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The Crystal Structure of $(+)_{350}$-(R)-Propylenediamine-N,N'-dimethylethylenediamineplatinum(II) Di-μ-(+)-tartrato(4−)-bis(antimonate(III)) Dihydrate

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The crystal of the title compound is monoclinic, with $a=9.415(3)$, $b=15.767(7)$, $c=8.786(3)$ Å, $\beta=94.25(4)°$, the space group of $P2_1$, and $Z=2$. The structure was determined from the counter intensity data by heavy-atom techniques and was refined by the block-diagonal least-squares calculations to R 0.050 for 2604 non-zero reflections. The Pt atom has a square-planar coordination by 4N atoms, the secondary N atoms of which are of the S absolute configuration.

Few studies have been made of the optical resolution of the platinum(II) complexes as well as of the correlation between the optical activity and structure of the Pt(II) chelates. Ito *et al.*[1] studied the absorption and circular dichroism (CD) spectra of a number of Pt(II) chelates of optically active diamines. The resolution and racemization reaction of some N-methylethylenediamineplatinum(II) substances were investigated by Buckingham *et al.*[2] and Goddard *et al.*[3] Recently, Bosnich[4] reported on the conformational and vicinal effects which were observed in the CD spectra of N-methyl-substituted ethylenediamine and propylenediamine complexes of Pt(II). As a part of our studies of the CD-structure correlation, we have been attempting for several years to resolve several mixed ligand complexes of Pt(II). This report will describe the absolute configuration of the complex cation of $(+)_{350}$-[Pt(R-pn)(Me$_2$en)][Sb$_2$(+)-tart$_2$]·2H$_2$O (R-pn: (R)-(−)-propylenediamine; Me$_2$en: N,N'-dimethylethylenediamine; [Sb$_2$(+)-tart$_2$]: di-μ-(+)-tartrato(4−)-bis(antimonate(III))), which was obtained in the course of our studies; we will also show the crystal structure of this compound.

Experimental

Preparation of $(+)_{350}$-*[Pt(R-pn)(Me$_2$en)][Sb$_2$(+)-tart$_2$]·2H$_2$O.* [PtCl$_2$(Me$_2$en)] was prepared following a method which is analogous to that used for [PtCl$_2$en].[5] A mixture of [PtCl$_2$(Me$_2$en)] (0.57 g) and an excess of (R)-propylenediamine ((R)-(−)-pn) in water (15 ml) was heated at 90 ° until the solution became clear. The solution was evaporated to near dryness, whereby the excess of diamine was removed. The resulting [Pt(R-pn)(Me$_2$en)]Cl$_2$ is highly hygroscopic and could not be isolated. Ag$_2$[Sb$_2$(+)-tart$_2$] (1.05 g) was added to "[Pt(R-pn)(Me$_2$en)]Cl$_2$" in 20 ml of water, and the suspension was warmed for 0.5 h in the dark. The AgCl was then filtered off and washed with hot water (10 ml). The filtrate and washing were combined, and the resultant solution was evaporated to dryness under reduced pressure. The product was dissolved in 14 ml of hot water acidified with a drop of acetic acid. The solution was filtered, and a small amount of unidentified precipitates was removed; then the solution was allowed to stand at room temperature for two days. The colorless crystals thus obtained were recrystallized from hot water involving a drop of acetic acid. They were filtered, and subsequently washed with ethanol and acetone. Yield, 0.51 g (23%).

Found: C, 19.21; H, 3.38; N, 5.68%. Calcd for $(+)_{350}$-[Pt(R-H$_2$NCH$_2$CH(CH$_3$)NH$_2$)(H$_3$CNHCH$_2$CH$_2$NHCH$_3$)]-[Sb$_2$(+)-(C$_4$H$_2$O$_6$)$_2$]·2H$_2$O: C, 19.39; H, 3.23; N, 6.03%.

An optical rotation measurement was made on 0.0104 g of the compound in 10 ml of 0.02 M acetic acid at 350 nm, using a JASCO J-20 Automatic Recording Spectropolarimeter; $[\alpha]_{350}$, +510°.

X-Ray Data Collection. The crystals of $(+)_{350}$-[Pt(R-pn)(Me$_2$en)][Sb$_2$(+)-tart$_2$]·2H$_2$O are colorless, needle-shaped, and stable in the air. The specimen employed for data collection had dimensions of 0.23×0.15×0.13 mm and was mounted on a glass fibre. Preliminary X-ray photographic studies, using oscillation, Weissenberg, and precession techniques, revealed the approximate unit cell dimensions, the Laue symmetry of 2/m, and the systematic absences of $0k0$ for $k=2n+1$. These extinctions indicate that the space group is $P2_1$, since the compound is optically active. Crystal data: $C_{15}H_{30}O_{14}N_4Sb_2Pt$, monoclinic, $a=9.415(3)$, $b=15.767(7)$, $c=8.786(3)$ Å, $\beta=94.25(4)°$, $U=1300.7$ Å^3, $Z=2$, $D_c=2.40$, $D_m=2.37$ g·cm^{-3}, space group $P2_1$, $\lambda(\mathrm{Mo}K\alpha)=0.71069$ Å, $\mu(\mathrm{Mo}K\alpha)=78.0$ cm^{-1}.

The cell dimensions were determined by a least-squares fit using 22 θ values measured accurately on a Philips PW1100 diffractometer. Intensity data with $6°\leq 2\theta \leq 55°$ were collected at room temperature by the use of graphite-monochromated Mo$K\alpha$ radiation. The ω-2θ scan technique was employed. The scan range was $(0.7+0.2\tan\theta)°$, and the scan speed, 1.0°/min; the background was counted for 20 s at each end of the scan. Three standard reflections, 600, $0\bar{4}0$, 003, measured every 240 min, showed no appreciable decay. A total of 2604 intensities with $I_{\mathrm{top}}-2\sqrt{I_{\mathrm{top}}}>I_{\mathrm{back}}$ were classified as observed; I_{top} is the intensity (counts/s) measured at the top of the peak, and I_{back} is the mean background intensity (counts/s) obtained from the preliminary background measurements for 5 s on each side of the peak. Corrections for Lorentz-polarization and absorption effects were made, and the relative structure factors were derived.[6]

Structure Determination

The structure was solved by heavy-atom techniques. Six cycles of block-diagonal least-squares refinement with the isotropic temperature factor for each atom gave an R of 0.069. Nine cycles of the refinement, based on the anisotropic temperature factors for Pt and Sb atoms, resulted in $R=0.050$. The minimized function was $\sum w(F_o-|F_c|)^2$ $(=\sum w\Delta F^2)$. The weighting scheme, $w=(39.16/F_o)^2$ for $F_o>39.16$, $w=1$ for $23.30\leq F_o\leq 39.16$, and $w=0.8$ for $F_o<23.30$, was used to make $w\Delta F_o^2$ approximately constant over the whole range of F_o. The corrections for the anomalous dispersion effect were applied for the Pt and Sb atoms.[7] The

Table 1. Final atomic coordinates and temperature factors, with estimated standard deviations in parentheses

	x	y	z	B(Å^2)
Pt	0.01070(5)	0	0.19076(6)	a)
N(1)	0.0269(16)	−0.0915(10)	0.0369(17)	2.8(2)
N(2)	0.0042(15)	−0.0773(9)	0.3409(16)	2.5(2)
N(3)	0.1746(18)	0.0890(11)	0.3458(19)	3.2(3)
N(4)	0.1963(18)	0.0766(11)	0.0355(19)	3.2(3)
C(1)	−0.0493(20)	−0.1621(13)	0.1155(22)	3.1(3)
C(2)	−0.1143(18)	−0.1258(11)	0.2537(20)	2.5(3)
C(3)	−0.1678(24)	−0.1959(15)	0.3545(26)	3.8(4)
C(4)	0.2883(24)	0.1433(15)	0.2719(26)	3.9(4)
C(5)	0.2317(24)	0.1590(15)	0.1080(26)	3.9(4)
C(6)	0.2410(37)	0.0550(23)	0.4950(39)	6.3(7)
C(7)	0.1111(26)	0.0854(16)	−0.1151(28)	4.2(4)
Sb(1)	0.55343(13)	0.36078(8)	−0.14028(15)	a)
Sb(2)	0.74737(14)	0.11255(9)	0.17924(16)	a)
O(1)	0.4116(14)	0.3521(9)	0.0388(15)	3.3(2)
O(2)	0.6900(12)	0.3538(8)	0.0405(14)	2.7(2)
O(3)	0.4087(15)	0.3560(11)	0.2915(16)	3.8(3)
O(4)	0.9057(15)	0.2097(10)	0.2373(18)	3.7(3)
O(5)	0.6235(13)	0.2050(8)	0.2373(15)	2.8(2)
O(6)	0.9194(17)	0.3402(11)	0.3379(18)	4.1(3)
O(7)	0.5094(13)	0.2395(9)	−0.1648(14)	2.9(2)
O(8)	0.7320(15)	0.3183(9)	−0.2646(16)	3.2(2)
O(9)	0.8176(18)	0.2063(11)	−0.3736(19)	4.3(3)
O(10)	0.5524(16)	0.0639(10)	0.0706(17)	3.8(3)
O(11)	0.7672(15)	0.1430(9)	−0.0327(16)	3.3(2)
O(12)	0.4361(18)	0.0460(11)	−0.1558(19)	4.2(3)
C(8)	0.4711(18)	0.3538(12)	0.1722(20)	2.8(3)
C(9)	0.6335(18)	0.3555(11)	0.1891(19)	2.5(3)
C(10)	0.6864(18)	0.2814(11)	0.2862(19)	2.4(3)
C(11)	0.8495(19)	0.2796(11)	0.2894(20)	2.7(3)
C(12)	0.7271(19)	0.2386(13)	−0.3000(21)	3.0(3)
C(13)	0.6054(20)	0.1869(13)	−0.2467(23)	3.1(3)
C(14)	0.6638(18)	0.1139(12)	−0.1458(19)	2.6(3)
C(15)	0.5394(21)	0.0715(13)	−0.0751(22)	3.2(3)
H_2O(1)	0.1240(26)	−0.4543(17)	0.4581(27)	7.1(5)
H_2O(2)	0.1452(16)	0.4229(10)	0.2471(18)	3.8(3)

a) Anisotropic temperature factors ($\times 10^5$) in the form of $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$ with parameters:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	510(4)	195(2)	700(5)	3(7)	361(8)	−41(8)
Sb(1)	850(12)	234(4)	1136(16)	77(12)	−130(22)	104(13)
Sb(3)	932(14)	279(5)	1351(18)	303(13)	688(26)	365(15)

scattering factors for neutral Pt, Sb, O, N, and C atoms were taken from the International Tables for X-Ray Crystallography.[7] The hydrogen atoms could not be located in a difference Fourier synthesis computed at this stage. The maximum shift of parameters in the final cycle was $<0.1\ \sigma$. The absolute configuration of the complex cation was determined on the basis of the known configurations of the (+)-tartrate ion and (*R*)-propylenediamine molecule. The final atomic coordinates, which give the absolute structure of the crystal, are presented in Table 1, together with their temperature factors. The observed and calculated structure factors are preserved at the Chemical Society of Japan (Document Number 7627). All the calculations were performed on a FACOM 270-30 computer at Osaka City University. The programs used included a local version of the UNICS.[8]

Results and Discussion

The absolute configuration of the complex cation is shown in Fig. 1, while the crystal structure viewed along the b axis is presented in Fig. 2. The Pt atom has a square-planar coordination by 4 N atoms. The O(8)($1-x$, $-1/2+y$, $-z$) occupies the apical position of a square pyramid whose basal plane is defined by Pt, N(1), N(2), N(3), and N(4), the Pt···O(8) distance being 3.31 Å. Both of the asymmetric second-

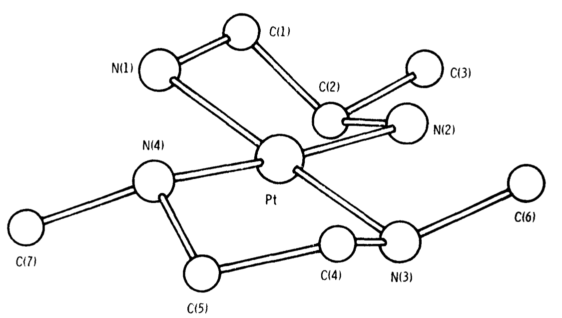

Fig. 1. The absolute configuration of the complex cation in $(+)_{350}$-[Pt(*R*-pn)(Me_2en)][Sb_2(+)-$tart_2$]·$2H_2O$.

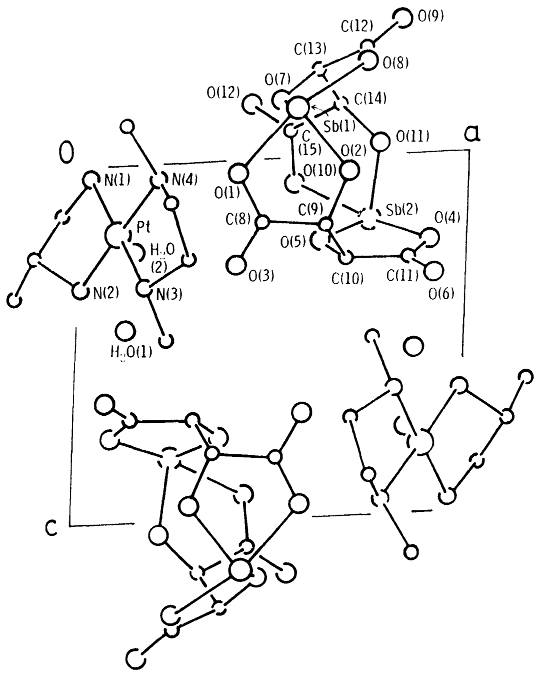

Fig. 2. The crystal structure viewed along the b axis.

ary N atoms of the Me_2en molecule have the *S* absolute configuration, and both the N-CH_3 groups are equatorial with respect to the 5-membered chelate ring (λ conformation) composed of the Me_2en ligand and the Pt atom.

In the solution of [Pt(*R*-pn)(Me_2en)]Cl_2 we prepared, the complex cation can exist in three isomers, (*R*,*R*), (*S*,*S*), and (*R*,*S*), where *R* or *S* denotes the absolute configuration of the asymmetric nitrogen center; the relative amounts of these isomers will be dependent upon the conformational energies of the respective isomers. The [Sb_2(+)-$tart_2$]$^{2-}$ anion chooses the (*S*,*S*) isomer to yield the least soluble diastereoisomer $(+)_{350}$-[Pt(*R*-pn)(Me_2en)][Sb_2(+)-$tart_2$]·$2H_2O$. The *S* isomer was also found in the least soluble diastereoisomer, $(+)_{350}$-[Pt(NH_3)$_2$(Me_3en)][Sb_2(+)-$tart_2$]·H_2O[9] (Me_3en: *N*,*N*,*N'*-trimethylethylenediamine). Thus, the dissymmetric [Sb_2(+)-$tart_2$]$^{2-}$ anion is likely to have a preference for the *S* and/or (*S*,*S*) isomer over the *R* and/or (*R*,*R*) isomer when the planar Pt(II) chelate of *N*-methyl-substituted ethylenediamine is given.

Table 2. Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

Pt-N(1)	2.06(2)	N(1)-Pt-N(2)	81.9(6)
Pt-N(2)	2.06(2)	N(3)-Pt-N(4)	84.2(7)
Pt-N(3)	2.04(2)	Pt-N(1)-C(1)	111(1)
Pt-N(4)	2.07(2)	Pt-N(2)-C(2)	109(1)
		Pt-N(3)-C(4)	108(1)
N(1)-C(1)	1.52(3)	Pt-N(3)-C(6)	116(2)
N(2)-C(2)	1.51(2)	Pt-N(4)-C(7)	114(1)
N(3)-C(4)	1.54(3)	Pt-N(4)-C(5)	109(1)
N(3)-C(6)	1.50(4)	C(4)-N(3)-C(6)	108(2)
N(4)-C(5)	1.48(3)	C(5)-N(4)-C(7)	113(2)
N(4)-C(7)	1.50(3)	N(1)-C(1)-C(2)	109(2)
		N(2)-C(2)-C(1)	106(1)
C(1)-C(2)	1.52(3)	N(2)-C(2)-C(3)	110(2)
C(2)-C(3)	1.53(3)	C(1)-C(2)-C(3)	111(2)
C(4)-C(5)	1.52(3)	N(3)-C(4)-C(5)	106(2)
		N(4)-C(5)-C(4)	109(2)

The bond lengths and angles are given in Table 2. The Pt–N bond lengths are in the range of 2.04—2.07 Å and seem slightly longer than the mean Pt–N bond length of 2.04 Å in [Pt en_2][Mo O(H_2O)(CN)$_4$]·$2H_2O$.[10] The coordination angle in the Pt—Me_2en chelate ring is 84.2°, while that in the Pt—(*R*)-pn chelate ring is 81.9°; the latter is smaller than the values reported in Refs. 9 and 10. The deviations of the atoms from the plane defined by 4 N atoms are as follows: Pt, −0.004; N(1), −0.007; N(2), 0.007; N(3), −0.007; N(4), 0.007; C(1), −0.045; C(2), 0.636; C(3), 0.402; C(4), −0.403; C(5), 0.324; C(6), −0.947; C(7), 0.893 Å. The equation of the plane is $-0.843X+0.512Y-0.168Z=-0.979$, where the coordinates are referred to the orthogonal axes, a, b, and c*. The geometry and dimensions of the [Sb_2(+)-$tart_2$]$^{2-}$ anion agree well with those in K_2[Sb_2(+)-$tart_2$]·$3H_2O$.[11]

The crystal consists of the [Pt(*R*-pn)(Me_2en)]$^{2+}$ cations, [Sb_2(+)-$tart_2$]$^{2-}$ anions, and water molecules. A [Pt(*R*-pn)(Me_2en)]$^{2+}$ cation (*x*, *y*, *z*) is surrounded trigonally by three [Sb_2(+)-$tart_2$]$^{2-}$ anions (*x*, *y*, *z*; 1−*x*, −1/2+*y*, −*z*; −1+*x*, *y*, *z*). The possible

Table 3. Possible hydrogen bonds

Atoms			Interatomic distances		Positions[a] of	
A	— H	··· B	A···B	H[b]···B	A	B
N(1)	H	O(2)	2.93(2)	1.95	1	2
N(1)	H	H_2O(2)	2.88(2)	1.97	1	3
N(2)	H	H_2O(1)	2.94(3)	1.93	1	4
N(4)	H	O(12)	2.95(2)	2.07	1	1
H_2O(1)		O(9)	2.71(3)		1	2
H_2O(1)		H_2O(2)	2.70(3)		1	6
H_2O(2)		O(1)	2.70(2)		1	1

a) The numerals refer to the following equivalent positions: 1 *x*, *y*, *z*; 2 1−*x*, −1/2+*y*, −*z*; 3 −*x*, −1/2+*y*, −*z*; 4 −*x*, 1/2+*y*, 1−*z*; 5 −1+*x*, *y*, *z*; 6 *x*, −1+y, *z*. b) The coordinates of the H atoms were calculated on the assumption that the N-H distance was 1.03Å.

hydrogen bonds are summarized in Table 3. Both primary amino groups take part in the formation of the N–H···O hydrogen bonds, while, with respect to the secondary amino groups, only one of the two participates in the N–H···O hydrogen bond, which is rather weak in view of the H···O distance (2.07 Å).

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