Preparation and Molecular Structure of *cis*-β,*trans*(*sec*-*N*,*P*)-{(2-Aminoethyl)dimethylphosphine}(3,7-diazanonane-1,9-diamine)cobalt(III) Bromide Dihydrate

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Synopsis. The reaction of *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ (2,3,2-tet: 3,7-diazanonane-1,9-diamine) with (2-aminoethyl)-dimethylphosphine (edmp) afforded only one geometrical isomer of $[Co(edmp)(2,3,2\text{-tet})]^{3+}$, the structure of which was determined by X-ray analysis to have the *cis*-β,*trans*-(*sec*-*N*,*P*) configuration.

Formation of cobalt(III)–phosphine complexes is often specific or selective concerning geometrical isomerism.[1,2] This note reports preparation and X-ray structure analysis of $[Co(edmp)(2,3,2\text{-tet})]^{3+}$ (edmp: (2-aminoethyl)dimethylphosphine, 2,3,2-tet: 3,7-diazanonane-1,9-diamine) which is only one geometrical isomer formed by the reaction of *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ with edmp.

Experimental

Preparation of the Complex. To an oxygen-free dimethyl sulfoxide solution (100 cm^3) of *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$[3] (340 mg, 0.84 mmol) was added an oxygen-free methanol solution (5 cm^3) of edmp[1] (91 mg, 0.87 mmol) with stirring under nitrogen atmosphere. After stirring for 2 h, the resulting orange solution was mixed with water (400 cm^3) and diethyl ether (100 cm^3) to extract unreacted edmp. The orange aqueous-dimethyl sulfoxide solution was diluted to 1 dm^3 with water and poured on a column ($\phi 2.5 \times 150$ cm^2) of SP-Sephadex C-25. The product adsorbed was eluted with 0.2 mol dm^{-3} NaCl, giving two bands. The first yellow eluate was *fac*-$[Co(edmp)_3]^{3+}$.[1] The second orange eluate was evaporated to dryness under reduced pressure. The residue was extracted with methanol (200 cm^3). The extract was diluted with water (1 dm^3) and the solution was poured on a column ($\phi 2.5 \times 15$ cm^2) of SP-Sephadex C-25. The complex adsorbed was eluted with 1 mol dm^{-3} KBr. The eluate was concentrated in a vacuum desiccator over P_4O_{10} to yield red-orange crystals, which were recrystallized from water and dried in air. Yield: *ca.* 50%. Found: C, 22.39; H, 5.93; N, 12.11%. Calcd for $[Co(edmp)(2,3,2\text{-tet})]Br_3 \cdot 2H_2O = C_{11}H_{36}N_5Br_3CoO_2P$: C, 22.02; H, 6.05; N, 11.67%. The complex in aqueous solution shows two d-d absorption bands at 21980 cm^{-1} ($\log \varepsilon = 2.37$) and 28740 cm^{-1} ($\log \varepsilon = 2.41$).

X-Ray Analysis. Crystal data: monoclinic, $P2_1/a$, $a = 17.719(2)$, $b = 8.776(1)$, $c = 14.966(1)$ Å, $\beta = 108.01(1)°$, $V = 2213.2(4)$ Å^3, $Z = 4$, $D_m = 1.803$, $D_x = 1.801$ g cm^{-1}, μ(Mo $K\alpha$) = 6.63 mm^{-1}. A specimen with dimensions $0.32 \times 0.34 \times 0.37$ mm^3 was used for the X-ray work. Diffraction data were collected on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Within the range $2\theta < 60°$, 3687 independent reflections with $F_o > 3\sigma(F_o)$ were obtained. Intensities were corrected for Lorentz and polarization factors, and for absorption.

The structure was solved by the direct method (MULTAN). The method used in the solution and refinement of the structure were standard and have been described previously.[4] Hydrogen atoms except for those bonded to one of water molecules of crystallization were located by the difference syntheses, and were included in the final refinement with the isotropic temperature factors. The final R indices were $R = 0.044$ and $R_w = 0.043$. Table 1 lists the atomic parameters.[5] The $F_o - F_c$ data, final thermal parameters, and hydrogen atomic coordinates are preserved by the Chemical Society of Japan (Document No. 8322).

Table 1. Fractional coordinates ($\times 10^5$) with B_{eq}

Atom	x	y	z	B_{eq}/Å^2
Br(1)	40675(3)	18613(7)	44140(4)	4.1
Br(2)	14171(4)	2287(6)	28560(5)	4.2
Br(3)	34800(3)	85424(8)	5943(4)	3.9
Co	22676(3)	49733(7)	24400(4)	1.5
P	9522(7)	53602(13)	19744(8)	2.0
N(1)	21091(22)	29983(43)	17679(26)	2.4
N(2)	34350(21)	44867(44)	26961(24)	2.2
N(3)	24885(20)	68967(40)	31936(24)	1.9
N(4)	22829(20)	39577(40)	36157(24)	2.0
N(5)	22264(20)	60836(44)	12609(24)	2.2
C(1)	28715(31)	22073(58)	18669(37)	3.3
C(2)	34954(29)	33893(63)	19620(36)	3.2
C(3)	40523(27)	56984(65)	28415(35)	3.1
C(4)	39689(28)	68929(63)	35329(35)	3.2
C(5)	32094(29)	77763(54)	32107(33)	2.7
C(6)	24608(26)	65486(54)	41709(29)	2.3
C(7)	26902(27)	49339(55)	44270(29)	2.4
C(8)	15748(30)	72228(55)	9203(33)	2.8
C(9)	8059(27)	64172(62)	8816(33)	3.1
C(10)	3328(29)	36911(61)	16604(39)	3.6
C(11)	4932(28)	64326(64)	26840(35)	3.2
O(1)	-9162(24)	63131(63)	-43288(32)	6.4
O(2)	-3070(49)	334(90)	7625(53)	13.9

Table 2. Bond lengths (l/Å) and angles (ϕ/°) and their estimated standard deviations

Co	-P	2.243(1)		N(2)	-C(3)	1.492(7)	
Co	-N(1)	1.980(4)		N(3)	-C(5)	1.486(6)	
Co	-N(2)	2.029(4)		N(3)	-C(6)	1.510(6)	
Co	-N(3)	2.000(4)		N(4)	-C(7)	1.479(6)	
Co	-N(4)	1.965(4)		N(5)	-C(8)	1.493(7)	
Co	-N(5)	1.997(4)		C(1)	-C(2)	1.490(8)	
P	-C(9)	1.828(6)		C(3)	-C(4)	1.512(8)	
P	-C(10)	1.803(6)		C(4)	-C(5)	1.498(8)	
P	-C(11)	1.791(6)		C(6)	-C(7)	1.491(7)	
N(1)	-C(1)	1.495(7)		C(8)	-C(9)	1.520(8)	
N(2)	-C(2)	1.490(7)					
P	-Co -N(1)	90.2(1)		Co	-P -C(10)	116.6(2)	
P	-Co -N(4)	94.1(1)		Co	-N(5) -C(8)	116.2(3)	
P	-Co -N(2)	172.5(1)		Co	-N(2) -C(3)	122.4(3)	
P	-Co -N(3)	92.9(1)		Co	-N(3) -C(6)	108.4(3)	
P	-Co -N(5)	84.3(1)		C(9)	-P -C(10)	105.8(3)	
N(1)	-Co -N(3)	175.9(2)		C(9)	-P -C(11)	107.4(3)	
N(2)	-Co -N(3)	93.5(2)		C(10)	-P -C(11)	103.3(3)	
N(3)	-Co -N(4)	86.1(2)		P	-C(9) -C(8)	108.9(4)	
N(1)	-Co -N(4)	91.1(2)		C(2)	-N(2) -C(3)	110.6(4)	
N(2)	-Co -N(4)	90.3(2)		C(5)	-N(3) -C(6)	111.9(4)	
N(3)	-Co -N(5)	91.9(2)		N(1)	-C(1) -C(2)	108.0(4)	
N(1)	-Co -N(2)	83.6(2)		N(2)	-C(2) -C(1)	107.5(4)	
N(1)	-Co -N(5)	91.0(2)		N(2)	-C(3) -C(4)	111.8(4)	
N(2)	-Co -N(5)	91.5(2)		C(3)	-C(4) -C(5)	114.0(5)	
N(4)	-Co -N(5)	177.4(2)		N(3)	-C(5) -C(4)	114.8(4)	
Co	-P -C(9)	101.6(2)		N(3)	-C(6) -C(7)	110.7(4)	
Co	-N(1) -C(1)	112.1(3)		N(4)	-C(7) -C(6)	108.3(4)	
Co	-N(2) -C(2)	107.4(3)		N(5)	-C(8) -C(9)	106.9(4)	
Co	-N(3) -C(5)	117.7(3)		Co	-N(4) -C(7)	109.9(3)	
Co	-P -C(11)	120.9(2)					

Results and Discussion

Figure 1 shows a perspective view of the complex ion. The 2,3,2-tet ligand coordinates to the cobalt(III) ion with the four nitrogen atoms to form *cis*-β

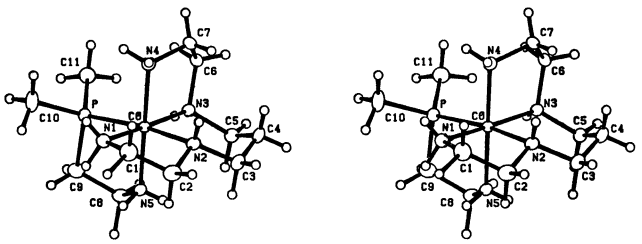

Fig. 1. A stereo view of $[Co(edmp)(2,3,2\text{-tet})]^{3+}$.

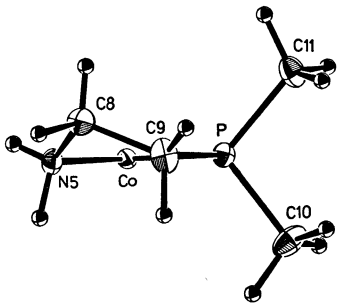

Fig. 2. Conformation of the edmp chelate ring.

configuration, and the phosphorus atom of edmp takes the position *trans* to the secondary amine (N2) of 2,3,2-tet. The bond distances and angles are listed in Table 2. The Co–N(2) distance of 2.029(4) Å is the longest among those reported for analogous 2,3,2-tet complexes, $(+)_{470}$-*Λ-cis-β*-$[Co(NO_2)_2\{(R)\text{-}NH_2CH_2CH_2NHCH(CH_3)CH_2CH_2NHCH_2CH_2NH_2\}]Br$ (2.004(4) Å)[6] and $(-)_{546}$-*Λ-cis-β*-$[Co(C_2O_4)\{(R,R)\text{-}NH_2CH_2CH_2NHCH(CH_3)CH_2CH(CH_3)NHCH_2CH_2NH_2\}]ClO_4$ (1.99(1) Å).[7] The elongation of the Co–N(2) bond can be attributed to trans influence of the phosphorus atom of edmp. Similar elongations of Co–N bonds have been observed in $(+)_{589}$-*Λ-fac*-$[Co(edmp)_3]Br_3\cdot 3H_2O$ (2.041 Å)[1] and $(+)_{589}$-*Λ*-$[Co(en)_2\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}]Br_3\cdot 1.5H_2O$ (2.032 Å).[8] The Co–P distance of 2.243 Å is similar to 2.237(5)[1] and 2.256(3) Å[8] in the complexes given above.

The chelate rings of 2,3,2-tet and edmp in the *Λ*-complex adopt (*δ*-gauche)(chair)(*δ*-gauche) and pseudo *δ*-gauche conformations, respectively (Figs. 1 and 2). Bond angles around the phosphorus atom deviate argely from the normal tetrahedral angle; Co–P–C(11):120.9(2)°, Co–P–C(10):116.6(2)°, Co–P–C(9):101.6(2)°, and C(10)–P–C(11):103.3(3)°. These deviations seem to come from a crowded structure around the phosphorus atom.

The other *cis-β,cis(sec-N,P)* isomer was not formed. Molecular models indicate that this isomer has big steric hindrance among one methyl group and axial hydrogen atoms on C(3) and C(5). Attempts to prepare $[Co\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}(2,3,2\text{-tet})]^{3+}$, which has the $-P(CH_3)_2$ group at the *cis(sec-N,P)* position, were unsuccessful, no reaction taking place between *trans*-$[CoCl_2(2,3,2\text{-tet})]^+$ and the diphosphine ligand. No *cis-α* isomer of a 2,3,2-tet complex has been reported probably because of strong preference of the chair conformation of the six-membered chelate ring. Thus the $[Co(edmp)(2,3,2\text{-tet})]^{3+}$ complex forms only one geometrical isomer of the *cis-β,trans(sec-N,P)* configuration.

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References

1) I. Kinoshita, K. Kashiwabara, J. Fujita, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **54**, 2683 (1981).

2) K. Kashiwabara, K. Katoh, T. Ohishi, J. Fujita, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **55**, 149 (1982).

3) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, **1966**, 1311; H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

4) T. Ito, K. Toriumi, and H. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 1096 (1981).

5) The value of B_{eq} for O(2) of water of crystallization is relatively large. When the occupancy factor of O(2) was assumed to be 0.5 in the least-squares calculation, a normal thermal parameter ($B_{eq}=6.0$ Å^2) was obtained. The values observed in elemental analysis are closer to the values calculated as the sesqui hydrate (C, 22.35; H, 5.97; N, 11.85%) rather than those for the dihydrate (see text). These facts indicate that about 25% of water of crystallization are lost randomly from the crystal lattice.

6) P. W. R. Corfield, J. C. Dabrowiak, and E. S. Gore, *Inorg. Chem.*, **12**, 1734 (1973).

7) S. Yano, A. Fujioka, M. Yamaguchi, and S. Yoshikawa, *Inorg. Chem.*, **17**, 14 (1978).

8) S. Ohba, Y. Saito, T. Ohishi, K. Kashiwabara, and J. Fujita, *Acta Crystallogr., Sect. C*, **39**, 49 (1983).