Preparation and Structure of {Bis(3-aminopropyl)amine}(*r*-1, *c*-3, *c*-5-cyclohexanetriamine)cobalt(III) Complex

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Synopsis. {Bis(3-aminopropyl)amine}(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) complex was prepared and the crystal structure of its iodide has been analyzed by X-ray diffraction. The complex cation has a facial configuration and an exo-type of N(secondary)–H bond orientation in bis(3-aminopropyl)amine. There is only a little distortion in the octahedron of this complex cation.

Although the complexes of five-membered rings of diethylenetriamine (dien) ligand have been extensively studied, reports on those of six-membered ring bis(aminopropyl)amine (dpt) are relatively few.

In a previous paper, the authors described the preparation of *mer*-$[Co(dpt)_2]^{3+}$ complex and the resolution to their optical isomers.[1] We also reported the structure of a bis-type complex of *r*-1,*c*-3,*c*-5-cyclohexanetriamine (chta), which takes a facial position and forms six-membered rings.[2]

The title complex, which is the mixed complex of chta and dpt, has necessary a facial geometry and exo and endo isomers in dpt as shown in Fig. 1.

In this paper, the authors will report the preparation of {bis(3-aminopropyl)amine}(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) complex, $[Co(chta)(dpt)]^{3+}$, and the crystal structure of its iodide.

Experimental

Preparation. To 80 mg of finely ground $[CoCl_3(chta)]$,[3] 5 ml of dpt solution (45 mg dpt/ml ethanol) was added, and the solution was stirred for 5 h on a water bath. The reddish-orange solution was diluted with a small amount of water and filtered to remove unreacted materials. The filtrate was poured into a column (ϕ 40 mm, h 300 mm) containing SP-Sephadex C-25 resin of Na^+ form. After the column was washed with 1 dm^3 water, elution was carried out with 1.0 mol dm^{-3} hydrochloric acid. A faster red layer and a slower reddish-orange layer descended. The reddish-orange fraction was concentrated to a small volume by an evaporator at 35 °C. With addition of ethanol to this solution, orange powders were obtained. Yield 21 mg (18%). Found: C, 32.50; H, 7.49; N, 18.87%. Calcd for $CoCl_{12}N_6H_{32}Cl_3\cdot H_2O$: C, 32.48; H, 7.72; N, 18.94%. Absorption maxima of ligand field bands and their extinction coefficients are as follows: ,20300 cm^{-1} (log ε=1.90), 28300 cm^{-1} (log ε=1.94). The crystal for X-ray analysis was grown from an aqueous solution, after the chloride was converted into iodide with an I^- form anion-exchange resin.

Crystal Structure Determination. The crystal data are as follows: $[Co(chta)(dpt)]I_3\cdot H_2O$, $CoC_{12}N_6H_{32}I_3\cdot H_2O$, *F. W.*= 818.09, monoclinic, space group *P*2/*a*,[4] $a=23.424(7)$, $b=12.079(3)$, $c=9.761(3)$ Å, $\beta=123.93(11)°$, $V=2291.6(1)$ Å^3, $D_x=2.03$ Mg m^{-3}, $D_m=2.05$ Mg m^{-3}, $Z=4$. A polyhedral crystal of approximately spherical shape with the radius of 0.5 mm was used for the X-ray intensity measurement. The intensity was measured on a Rigaku AFC-5 four-circle diffractometer (Keio University) with graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda=0.7093$ Å) up to 2θ of 55°. The θ-2θ scan technique was employed. Independent 4482 reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure determination. Corrections were made for the Lorentz and polarization factors, but no correction for absorption and extinction was applied. The structure was analyzed by the Patterson method by means of UNICS.[5] The calculation was carried out on a UNIVAC 1100 computer at Rikkyo University Computer Center. Scattering factors were taken from International Tables for X-ray Crystallography.[6] The refinement was carried out using the block-diagonal least-squares program HBLS IV based on $\Sigma w(|F_o|-k|F_c|)^2$, $w=1$, with anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogen atoms. Fifteen among thirty-two hydrogen atoms (except those of the water molecule) were found from different synthesis. The remaining seventeen hydrogen atoms were located at sites calculated by assuming a tetrahedral geometry around C and N and fixed bond lengths. The atomic and thermal parameters of the complex are given in Table 1.[7] The R and R_2 values were 4.09 and 4.60%, respectively. A perspective drawing of the complex cation is shown in Fig. 2.

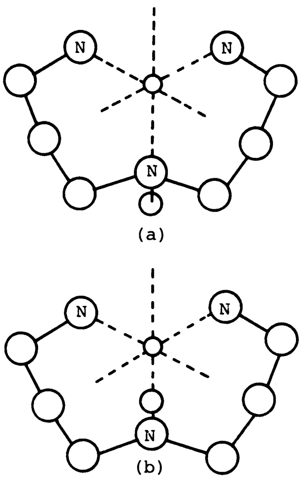

Fig. 1. Coordination mode of bis(3-aminopropyl)amine. (a) exo (b) endo.

Results and Discussion

The chta and dpt ligands coordinate with six nitrogen atoms from above and below cobalt atom to form an octahedral complex. Each ligand spreads across a face of the octahedron, that is, it coordinates in facial positions as expected. In the dpt chelate, N-(secondary)–H (N(5)–H) bond orientation has apparently an exo-type (Fig. 1-(a)). In the chta chelate, triplet six-membered chelate rings have stable chair-

Table 1. Final Atomic Coordinates ($\times 10^5$ for I and Co, $\times 10^4$ for N, C, and O), with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Thermal Parameters

Atom	x	y	z	B_{eq}/Å^2 a)
I(1)	45741(3)	15598(5)	62913(7)	3.1_0
I(2)	39326(3)	47072(4)	16768(6)	2.6_8
I(3)	18670(3)	45524(5)	20682(6)	3.1_2
Co	10394(4)	23261(7)	46387(10)	1.3_3
N(1)	2033(3)	1947(5)	5877(7)	2.1_1
N(2)	1107(3)	2438(5)	6755(7)	1.2_3
N(3)	1276(3)	3913(4)	4805(7)	1.8_8
N(4)	31(3)	2693(5)	3436(7)	2.3_1
N(5)	954(3)	2199(5)	2473(7)	2.0_1
N(6)	792(3)	723(5)	4538(7)	2.0_0
C(1)	2530(4)	2602(6)	7424(9)	2.4_7
C(2)	2358(4)	2452(7)	8686(9)	2.9_1
C(3)	1695(4)	3026(6)	8175(8)	2.5_9
C(4)	1672(4)	4229(6)	7708(9)	2.9_1
C(5)	1851(4)	4368(6)	6451(9)	2.5_6
C(6)	2522(4)	3806(6)	6973(9)	2.6_7
C(7)	−321(4)	3501(7)	2059(11)	3.3_7
C(8)	−2(4)	3583(7)	1066(10)	3.2_4
C(9)	266(4)	2480(8)	931(9)	3.4_3
C(10)	1216(4)	1158(6)	2174(10)	2.7_2
C(11)	856(4)	135(6)	2209(10)	2.9_3
C(12)	1056(4)	−138(6)	3913(10)	2.7_7
O(1)	2806(4)	2229(7)	4371(11)	5.6_5

a) $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cdot\cos\beta)$

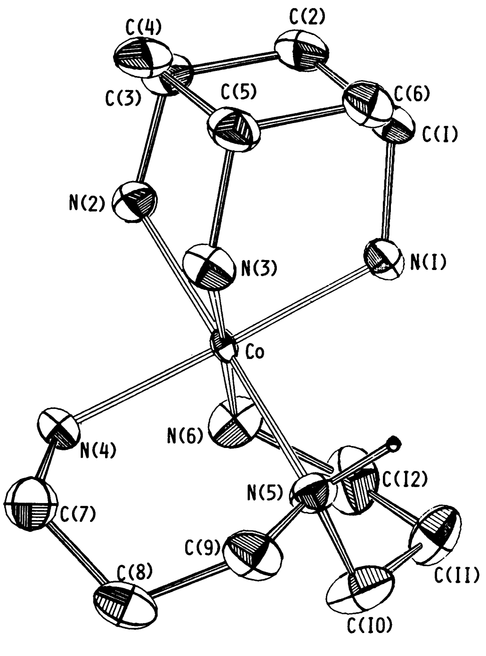

Fig. 2. Perspective drawing of the [Co(chta)(dpt)]$^{3+}$ cation.

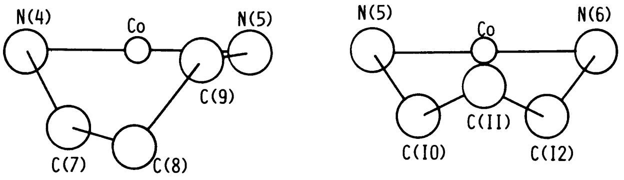

Fig. 3. Conformation of dpt chelate rings.

Table 2. Bond Distances (l/Å) in the Chelate Rings with Their Standard Deviations in Parentheses

Co-N(1)	1.910(5)	C(1)-C(2)	1.494(15)
Co-N(2)	1.989(7)	C(2)-C(3)	1.456(12)
Co-N(3)	1.972(5)	C(3)-C(4)	1.515(11)
Co-N(4)	1.933(6)	C(4)-C(5)	1.499(15)
Co-N(5)	2.020(7)	C(5)-C(6)	1.462(12)
Co-N(6)	2.002(6)	C(6)-C(1)	1.517(11)
		C(7)-C(8)	1.496(17)
N(1)-C(1)	1.459(8)	C(8)-C(9)	1.512(13)
N(2)-C(3)	1.495(8)	C(10)-C(11)	1.488(12)
N(3)-C(5)	1.483(11)	C(11)-C(12)	1.498(14)
N(4)-C(7)	1.474(8)		
N(5)-C(9)	1.485(11)		
N(5)-C(10)	1.497(11)		
N(6)-C(12)	1.487(12)		

Table 3. Bond Angles (ϕ/°) in the Chelate Rings with Their Standard Deviations in Parentheses

N(1)-Co-N(2)	89.8(3)	Co-N(1)-C(1)	118.2(6)
N(1)-Co-N(3)	89.6(2)	Co-N(2)-C(3)	119.9(6)
N(2)-Co-N(3)	89.6(3)	Co-N(3)-C(5)	118.9(4)
		Co-N(4)-C(7)	123.4(6)
N(4)-Co-N(5)	90.5(3)	Co-N(5)-C(10)	117.1(6)
N(4)-Co-N(6)	88.4(3)	Co-N(6)-C(12)	121.0(6)
N(5)-Co-N(6)	91.0(3)		
		C(6)-C(1)-C(2)	112.8(8)
N(1)-Co-N(5)	91.0(3)	C(1)-C(2)-C(3)	111.7(6)
N(1)-Co-N(6)	90.9(2)	C(2)-C(3)-C(4)	113.4(8)
N(1)-Co-N(4)	178.4(3)	C(3)-C(4)-C(5)	111.8(8)
N(2)-Co-N(4)	88.8(3)	C(4)-C(5)-C(6)	112.5(6)
N(2)-Co-N(6)	88.3(3)	C(5)-C(6)-C(1)	111.7(8)
N(2)-Co-N(5)	179.0(3)		
N(3)-Co-N(4)	91.1(3)	N(1)-C(1)-C(2)	110.2(7)
N(3)-Co-N(5)	91.1(3)	N(1)-C(1)-C(6)	109.5(6)
N(3)-Co-N(6)	177.8(3)	N(2)-C(3)-C(2)	109.7(7)
		N(2)-C(3)-C(4)	108.7(5)
		N(3)-C(5)-C(4)	109.7(7)
		N(3)-C(5)-C(6)	109.7(7)
		N(4)-C(7)-C(8)	113.4(7)
		C(7)-C(8)-C(9)	112.0(8)
		C(8)-C(9)-N(5)	112.1(6)
		C(9)-N(5)-C(10)	108.7(6)
		N(5)-C(10)-C(11)	112.9(9)
		C(10)-C(11)-C(12)	112.0(6)
		C(11)-C(12)-N(6)	110.8(6)

conformation. In contrast to this, the double fused six-membered dpt chelate rings take chair and skew-boat conformations (Fig. 3) which are the same as that observed in *s-fac*-[Co(dien)(dpt)](S_2O_6)(ClO_4)·H_2O.[8] There is a little difference in the Co–N distances between chta and dpt chelates in the [Co(chta)(dpt)]$^{3+}$ complex, but these values agree with the results obtained for the complex having six-membered chelate rings[9] (Table 2). The N–Co–N angles in the chelate rings are close to 90° (Table 3), distinct from other complexes containing facial type dpt (for example, in *s-fac*-[Co(dien)(dpt)]$^{3+}$,[8] 96.2°, 87.9°, and 92.5°, in *u-fac*-[Co(dien)(dpt)]$^{3+}$,[10] 96.6°, 88.7°, and 90.5°, and in [$Co_2(OH)_3(dpt)_2$]$^{3+}$,[11] 95.5°, 98.4°, and 93.1°) and comparable to those of chta complex (in [$Co(chta)_2$]$^{3+}$,[2] 90.1°, 90.0°, and 89.9°). The trans N–Co–N angles are slightly smaller than 180° and the non-chelate N–Co–N angles are slightly larger or smaller than 90°. These facts indicate that six nitrogen atoms form a slightly distorted octahedron around cobalt atom; the axis perpendicular to facial plane of octahedron elongates. In the complexes containing dpt, *s-fac-*,[8] *mer-*,[12] *u-fac*-[Co(dien)(dpt)]$^{3+}$,[10] and *mer*-[$Co(dpt)_2$]$^{3+}$,[13] there exists a considerable deviation from 90° in their N–Co–N angles of six-membered chelate rings. However, in the title complex, [Co(chta)(dpt)]$^{3+}$, the octahedral configuration is retained. It is known that chta ligands in [$Co(chta)_2$]$^{3+}$ [2] form a robust octahedron with cobalt atom. It seems that the particular structure of the title dpt complex is due to combination of dpt with chta and that distortion is fairly reduced by soft conformation of six-membered dpt chelate rings to retain octahedra of CoN_6 chromophores.

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