July, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **60**, *2683—2685 (1987)* 2683

Crystal Structure of $(+)^{CD}_{490}$*mer*-Bis{bis(3-aminopropyl)amine-cobalt(III)} Hexacyanocobaltate(III) Dihydrate, $(+)^{CD}_{490}$*mer*-$[Co(dpt)_2][Co(CN)_6]\cdot 2H_2O$

Minoru Ishii,* Michiko Umehara, Kazumasa Harada, and Masayoshi Nakahara
Department of Chemistry, College of Science, Rikkyo (St. Paul's) University,
Nishiikebukuro 3, Toshima-ku Tokyo 171

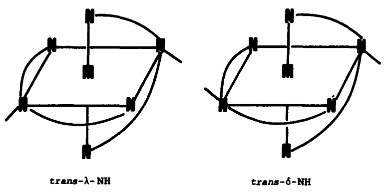
(Received November 11, 1986)

Synopsis. The structure of optically active title compound was determined by X-ray diffraction. The absolute configuration is *trans*-*δ*-NH. A pair of two-fused six-membered rings is extended. The geometry of the octahedron is distorted by the presence of the six-membered chelate rings.

The linear triamine bis(3-aminopropyl)amine ($NH_2CH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$, abbreviated as dpt) acts as a terdentate ligand and coordinates to the central metal ion in two topological modes. The cobalt complex, $[Co(dpt)_2]^{3+}$, which contains four six-membered chelate rings, can exist in three geometrical isomers, mer-, sym-fac-, and unsym-fac-isomers. As for the mer-isomers, an optical isomer due to the alternative disposition of N-H bond of the secondary nitrogen atom in dpt ligands is presumed (Fig. 1). The *mer*-$[Co(dpt)_2]^{3+}$ has been prepared and resolved by the present authors,[1] and the structure of optically nonactive complex, $[Co(dpt)_2](ClO_4)_3$, was determined by X-ray analysis by Hambley et al.[2] However, no report has been published on an optically active one. This paper reports the molecular structure of $(+)^{CD}_{490}$*mer*-$[Co(dpt)_2][Co(CN)_6]\cdot 2H_2O$.

Experimental

The $[Co(dpt)_2]^{3+}$ complex was prepared by the method described in a previous paper.[1] The product was dissolved in a small amount of water, and the solution was poured into a column of 2 cm diameter and 120 cm length containing SP-Sephadex C-25 resin (H^+ form). When the elution was carried out with a sodium bis[$(+)_{589}$tartrato]-diantimonate(III) solution of 0.20 mol dm^{-3} at pH≈2, adjusted with HCl,[2] and at a temperature below 7 °C, two reddish purple bands were separated as shown in Fig. 2. These bands were optically active.[3] The elute corresponding to the faster layer was collected and poured into a column (2×ca. 25 cm) of SP-Sephadex C-25 (H^+ form). After the column was washed with 1.0 dm^3 of 0.1 mol dm^{-3} hydrochloric acid, an elute with 1.0 mol dm^{-3} hydrochloric acid was obtained. Crystals were allowed to grow from the elute on addition of equivalent $K_3[Co(CN)_6]$.



trans-λ-NH trans-δ-NH

Fig. 1. Two optical isomers of *mer*-$[Co(dpt)_2]^{3+}$.

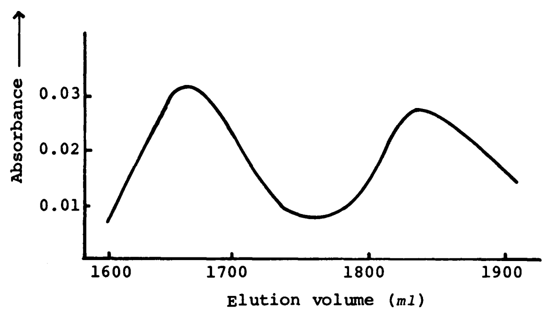


Fig. 2. Elution curve of *mer*-$[Co(dpt)_2]^{3+}$ (516 nm).

Crystal Structure Determination. The crystal is reddish purple, transparent hexagonal prism and of monoclinic structure. The absence of systematic (0*k*0) patterns for $k=2n+1$ indicated that the possible space group is $P2_1$ or $P2_1/m$. Since the crystal is optically active, the space group seems to be $P2_1$.

Crystal Data: $(+)^{CD}_{490}$*mer*-$[Co(dpt)_2][Co(CN)_6]\cdot 2H_2O$, $Co_2C_{18}H_{38}N_{12}O_2$ *F.W.* = 572.44, monoclinic, space group $P2_1$, a=9.528(2), b=16.464(2), c=8.997(2) Å, β=113.50(2)°, V=1294.3(5) Å^3, Z=2, D_m=1.45 Mg m^{-3}, D_c=1.47 Mg m^{-3}.

A crystal with dimensions of ca. 0.4×0.2×0.4 mm was used for X-ray diffraction intensity measurements. The intensity was determined by a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo *Kα* radiation (λ=0.7107 Å) up to 2θ of 55°. Independent 3634 reflections containing Bijvoet pairs with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination. The usual corrections were made for the Lorentz and polarization effects, but no correction was applied for absorption. The calculation was carried out on a FACOM M-360 computer at Rikkyo University. The structure was solved by the Patterson-Fourier method with UNICS III computation program system.[4] The positions of cobalt atoms were deduced from three-dimensional Patterson maps and those of other non-hydrogen atoms were derived from the Fourier map. The scattering factors were taken from Ref. 5). The refinements by the block diagonal least-squares with anisotropic thermal parameters gave *R* of 0.032. The absolute structure was de-

Table 1. Determination of the Absolute Configuration

h	*k*	*l*	$\lvert F_c(hkl)\rvert$	Obs.	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$
0	8	0	45	>	43
0	6	0	39	<	42
2	5	0	21	<	23
3	5	0	57	>	54
−8	1	2	21	<	23
−8	3	4	15	>	12
−5	1	6	36	>	33
−4	1	1	40	>	37
−4	4	4	15	>	13
−3	2	4	58	<	59

Table 2. Final Atomic Coordinates ($\times 10^4$ for Co, N, C, and O, $\times 10^3$ for H) and Their Equivalent Isotropic Thermal Parameters

Atom	x	y	z	B_{eq}/Å^2
Co(1)	6171(1)	7500(0)	3098(1)	1.4
Co(2)	281(1)	4732(0)	596(1)	1.6
N(1)A	4537(3)	7418(2)	3999(4)	1.9
N(2)A	7779(4)	6845(2)	4932(4)	1.9
N(3)A	7536(3)	7568(2)	1925(4)	2.3
N(4)A	5430(4)	6416(2)	2029(4)	2.1
N(5)A	4614(4)	8164(2)	1264(4)	2.1
N(6)A	6947(4)	8488(2)	4447(4)	2.0
C(1)A	4831(5)	7148(3)	5680(5)	2.8
C(2)A	5995(5)	6484(3)	6267(5)	3.1
C(3)A	7556(5)	6781(3)	6473(5)	2.6
C(4)A	9436(4)	7054(3)	5381(5)	2.8
C(5)A	9940(5)	7034(3)	3989(6)	3.6
C(6)A	9232(5)	7702(3)	2792(6)	3.4
C(7)A	4411(5)	6305(3)	297(5)	2.9
C(8)A	3215(5)	6961(3)	−330(5)	3.2
C(9)A	3902(5)	7787(3)	−365(5)	3.1
C(10)A	5007(5)	9027(3)	1007(6)	3.0
C(11)A	5530(5)	9538(2)	2501(6)	3.1
C(12)A	7043(5)	9285(3)	3747(6)	3.2
C(1)C	−1147(4)	4031(3)	−920(5)	2.1
C(2)C	628(4)	5159(2)	−1184(5)	2.2
C(3)C	1845(4)	3951(2)	934(5)	2.0
C(4)C	−136(4)	4264(2)	2305(5)	2.1
C(5)C	−1271(4)	5510(2)	397(5)	2.1
C(6)C	1794(4)	5444(2)	2022(5)	2.2
N(1)C	−1965(4)	3610(3)	−1866(5)	3.5
N(2)C	813(5)	5381(2)	−2302(5)	3.4
N(3)C	2808(5)	3495(2)	1155(5)	3.1
N(4)C	−425(4)	3976(2)	3304(5)	3.3
N(5)C	−2182(4)	5960(2)	379(5)	3.7
N(6)C	2723(5)	5873(3)	2830(5)	3.7
O(1)W	8033(4)	5053(2)	4675(4)	4.0
O(2)W	5374(5)	4116(3)	4281(5)	5.7
N(2)AH	762(4)	629(2)	460(5)	2.4
N(5)AH	397(5)	824(3)	168(6)	4.3

termined by the anomalous-scattering technique. The enantiomeric structure was refined in the same way at this stage and converged at residuals R of 0.042. As is shown in Table 1, the comparison of the observed and calculated differences between $|F(hkl)|$ and $|F(h\overline{kl})|$ indicated that $(+)^{\mathrm{CD}}_{490}$-isomer has the absolute configuration illustrated in Fig. 3.

The final refinement was carried out using the block diagonal least-squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms. The positions of twenty-nine hydrogen atoms among thirty-four, except those of water, were found from a difference synthesis. The final R and R_2 values were 0.022 and 0.028, respectively. The final atomic parameters and thermal parameters are given in Table 2.[6)]

Results and Discussion

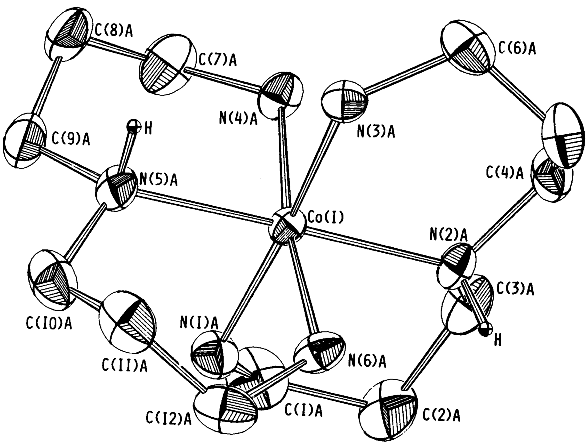


Fig. 3. Perspective drawing of the $[Co(dpt)_2]^{3+}$. The hydrogen atoms except for the secondary amine are not shown.

A perspective drawing of the complex cation is shown in Fig. 3. Two molecules of dpt ligands coordinate with six nitrogen atoms to form an octahedral complex. Each ligand occupies a meridional position as expected. The absolute structure shown in Fig. 3 was assigned to *trans*-δ-NH[7)]$(\overrightarrow{\Lambda})$.[8)]

The bond lengths and angles in the complex cation are listed in Table 3. The Co–N bond lengths (the longest value is 2.053(3) Å for Co(1)–N(2) and the shortest is 1.979(4) Å for Co(1)–N(3)) agreed with the observations for the $[Co(diamine)_3]^{3+}$- and $[Co(triamine)_2]^{3+}$-type complexes containing six-membered chelate rings.[9)] Co(1)–N(secondary) length is, however, longest in other values, in contrast to the cases of $(+)_{589}$*mer*-$[Co(dien)_2]Br_3\cdot 1.6H_2O$[6)] and $(-)_{589}$*unsym-fac*-$[Co(dien)_2][Co(CN)_6]\cdot 2H_2O$.[10)] All of the N(secondary)–Co–N(terminal) angles in the dpt chelates are larger than 90°. These results indicate that the six-membered chelate rings are considerably extended. As for the $[Co(triamine)_2]^{3+}$-type complexes containing six-membered chelate ring, such as $[Co(chta)_2]I_3$[11)] and $(-)^{\mathrm{CD}}_{474}$*mer*-$[Co(aepn)(dien)]I_3\cdot H_2O$[12)] (chta: *r*-1,*c*-3,*c*-5-cyclohexanetriamine, aepn: *N*-(2-aminoethyl)-1,3-propanediamine), octahedrons of chromophores are not distorted, although these complexes have many six-membered chelate rings. In contrast to these complexes, a pair of two-fused six-membered chelates coordinate to form a distorted octahedral complex in $[Co(dpt)_2]^{3+}$. The reddish purple coloration of $[Co(dpt)_2]^{3+}$ is unusual as CoN_6 chromophores. The maxima of the absorption spectra (19400 and 27200 cm^{-1}) are at lower energy sides than other CoN_6 complexes, and imply that this octahedron is distorted. The structure described above is consistent with the speculations based on the absorption spectrum.

References

1) S. Yamada, M. Umehara, M. Ishii, and M. Nakahara, *Nippon Kagaku Kaishi*, **1983**, 1733.

2) T. W. Hambley, G. H. Searle, and M. R. Snow, *Aust. J. Chem.*, **35**, 1285 (1982).

3) The values reported in the Ref. 1 should be corrected

Table 3. Bond Distances and Angles within the Complex Cation, *mer*-[Co(dpt)$_2$]$^{3+}$, with Their Estimated Standard Deviations in Parentheses

Bond distance	l/Å	Bond angle	ϕ/°
Co(1)-N(1)A	2.026(4)	N(1)A-Co(1)-N(2)A	95.2(1)
Co(1)-N(2)A	2.053(3)	N(1)A-Co(1)-N(3)A	172.1(2)
Co(1)-N(3)A	1.979(4)	N(1)A-Co(1)-N(4)A	87.7(2)
Co(1)-N(4)A	2.016(4)	N(1)A-Co(1)-N(5)A	86.1(1)
Co(1)-N(5)A	2.042(4)	N(1)A-Co(1)-N(6)A	88.2(2)
Co(1)-N(6)A	1.987(4)	N(2)A-Co(1)-N(3)A	91.1(2)
		N(2)A-Co(1)-N(4)A	85.7(1)
N(1)A-C(1)A	1.493(6)	N(2)A-Co(1)-N(5)A	178.6(1)
N(2)A-C(3)A	1.489(6)	N(2)A-Co(1)-N(6)A	87.9(1)
N(2)A-C(4)A	1.505(6)	N(3)A-Co(1)-N(4)A	88.6(2)
N(3)A-C(6)A	1.504(7)	N(3)A-Co(1)-N(5)A	87.6(2)
N(4)A-C(7)A	1.483(6)	N(3)A-Co(1)-N(6)A	96.6(2)
N(5)A-C(9)A	1.483(6)	N(4)A-Co(1)-N(5)A	94.9(1)
N(5)A-C(10)A	1.510(6)	N(4)A-Co(1)-N(6)A	171.8(2)
N(6)A-C(12)A	1.474(6)	N(5)A-Co(1)-N(6)A	91.7(1)
C(1)A-C(2)A	1.495(7)	Co(1)-N(1)A-C(1)A	124.2(3)
C(2)A-C(3)A	1.504(7)	Co(1)-N(2)A-C(3)A	116.6(3)
C(4)A-C(5)A	1.510(7)	Co(1)-N(2)A-C(4)A	117.6(3)
C(5)A-C(6)A	1.499(8)	Co(1)-N(3)A-C(6)A	122.0(3)
C(7)A-C(8)A	1.506(7)	Co(1)-N(4)A-C(7)A	124.7(3)
C(8)A-C(9)A	1.515(7)	Co(1)-N(5)A-C(9)A	118.3(3)
C(10)A-C(11)A	1.494(7)	Co(1)-N(5)A-C(10)A	118.9(3)
C(11)A-C(12)A	1.490(8)	Co(1)-N(6)A-C(12)A	122.7(3)
		N(1)A-C(1)A-C(2)A	112.9(4)
		N(2)A-C(3)A-C(2)A	114.2(4)
		N(2)A-C(4)A-C(5)A	114.7(4)
		N(3)A-C(6)A-C(5)A	110.3(4)
		N(4)A-C(7)A-C(8)A	112.7(4)
		N(5)A-C(9)A-C(8)A	112.8(4)
		N(5)A-C(10)A-C(11)A	114.0(4)
		N(6)A-C(12)A-C(11)A	111.4(4)
		C(1)A-C(2)A-C(3)A	111.4(4)
		C(4)A-C(5)A-C(6)A	112.3(4)
		C(7)A-C(8)A-C(9)A	112.5(4)
		C(10)A-C(11)A-C(12)A	113.3(4)

as follows: at 490 nm, in 1 mol dm^{-3} HCl: *trans*-δ-NH, $\Delta\varepsilon=+0.16$; *trans*-λ-NH, $\Delta\varepsilon=-0.13$.

4) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 73, and 78.

6) The observed and calculated structure factors, anisotropic thermal parameters for non-hydrogen atoms, and atomic parameters for hydrogen atoms are deposited at Bull. Chem. Soc. Jpn. (Document No. 8743).

7) K. Okiyama, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **35**, 2389 (1979).

8) T. Dambus and G. Shaffer, *Inorg. Chem.*, **22**, 2406 (1983).

9) R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 2438 (1973).

10) M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).

11) M. Ishii, M. Umehara, T. Nomura, and M. Nakahara, *Chem. Lett.*, **1983**, 541.

12) M. Ishii, S. Sato, Y. Saito, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **57**, 3094 (1984).