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CRYSTAL STRUCTURE OF $(-)_{474}$-*mer*-{N-2-AMINOETHYL-(1,3-PROPANEDIAMINE)}(DIETHYLENETRIAMINE)COBALT(III) IODIDE MONOHYDRATE

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The molecular structure of the title compound was determined to be (S)-*mer*-I type by X-ray diffraction. The N(secondary)-H bond in the diethylenetriamine (dien) is directed toward the six-membered chelate ring formed by the N-2-aminoethyl-(1,3-propanediamine) (aepn). The six-membered ring formed by the aepn takes a chair-form and its five-membered-ring is δ, while those of the two five-membered rings of the duen are λ and δ, respectively.

N-2-Aminoethyl-(1,3-propanediamine) acts as a terdentate and forms fused five- and six-membered chelate rings. The title complex was synthesized in order to study stereochemistry of such fused ring systems. This letter deals with the preparation, the absorption and circular dichroism spectra of the *mer*-{N-2-aminoethyl-(1,3-propanediamine)}(diethylenetriamine)cobalt(III) complex (*mer*-$[Co(aepn)(dien)]^{3+}$) and also with the absolute configuration of the isomer determined by x-ray diffraction.

To 2.7 g of finely grounded *mer*-$[CoCl_3(dien)]$[1)], suspended in 5 m*l* of DMSO, 1.5 g of N-2-aminoethyl-(1,3-propanediamine)(aepn) was added and stirred for 3 h at room temperature. The resulting orange solution, once filtrated, poured into a column containing SP-Sephadex C-25 resin in Na^+ form (2 x 100 cm). When the elution was carried out with a 0.2 M Na_2SO_4 solution and then with the buffer solution (pH 2: $Na_2SO_4 + H_2SO_4$), finally four bands colored orange (the elution order; I, II, III, IV) descended[2)]. The eluate containing the fastest layer(I) was collected and once more charged on a column of SP-Sephadex C-25 resin in Na^+ form (2 x 100 cm). By elution with a 0.2 M sodium bis[$(-)_{589}$-tartarato]diantimonate(III) solution, two bands descended. The effluent of the first band was concentrated to a small volume, was filtered, and then kept in a refrigerator. The orange crystals precipitated were recrystallized from warm water.

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 %.

Fig. 1 shows the absorption and CD spectra of *mer*-$[Co(aepn)(dien)]^{3+}$.

The orange-red crystals of the $(-)_{474}$-isomer are monoclinic with space group P2 ; a=9.662(3), b=14.602(2), c=8.201(3) A and β=112.87(4)°, V=1065.9(4) A , Dx=2.11 g cm^{-3}, Dm=2.19 g cm^{-3} and Z=2. A crystal having dimensions of about 0.4 x 0.2 x 0.15 mm was used for the intensity measurement. Intensities were collected on a PHILIPS 1100 four-circle diffractometer with graphite-monochromated Mo Kα radiation up to 2θ=70°, the θ-2θ scan technique being employed. Independent 2441 reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure determination. The usual corrections were made for Lorentz, polarization and absorption factors, but no correction was applied for extinction. The structure was solved by Patterson-Fourier methods with a local version of UNICS[3)]. The final refinement was carried out using full-matrix least-squares program LINUS[4)#] with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The final R and R_2 values were 0.060 and 0.073, respectively. The absolute structure was determined by the anomalous-scattering technique. Some hkl and $h\bar{k}l$ pairs were examined on Weissenberg photographs recorded using Cu Kα radiation. In Table 1 the observed and calculated differences are compared, for which $|F(hkl)|$ and $|F(h\bar{k}l)|$ differed by more than 10 % The concordance in Table 1 indicated that $(-)_{474}$-isomer has the absolute configuration illustrated in Fig. 3. The enantiomeric structure was refined in the same way and converged at residuals R=0.061 and R_2=0.074. Application of the R factor ratio test showed that the latter can be rejected

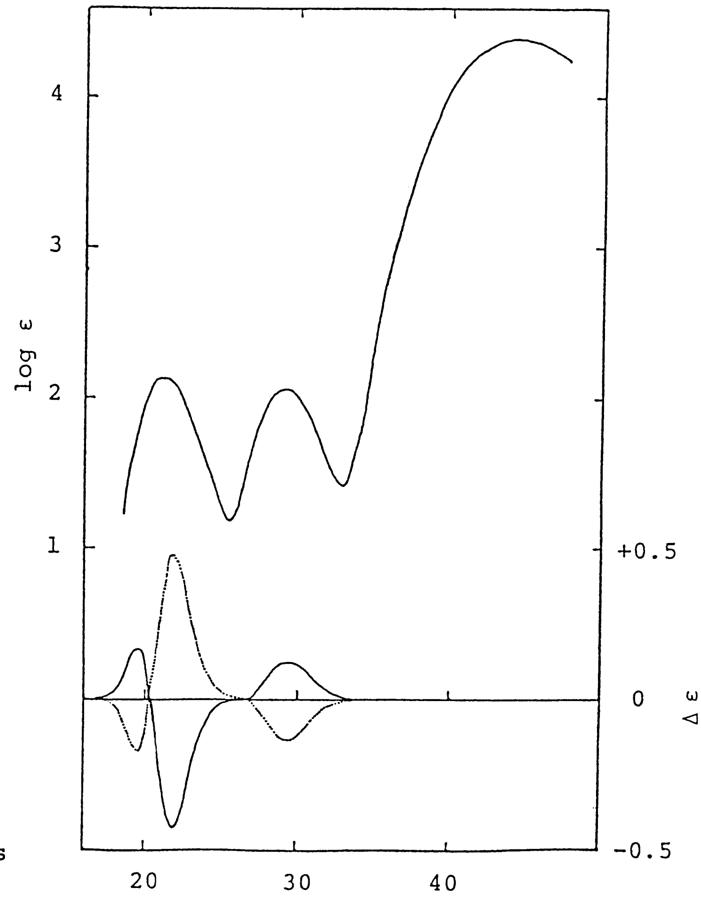

Fig. 1 Absorption and CD spectra of the *mer*-[Co(aepn)(dien)]$(ClO_4)_3$
a) $(-)_{474}$ isomer (————)
b) $(+)_{474}$ isomer (••••••••)

Table 1 Determination of the absolute configuration

h k l	Fc(*hkl*)	Observed	Fc(*hk̄l*)
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

[#] The calculations were carried out on a FACOM M-160F computer at the Institute for Solid State Physics (The University of Tokyo) and partially on a HITAC 200H computer at the Computer Center of the University of Tokyo.

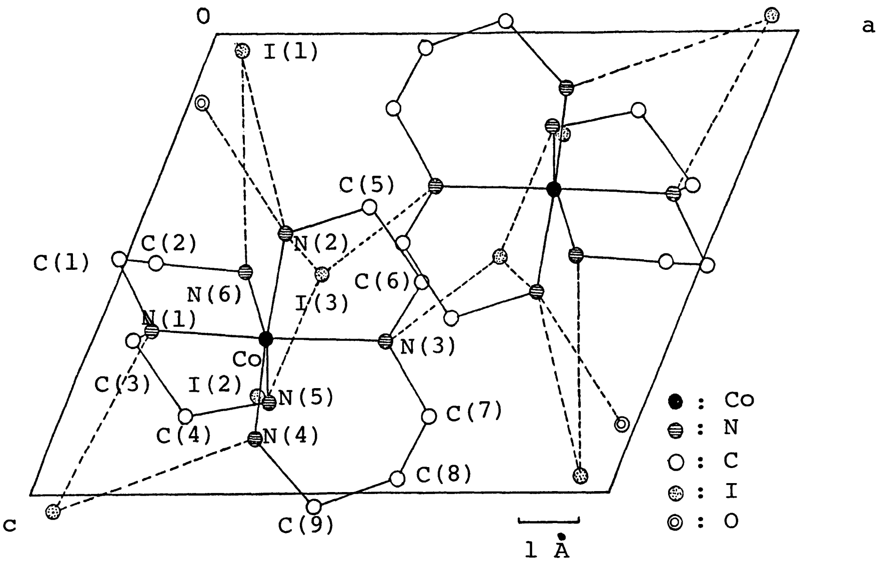

Fig. 2 A projection of the crystal structure along b

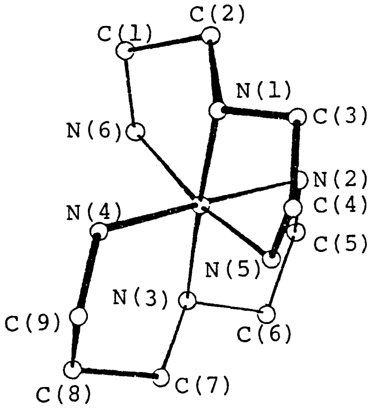

Fig. 3 A perspective drawing of the complex cation

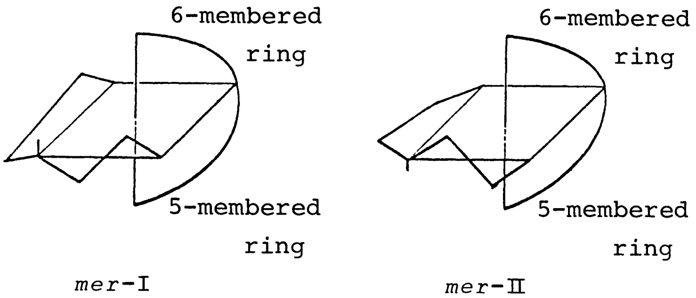

Fig. 4 The geometrical isomers of the *mer*-[Co(aepn)(dien)]$^{3+}$

at the 0.05 confidence level in favor of the former$^{5)}$. A projection of the crystal structure along b and a perspective drawing of the complex cation are shown in Figs. 2 and 3, respectively. The two ligands coordinate to the central cobalt atom in the meridional (*mer*) positions by their six nitrogen atoms forming a distorted octahedral complex. In this situation, there are two types of geometrical isomers, distinguished with N(secondary)-H bond orientation in dien (Fig. 4). The present structure corresponds to the type I. The absolute configuration of the asymmetric nitrogen atom (N(3)) was determined to be *S*, and the conformation of the five-membered moiety is δ. The conformation of the two five-membered chelate rings in the dien are λ and δ, respectively. Presence of the six-membered chelate ring does not much distort the octahedral geometry of the complex ion. The Co-N(secondary) bond (1.939(12) Å) in the dien is significantly shorter than the Co-N(terminal) bonds (1.988(11), 1.984(11) Å). This agrees with the results observed for the *mer*-[Co (dien)$_2$]Br$_3$•1.6 H$_2$O[6)] and *unsym-fac*-[Co(dien)$_2$]Br$_3$[7)]. In constant to this, the three Co-N distances in the aepn are practically the same (Co-N(secondary); 1.994(12) Å, Co-N(terminal); 2.006(13), 1.993(12) Å). The angles N(terminal)-Co-N(secondary) are smaller than 90° in the five-membered rings (84.9(5), 84.6(5), 85.3(5)°), and larger in the six-membered ring (91.2(5)°). Both the angles N(terminal)-Co-N(terminal) are significantly smaller than 180° (169.4(5)° in dien, 175.2(5)° in aepn), whereas the angle N(secondary)-Co-N(secondary) is nearly 180° (177.7(5)°). The three ligating N atoms of each ligand and the cobalt atom are nearly coplanar and the two planes formed by these ligands and cobalt atom are perpendicular. These facts suggest that the distortion of the complex molecule is is fairly alleviated owing to the flexibility of the six-membered chelate ring.

Table 2 Atomic parameters with their standard deviations in parenthes

	X	Y	Z	UEQ (A^2)
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	0.6612 (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)

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

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