, and the N(secondary)-H bond is oriented toward the six-membered chelate ring formed by *N*-(2-aminoethyl)-1,3-propanediamine.

Two linear triamines, *N*-(2-aminoethyl)-1,3-propanediamine ($NH_2CH_2CH_2CH_2NHCH_2CH_2NH_2$: abbreviated as aepn) and diethylenetriamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$; abbreviated as dien), can act as terdentate ligands and coordinate to the central metal ion in two topological modes. The cobalt(III) complex, $[Co(aepn)(dien)]^{3+}$, which contains three five-membered chelate rings and one six-membered ring, can exist in five geometrical isomers, as is shown in Fig. 1. The two *mer*-isomers differ in the orientation of the N(secondary)-H bond in the dien ligand. Further, the optical isomers arising from the alternative disposition of the N-H bond of the secondary nitrogen atom in aepn (*R*/*S*) can be expected for each of the two *mer*-geometries (Fig. 2).

Three *mer* type complexes, *mer*-$[Co(dien)_2]^{3+}$,[1] *mer*-[Co(dema)(dien)]$^{3+}$ (dema; *N*-menthylbis(2-aminoethyl)-amine),[2] and *mer*-$[Co(dpt)_2]^{3+}$ (dpt; bis(3-aminopropyl)amine),[3] have been prepared. The crystal structure of $(+)_{589}$*mer*-$[Co(dien)_2]Br_3 \cdot 1.6H_2O$ has previously been determined, and the absolute configuration of the complex ion has been identified as *trans*-λ-NH.[4]

Complexes with five-membered chelate rings have been extensively studied, but little is known concerning the complexes involving a six-membered chelate ring. Thus, it is of interest to study the stereochemistry

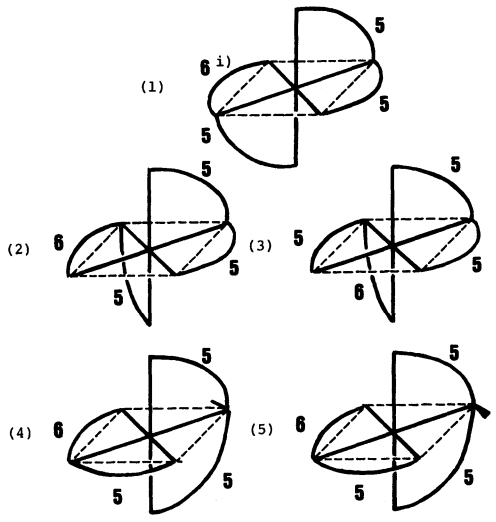

Fig. 1. Geometrical isomers of $[Co(aepn)(dien)]^{3+}$ (1): *sym-fac* type, (2),(3): *unsym-fac* type, (4),(5): *mer* type.
i) Numbers 5, 6 indicate the number of chelate ring members.

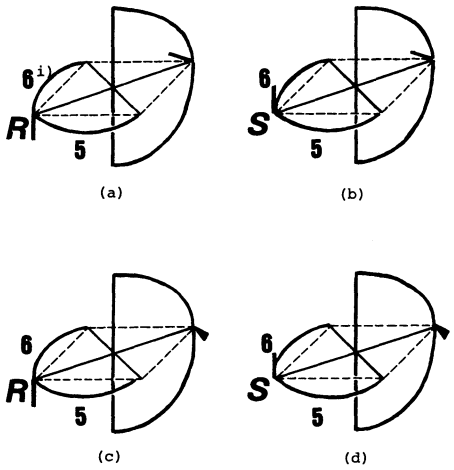

Fig. 2. Two types of *mer*-$[Co(aepn)(dien)]^{3+}$ and their antipodes (simplified).
mer-I type: (a) *trans*-δ-NH(*R*),[11] (b) *trans*-λ-NH(*S*)
mer-II type: (c) *trans*-λ-NH(*R*), (d) *trans*-δ-NH(*S*).
i) Numbers 5, 6 indicate the number of chelate ring members. ii) See Appendix.

of $[Co(aepn)(dien)]^{3+}$.

In this paper, the structure and the absolute configuration of $(-)^{CD}_{474}$ *mer*-{*N*-(2-aminoethyl)-1,3-propanediamine}(diethylenetriamine)cobalt(III) iodide monohydrate, $(-)^{CD}_{474}$ *mer*-[Co(aepn)(dien)]$I_3 \cdot H_2O$ are reported.

Experimental

The $[Co(aepn)(dien)]^{3+}$ complex was prepared by the method described in the literature.[5] Of the two fractions obtained by means of SP-Sephadex C-25 ion-exchange chromatography, the faster one was collected and resolved by this chromatography. The $(-)^{CD}_{474}$ isomer was converted into iodide in the anion-exchange region (I^- form, ϕ 1.0 cm×30 cm), and the effluent was evaporated to a few cm^3 under reduced pressure. Crystals were grown from an aqueous solution acidified with acetic acid, and elemental analyses gave:

Found: C, 15.87; H, 4.30; N, 12.54%. Calcd for $Co(C_9H_{28}N_6)I_3 \cdot H_2O$: C, 15.94; H, 4.46; N, 12.39%.

The crystals are orange-red, transparent hexagonal prisms. They are monoclinic. The observed systematic absences on Weissenberg photographs, *0, k, 0* for $k=2n$, indicated that the possible space group was $P2_1$ or $P2_1/m$. Since the crystal was optically active, the space group was uniquely determined to be $P2_1$.

Crystal data:

$(-)^{CD}_{474}$*mer*-[Co(aepn)(dien)]$I_3 \cdot H_2O$, $Co(C_9H_{28}N_6)I_3 \cdot H_2O$ $M_w=678.02$, monoclinic, $a=9.662(3)$, $b=14.602(2)$, $c=8.201(3)$ Å, $\beta=112.87(4)°$, $V=1065.9(4)$ Å^3, $Z=2$, $D_m=2.19$ ($D_c=2.11$) g cm^{-3}, μ for Mo $K\alpha$ ($\lambda=0.7107$ Å) = 51.10 cm^{-1}, space group $P2_1$.

A crystal with dimensions of *ca.* 0.4×0.2×0.15 mm^3 was used for the intensity measurements. The intensities were collected on a PHILIPS 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation up to $2\theta=70°$, the θ-2θ scan technique being employed. Independent 2441 reflections with $|F_o|<3\sigma(|F_o|)$ were used for the structure determination. The usual corrections were made for the Lorentz, polarization, and absorption factors, but no correction was applied for extinction. The structure was solved by the Patterson-Fourier method with a local version of UNICS.[6] The calculations were carried out on a FACOM M-160F computer at the Institute for Solid State Physics (The University of Tokyo) and on a HITAC 200H computer at the Computer Center of the University of Tokyo.

Determination and Refinement of the Structure

The positions of the I and Co atoms were deduced from three-dimensional Patterson maps, while the positions of all the non-hydrogen atoms were derived by the Fourier method. They were refined by the block-diagonal least-squares method with anisotropic thermal parameters. At the stage of $R=0.074$, eight hydrogen atoms among the twenty-eight hydrogen atoms (except for those of the water molecule) were found from a different synthesis. The positions of the remaining twenty hydrogen atoms were located theoretically. The final refinement was carried out using the full-matrix least-squares program LINUS[7] with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms. The final R and R_2 values were 0.060 and 0.073 respectively.[8]

The absolute structure was determined by the anomalous-scattering technique. Some $h\ k\ l$ and $h\ \bar{k}\ l$ pairs were examined on Weissenberg photographs recorded using Cu $K\alpha$ radiation. As is shown in Table 1, a comparison of the observed and calculated differences between $|F(hkl)|$ and $|F(h\bar{k}l)|$ indicates that the calculated values differ by more than 10%. The concordance in Table 1 indicates that the $(-)^{CD}_{474}$-isomer has the absolute configuration illustrated in Fig. 4. The enantiomeric structure was refined in the same way and converged at residuals $R=0.061$ and $R_2=0.074$. The application of the R-factor ratio test[9] showed that the latter can be rejected at the 0.05 significance level in favor of the former.

The final atomic parameters and thermal factors of non-hydrogen atoms and hydrogen atoms are given in Tables 2 and 3 respectively.[10]

Results and Discussion

A projection of the crystal structure along *b*, and

Table 1. Determination of the absolute configuration

$h\ k\ l$	$F_c(hkl)$	Observed	$F_c(\bar{h}kl)$
3 1 2	50.0	>	42.3
3 3 2	73.6	<	81.3
7 1 0	30.6	<	36.4
7 1 1	24.1	>	14.2
7 2 2	49.8	<	55.0

Table 2. Final atomic positional parameters and equivalent temperature factors for non-hydrogen atoms, with their estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}(Å^2)[a]
I (1)	0.0580(1)	0.4155(2)	0.0360(2)	0.051(1)
I (2)	0.3290(1)	0.1805(1)	0.7830(2)	0.042(<1)
I (3)	0.3524(2)	0.8072(1)	0.5169(2)	0.043(<1)
Co	0.3023(2)	0.5000(0)	0.6612(2)	0.020(1)
N (1)	0.0990(11)	0.5180(8)	0.6464(17)	0.022(4)
N (2)	0.2614(12)	0.5689(7)	0.4356(16)	0.021(4)
N (3)	0.5101(11)	0.4856(7)	0.6693(17)	0.020(4)
N (4)	0.3519(12)	0.4238(8)	0.8782(16)	0.021(4)
N (5)	0.3470(14)	0.6158(7)	0.7993(18)	0.023(5)
N (6)	0.2187(13)	0.3891(7)	0.5167(16)	0.021(4)
C (1)	−0.0108(16)	0.4723(11)	0.4920(21)	0.042(6)
C (2)	0.0607(16)	0.3722(9)	0.4991(23)	0.044(6)
C (3)	0.0734(19)	0.6181(11)	0.6670(26)	0.054(7)
C (4)	0.2151(19)	0.6484(10)	0.8310(23)	0.050(7)
C (5)	0.3877(15)	0.5533(10)	0.3793(22)	0.042(6)
C (6)	0.5299(15)	0.5539(10)	0.5420(21)	0.040(6)
C (7)	0.6384(16)	0.4881(13)	0.8377(23)	0.050(7)
C (8)	0.6273(15)	0.4141(13)	0.9690(23)	0.054(7)
C (9)	0.5024(18)	0.4331(12)	1.0268(21)	0.047(6)
O (W)	0.0213(38)	0.6677(37)	0.1454(74)	0.222(35)

a) $U_{eq}=1/3(U_{11}+U_{22}+U_{33}+2U_{13}\cos\beta)$.

a perspective drawing of the complex cation are shown in Figs. 3 and 4 respectively. The two ligands coordinate to the central cobalt atom in *mer* positions by means of their six nitrogen atoms, thus forming a slightly distorted octahedral complex. The complex

Table 3. Final atomic positional parameters and equivalent temperature factors for hydrogen atoms, with their estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}(Å^2)[a]
H1(N1)	0.084(0)	0.487(0)	0.747(0)	0.057(0)
H1(N2)	0.209(23)	0.651(16)	0.428(30)	0.067(64)
H2(N2)	0.165(0)	0.546(0)	0.342(0)	0.057(0)
H1(N3)	0.512(0)	0.419(0)	0.633(0)	0.057(0)
H1(N4)	0.260(0)	0.418(0)	0.907(0)	0.057(0)
H2(N4)	0.342(0)	0.359(0)	0.837(0)	0.057(0)
H1(N5)	0.433(0)	0.606(0)	0.912(0)	0.057(0)
H2(N5)	0.375(0)	0.664(0)	0.728(0)	0.057(0)
H1(N6)	0.220(0)	0.398(0)	0.394(0)	0.057(0)
H2(N6)	0.258(0)	0.320(0)	0.561(0)	0.057(0)
H1(C1)	−0.028(21)	0.536(15)	0.393(26)	0.056(53)
H2(C1)	−0.111(0)	0.468(0)	0.501(0)	0.057(0)
H1(C2)	0.004(0)	0.337(0)	0.388(0)	0.057(28)
H2(C2)	0.059(0)	0.337(0)	0.603(0)	0.057(0)
H1(C3)	0.068(0)	0.660(0)	0.564(0)	0.057(0)
H2(C3)	0.007(13)	0.651(9)	0.717(17)	0.011(28)
H1(C4)	0.230(0)	0.706(0)	0.844(0)	0.057(0)
H2(C4)	0.214(0)	0.620(0)	0.943(0)	0.057(0)
H1(C5)	0.375(0)	0.496(0)	0.312(0)	0.057(0)
H2(C5)	0.389(0)	0.606(0)	0.296(0)	0.057(0)
H1(C6)	0.516(28)	0.627(20)	0.553(31)	0.091(81)
H2(C6)	0.607(13)	0.520(9)	0.526(17)	0.010(28)
H1(C7)	0.745(22)	0.481(16)	0.842(26)	0.055(56)
H2(C7)	0.644(0)	0.550(0)	0.892(0)	0.057(0)
H1(C8)	0.724(0)	0.413(0)	1.075(0)	0.057(0)
H2(C8)	0.611(0)	0.353(0)	0.910(0)	0.057(0)
H1(C9)	0.504(0)	0.383(0)	1.132(0)	0.057(0)
H2(C9)	0.516(18)	0.506(14)	1.091(23)	0.047(0)

a) $U_{eq}=1/3(U_{11}+U_{22}+U_{33}+U_{13}\cos\beta)$.

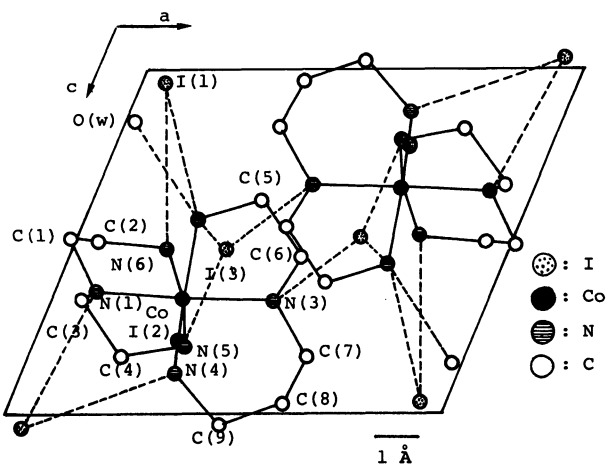

Fig. 3. A projection of the crystal structure along *b*.

cation, $(-)^{CD}_{474}$ *mer*-[Co(aepn)(dien)]$^{3+}$ corresponds to the *mer*-I type (Fig. 2 (a)). The absolute configuration of the asymmetric nitrogen atom (N(3)) was determined to be *R*.[11] The structure shown in Fig. 4 was assigned to *trans*-*δ*-NH(*R*) (Fig. 2 (a)).[12] The conformations of the two fused five-membered chelate rings in dien were *δ* and *λ*, in agreement with the observation for $(+)_{589}$ *mer*-$[Co(dien)_2]Br_3\cdot 1.6H_2O$.[4] The conformation of the six-membered chelate ring formed by aepn was chair (Fig. 5), and the conformation of its five-membered chelate ring was *δ*.

The bond distances and angles in the complex ion are listed in Table 4, together their estimated standard deviations.

The Co–N(secondary) bond distance in dien (Co–N(1)) is significantly shorter than the Co–N(terminal) bond distances (Co–N(5), Co–N(6)). Such a trend was also observed for $(+)_{589}$ *mer*-$[Co(dien)_2]Br_3\cdot 1.6H_2O$[4] and $(-)_{589}$*unsym-fac*-$[Co(dien)_2][Co(CN)_6]\cdot 2H_2O$.[13] In contrast to this, the three Co–N distances (Co–N(2), Co–N(3), and Co–N(4)) in aepn are within 1.0*σ* of each other.

The N(terminal)–Co–N(terminal) angles in the five-membered chelate rings (N(1)–Co–N(6), N(1)–Co–N(5), and N(2)–Co–N(3)) are smaller than 90°, in agreement with the result obtained for similar complexes containing five-membered chelate rings.[14]

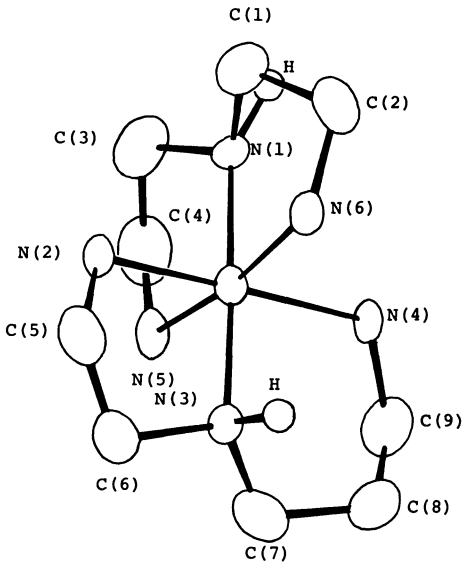

Fig. 4. A perspective drawing of the complex cation.

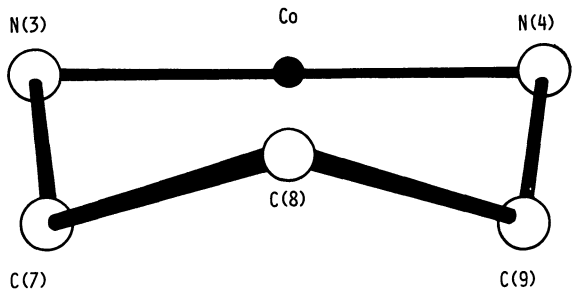

Fig. 5. Edge-on view of the chelate ring with respect to the plane formed by the Co and two N atoms.

TABLE 4. BOND DISTANCES AND ANGLES WITHIN THE COMPLEX CATION, *mer*-[Co(aepn)(dien)]$^{3+}$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond distance	l/Å	Bond distance	l/Å
Co-N (1)	1.939 (12)	N (3)-C (7)	1.454 (17)
Co-N (2)	2.006 (13)	N (4)-C (9)	1.497 (17)
Co-N (3)	1.994 (12)	N (5)-C (4)	1.476 (25)
Co-N (4)	1.993 (12)	N (6)-C (2)	1.497 (21)
Co-N (5)	1.988 (11)		
Co-N (6)	1.984 (11)	C (1)-C (2)	1.607 (21)
		C (3)-C (4)	1.565 (21)
N (1)-C (1)	1.460 (17)	C (5)-C (6)	1.498 (18)
N (1)-C (3)	1.503 (20)	C (7)-C (8)	1.558 (28)
N (2)-C (5)	1.481 (23)	C (8)-C (9)	1.485 (27)
N (3)-C (6)	1.509 (22)		
Bond angle	ϕ/°	**Bond angle**	ϕ/°
N (1)-Co-N (2)	92.4 (5)	N (1)-Co-N (6)	84.6 (5)
N (1)-Co-N (3)	177.7 (5)	N (2)-Co-N (3)	85.3 (5)
N (1)-Co-N (4)	91.0 (5)	N (2)-Co-N (4)	175.2 (5)
N (1)-Co-N (5)	84.9 (5)	N (2)-Co-N (5)	91.1 (5)
N (2)-Co-N (6)	88.3 (5)		
N (3)-Co-N (4)	91.2 (5)	C (1)-N (1)-C (3)	116.5 (11)
N (3)-Co-N (5)	94.5 (5)	C (6)-N (3)-C (7)	110.5 (11)
N (3)-Co-N (6)	96.0 (5)		
N (4)-Co-N (5)	92.4 (5)	N (1)-C (1)-C (2)	103.1 (10)
N (4)-Co-N (6)	88.8 (5)	N (1)-C (3)-C (4)	104.1 (11)
N (5)-Co-N (6)	169.4 (5)	N (2)-C (5)-C (6)	107.6 (13)
		N (3)-C (6)-C (5)	107.1 (11)
Co-N (1)-C (1)	111.7 (10)	N (3)-C (7)-C (8)	112.2 (14)
Co-N (1)-C (3)	109.4 (9)	N (4)-C (9)-C (8)	112.1 (14)
Co-N (2)-C (5)	108.6 (9)	N (5)-C (4)-C (3)	106.5 (14)
Co-N (3)-C (6)	107.7 (8)	N (6)-C (2)-C (1)	105.2 (11)
Co-N (3)-C (7)	120.3 (10)		
Co-N (4)-C (9)	119.8 (9)	C (7)-C (8)-C (9)	112.0 (15)
Co-N (5)-C (4)	111.3 (10)		
Co-N (6)-C (2)	110.8 (10)		

In the six-membered ring, this angle (N(3)–Co–N(4)) is slightly greater than 90°. The Co–N–C angles (Co–N(3)–C(7), Co–N(4)–C(9)) are larger by 10% than the other bond angles in the chelate ring. The six-membered chelate ring is thus flattened like those in $[Co(tn)_3]^{3+}$.[15]

The N(terminal)–Co–N(terminal) angles in both ligands (N(5)–Co–N(6), N(2)–Co–N(4)) are obviously smaller than 180°, whereas the N(secondary)–Co–N(secondary) angle (N(1)–Co–N(3)) is nearly 180°. The three ligating nitrogen atoms of each ligand and the cobalt atom are nearly co-planar, and the two coordination planes are perpendicular. These observations suggest that the presence of the six-membered chelate ring does not introduce much distortion into the octahedral geometry of the complex cation and that any such distortion is relieved by the flexibility of the six-membered ring.

The relevant interatomic distances of less than 3.9 Å between complexes, along with the estimated standard deviations, are listed in Table 5. The bond length of I(1)–N(4) (3.55(2) Å) is clearly shorter than the sum of the ionic radii. This might lead to the hydrogen bond formation of N–H···I.

TABLE 5. RELEVANT INTERATOMIC DISTANCES OUTSIDE THE COMPLEX ION, *mer*-[Co(aepn)(dien)]$^{3+}$, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Key operations			
i) x, y, z		ii) x, y, $1/2+z$	
Distance	l/Å	Distance	l/Å
$I(1)^{I}$-N(2)	3.82 (3)	$I(3)^{I}$-N(2)	3.68 (7)
-N2H1	2.99 (3)	-N2H1	2.62 (6)
-N(6)	3.65 (6)	-N(5)	3.64 (2)
N6H1	2.75 (3)	-N5H2	2.67 (1)
$I(2)^{I}$-N(4)	3.63 (6)	$I(1)^{II}$-N(1)	3.68 (7)
-N4H2	2.63 (8)	-N1H1	3.22 (7)
-N(6)	3.65 (7)	-N(4)	3.55 (2)
-N6H2	2.63 (8)	-N4H1	2.55 (7)

Appendix

Remarks on Chirality Specification. The four isomers of *mer*-[Co(aepn)(dien)]$^{3+}$ shown in Fig. 2 can be specified easily by means of common chirality descriptors. Without any consideration of the conformations of the chelate rings, the chirality of these isomers can be said to arise from the dissymmetric disposition of the two coordinated NH groups and from the dissymmetry around the secondary nitrogen atom of aepn. If we employ the same descriptor as was used for *mer*-[Co(dien)$_2$]$^{3+}$,[4] they can be denoted by:

(a) *trans*-δ-NH(R), (b) *trans*-λ-NH(S), (c) *trans*-λ-NH(R), (d) *trans*-δ-NH(S),

where δ or λ refers to the non-oriented N–N and H–H lines defined by the two N–H groups under consideration and where R or S represents the absolute configuration of the asymmetric nitrogen atom of aepn. Recently, Damhus and Schäffer proposed a new reference system consisting of oriented lines.[16] When this new system is employed, the four isomers can be represented as follows:

(a) $\vec{\Lambda}(R)$, (b) $\vec{\Delta}(S)$, (c) $\vec{\Delta}(R)$, (d) $\vec{\Lambda}(S)$.

References

1) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972).
2) M. Kojima, M. Iwasaki, 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) K. Okiyama, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **35**, 2389 (1979).
5) M. Ishii, S. Sato, Y. Saito, and M. Nakahara, *Chem. Lett.*, **1981**, 1613; M. Ishii, *Bull. Chem. Soc. Jpn.*, **57**, 3088 (1984).
6) T. Sakurai, UNICS, The Universal Crystallographic Computing System, Tokyo: The Crystallographic Society of Japan (1967).
7) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).
8) $R=\sum||F_o|-|F_c||/\sum|F_o|$, $R_2=\sum[w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$.
9) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
10) The complete F_o–F_c data are deposited as Document No. 8443 at the Office of the Editor of the Bulletin of the

Chemical Society of Japan.
11) In an earlier letter (Ref. 5), the symbol of the absolute configuration in aepn was incorrect. *R* in Ref. 5. should read *S*.
12) Remarks on the chirality specification may be found in the Appendix section in this paper.
13) M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).
14) For example, Refs.4 and 13 in this paper; M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 470 (1972); S. Sato and Y. Saito, *ibid.*, **33**, 860 (1977); M. Mikami, R. Kuroda, and Y. Saito, *ibid.*, **33**, 1485 (1977); S. Sato and Y. Saito, *ibid.*, **34**, 3352 (1978).
15) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 1016 (1969); R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 2438 (1973).
16) T. Damhus and C. Shäffer, *Inorg. Chem.*, **22**, 2406 (1983).