The Crystal Structure of $(+)_{350}$-Diammine-*N*,*N*,*N'*-trimethylethylenediamineplatinum(II) Di-*μ*-(+)-tartrato-(4-)bis(antimonate(III)) Monohydrate

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X-Ray structure analysis of the title compound has revealed that the asymmetric secondary nitrogen center in the complex cation has the *S* absolute configuration. The crystals are orthorhombic, with the space group $P2_12_12_1$ and with $Z=4$ in a unit cell with dimensions of: $a=18.783(6)$, $b=14.138(4)$, and $c=8.473(2)$ Å. The crystal structure has been determined from three-dimensional diffractometer data and refined by the least-squares method to R of 0.030 for 1971 independent reflections with $I>3\sigma(I)$. The Pt atom has a square-planar coordination by four N atoms, and the methyl group bonded to the secondary nitrogen is equatorial with respect to the chelate ring. Each complex cation is surrounded octahedrally by six di-*μ*-(+)-tartrato(4-)-bis(antimonate(III)) anions.

Although an optical resolution has been made for a large number of octahedral Co(III) complexes, there have been few reports concerning the resolution of the planar Pt(II) complexes. In order to study the correlation between the circular dichroism and the structure in dissymmetric planar metal complexes, we have prepared several Pt(II) chelates of *N*-substituted diamine and have attempted to resolve each of them into enantiomeric forms.

Of these chelates, $[Pt(NH_3)_2(Me_3en)]^{2+}$ (Me_3en, *N*,*N*,*N'*-trimethylethylenediamine) exists in two optical isomers: the one has a secondary nitrogen with the *R* configuration, while the other involves *S* asymmetric nitrogen. By the use of silver di-*μ*-(+)-tartrato(4-)-bis(antimonate(III)) ($Ag_2[Sb_2(+)\text{-}tart_2]$) as the resolving agent, the seemingly diastereoisomeric salt, $(+)_{350}$-$[Pt(NH_3)_2(Me_3en)][Sb_2(+)\text{-}tart_2]\cdot H_2O$, could be obtained as a less soluble fraction in an acidic solution. The circular dichroism of this compound is different from that of $K_2[Sb_2(+)\text{-}tart_2]$ in the 250—350 nm region. Although this indicate that there is some resolution, it is uncertain whether or not the resolution is complete. Fortunately, if the diastereoisomeric salt contains only one antipode of the enantiomeric pair, it is necessary to elucidate the absolute configuration of the complex in order to advance our study. Therefore, an X-ray structure analysis was performed on this compound.

Experimental

Details of the preparation of the title compound will be reported in the near future.

X-Ray Data Measurement. *Crystal Data*: $C_{13}H_{26}N_4O_{13}Sb_2Pt$, $M=884.96$, Orthorhombic, $a=18.783(6)$, $b=14.138(4)$, $c=8.473(2)$ Å, $U=2250(1)$ Å^3, $Z=4$, $D_m=2.59$ (by flotation), $D_c=2.61$ gcm^{-3}, Mo*Kα* radiation ($\lambda=0.71069$ Å), μ(Mo*Kα*) $=89.9$ cm^{-1}. Space group $P2_12_12_1$.

The Laue symmetry and the space group were determined from oscillation and Weissenberg photographs. The unit-cell parameters were obtained by the least-squares treatment of 19 θ values measured on a Philips diffractometer with Mo*Kα* radiation.

Data Collection. The intensities were measured by means of the ω-2θ scan method on a Philips PW 1100 four-circle diffractometer using a graphite monochrometer and Mo*Kα* radiation with a crystal with dimensions of $0.12\times0.13\times0.10$ mm. A scan speed of 0.017° s^{-1}, a scan width of $(0.9+0.2\tan\theta)°$, and two 20 s background counts were chosen. Three standard reflections (400, $0\bar{6}0$, and 004), monitored every 4 h throughout the data collection, showed no significant

Table 1. Final atomic coordinates and temperature factors

	x	y	z	B (Å^2)
Pt	0.23028(2)	0.22925(3)	0.49010(6)	a)
N(1)	0.2206(6)	0.3731(8)	0.5321(13)	2.1(2)
N(2)	0.1903(6)	0.2155(9)	0.7156(15)	2.7(2)
N(3)	0.2364(6)	0.0840(8)	0.4547(13)	2.3(2)
N(4)	0.2647(6)	0.2452(8)	0.2579(13)	2.3(2)
C(1)	0.1754(11)	0.3865(15)	0.6779(26)	5.0(4)
C(2)	0.8171(10)	0.3128(15)	0.7857(26)	4.6(4)
C(3)	0.1778(10)	0.4201(15)	0.4050(24)	4.5(4)
C(4)	0.2926(10)	0.4183(14)	0.5392(23)	4.3(4)
C(5)	0.2292(9)	0.1505(12)	0.8234(21)	3.5(3)
Sb(1)	0.47727(5)	0.40889(7)	0.30078(12)	a)
Sb(2)	0.57461(5)	0.53830(7)	−0.22411(11)	a)
C(6)	0.4067(7)	0.3390(10)	0.0125(19)	2.5(2)
C(7)	0.4834(7)	0.3117(9)	−0.0057(18)	2.0(2)
C(8)	0.5128(7)	0.3497(10)	−0.1598(17)	2.1(2)
C(9)	0.5940(7)	0.3345(10)	−0.1600(17)	2.1(2)
C(10)	0.6017(7)	0.5352(10)	0.3194(16)	1.8(2)
C(11)	0.5431(7)	0.5929(11)	0.2342(17)	2.3(3)
C(12)	0.5725(7)	0.6340(10)	0.0837(16)	2.1(2)
C(13)	0.5108(7)	0.6768(9)	−0.0120(18)	2.1(2)
O(1)	0.3883(5)	0.3802(8)	0.1403(13)	2.8(2)
O(2)	0.3637(7)	0.3166(9)	−0.0928(15)	4.1(3)
O(3)	0.5252(5)	0.3412(7)	0.1285(12)	2.4(2)
O(4)	0.4975(5)	0.4486(7)	−0.1770(11)	2.3(2)
O(5)	0.6340(5)	0.4083(7)	−0.1825(12)	2.6(2)
O(6)	0.6195(5)	0.2548(7)	−0.1390(11)	2.2(2)
O(7)	0.5862(5)	0.4505(8)	0.3592(12)	2.8(2)
O(8)	0.6605(6)	0.5707(8)	0.3411(13)	3.1(2)
O(9)	0.4829(5)	0.5357(7)	0.1994(11)	2.3(2)
O(10)	0.6094(4)	0.5654(6)	−0.0096(13)	2.3(2)
O(11)	0.5006(5)	0.6415(7)	−0.1484(13)	2.8(2)
O(12)	0.4737(5)	0.7394(8)	0.0422(12)	3.1(2)
H_2O	0.0720(7)	0.4372(9)	0.0669(15)	4.3(3)

a) Anisotropic temperature factors ($\times10^5$) in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$, with parameters:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	104(1)	197(2)	564(6)	6(3)	13(5)	−33(8)
Sb(1)	151(2)	247(4)	847(13)	34(6)	184(11)	164(14)
Sb(2)	197(3)	271(4)	628(12)	−63(6)	50(10)	107(13)

variation in intensity. Of the independent reflections measured in the $5° \leq 2\theta \leq 50°$ range, 1971 reflections with $I > 3\sigma(I)$ were considered to be observed and were used for the structure analysis ($\sigma^2(I) = CT + (t_c/t_b)(B_1+B_2) + (pI)^2$; CT, total integrated peak count obtained in a scan time t_c; B_1 and B_2, background counts each obtained in time $t_b/2$; $p = 0.04$; $I = CT\text{-}(t_c/t_b)(B_1+B_2)$). The intensity data were processed with the computer program of Hornstra and Stubbe.1) A spherical absorption correction ($r = 0.05$ mm) was applied.

Structure Determination and Refinement. The crystal structure was solved by the heavy-atom technique. The positional and thermal parameters were refined by the least-squares method, the function minimized being $\sum w(F_o - |F_c|)^2$. The weight for each reflection, w, was unity in the initial refinement; in the final one $w = 0.5$ for $F_o < 25.1$, $w = 1$ for $25.1 \leq F_o \leq 150.8$, and $w = (150.8/F_o)^2$ for $F_o > 150.8$. All the parameter shifts in the final cycle of the refinement were $< (1/10)\sigma$. The final R value was 0.030. The atomic scattering factors of the neutral Pt, Sb, O, N, and C were employed from Ref. 2. Real and imaginary parts of the anomalous dispersion correction were applied for Pt and Sb atoms.

The atomic coordinates listed in Table 1 correspond exactly to the absolute crystal structure, which was determined on the basis of the well-established absolute configuration of the $[Sb_2(+)\text{-}tart_2]$ anion. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7625). All the computations were carried out by means of the FACOM 270-30 computer at Osaka City University. The computer programs used in the calculations were as follows: RSSFR-4 (Fourier synthesis), HBLS-4 (least-squares calculation), and DAPH (interatomic distances and angles, least-squares plane, and coordinates of H atoms), all of which were adapted to the FACOM 270-30 computer.

Results and Discussion

The absolute configuration of the complex cation and the absolute crystal structure viewed down the c axis are shown in Figs. 1 and 2 respectively. The bond lengths and angles in the complex, along with some selected interatomic distances, are presented in Table 2.

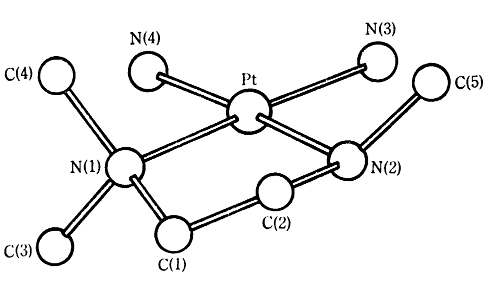

Fig. 1. The absolute configuration of the complex cation in $(+)_{350}$-$[Pt(NH_3)_2(Me_3en)][Sb_2\text{-}(+)\text{-}tart_2]\cdot H_2O$.

From the space group and the number of the formula units in the unit cell, it was inferred that the crystals involve only one antipode of the two optical isomers. The absolute configuration of the secondary nitrogen atom in the complex was elucidated to be S by the subsequent crystal structure analysis.

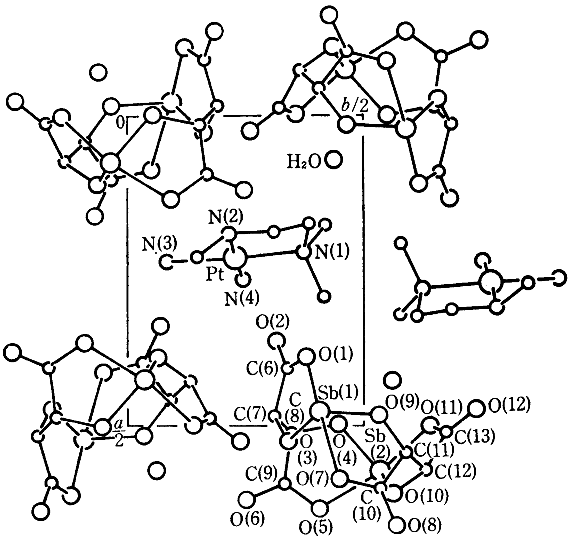

Fig. 2. The crystal structure viewed down the c axis.

TABLE 2. INTERATOMIC DISTANCES AND ANGLES

Bond lengths (Å)		Bond angles (°)	
Pt–N(1)	2.07(1)	N(1)–Pt–N(2)	84.4(5)
Pt–N(2)	2.06(1)	N(3)–Pt–N(4)	87.4(5)
Pt–N(3)	2.08(1)	Pt–N(1)–C(1)	108(1)
Pt–N(4)	2.08(1)	Pt–N(1)–C(3)	111(1)
N(1)–C(1)	1.51(3)	Pt–N(1)–C(4)	110(1)
N(1)–C(3)	1.50(2)	C(1)–N(1)–C(3)	103(1)
N(1)–C(4)	1.50(2)	C(1)–N(1)–C(4)	115(1)
N(2)–C(2)	1.50(3)	Pt–N(2)–C(2)	107(1)
N(2)–C(5)	1.49(2)	Pt–N(2)–C(5)	117(1)
C(1)–C(2)	1.40(3)	C(2)–N(2)–C(5)	110(1)
		N(1)–C(1)–C(2)	111(2)
		C(1)–C(2)–N(2)	115(2)

Atom		Interatomic distance (Å)	Positions$^{a)}$ of	
A	B		A	B
H[N(2)]$^{b)}$	O(3)	2.23	1	3
N(3)	O(5)	3.01(2)	1	2
N(3)	O(8)	3.13(2)	1	3
N(3)	O(10)	2.95(2)	1	5
N(4)	O(6)	2.91(2)	1	2
N(4)	O(8)	2.96(2)	1	5
H_2O	O(4)	3.00(2)	1	4
H_2O	O(6)	2.92(2)	1	2

a) Numerals refer to the following equivalent positions; 1: x, y, z. 2: $-1/2+x, 1/2-y, -z$. 3: $-1/2+x, 1/2-y, 1-z$. 4: $1/2-x, 1-y, 1/2+z$. 5: $1-x, -1/2+y, 1/2-z$. b) The coordinates of H atom linked to N(2) were calculated on the assumption that the N–H bond length is 1.03 Å.

The Pt atom has a square-planar coordination by four nitrogen atoms. The equation of the plane defined by the 4 N atoms is:

$$0.9403X + 0.0138Y + 0.3400Z = 5.484^{3)}$$

The deviations (Å) of atoms from the plane are as follows: Pt, −0.040; N(1), −0.02; N(2), 0.02; N(3), −0.02; N(4), 0.02; C(1), 0.36; C(2), −0.15; C(3), 1.09; C(4), −1.32, and C(5), −0.97. The N-CH_3 bond in the secondary amino group is equatorial with respect to the five-membered chelate ring.

The Pt–NH_3 bond lengths agree with those in *trans-*

$[PtCl_2(NH_3)_2]$ (2.05(4) Å)[4] and $[Pt(NH_3)_4][Re_2O_3(CN)_8]$ (2.047—2.059(9) Å)[5] within the limits of experimental error, though they seem to be slightly longer than those cited for comparison. The bond lengths of Pt–N(1) (tertiary amino group) and Pt–N(2) (secondary) are almost equal, but are somewhat longer than those of Pt–N (primary) found in $[Pten_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ (2.024(6) and 2.036(4) Å).[6] The C–C single bond in the complex cation is unusually short. However, all the bond lengths and angles in the $[Sb_2(+)\text{-tart}_2]$ anion are normal and are in good agreement with the corresponding ones in $K_2[Sb_2(+)\text{-tart}_2]\cdot 3H_2O$.[7] The abnormal C–C bond length presumably results from errors in absorption correction for the intensity data.

The complex cation is surrounded octahedrally by six $[Sb_2(+)\text{-tart}_2]$ anions. Since no hydrogen atoms could be located, it is difficult to point out unequivocally the hydrogen bonds in which the NH_3 or H_2O molecule participates. Some possible hydrogen bonds are shown in Table 2. However, the hydrogen bonding in the present crystal seems to be rather weak from the viewpoint of the interatomic distance between proton donor and acceptor.

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