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The Absolute Configuration and Circular Dichroism of the $(-)_{260}$-Diammine((*S*)-1-*N*-methyl-1,2-propanediamine)platinum(II) Ion, $(-)_{260}$-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]^{2+}$

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The optical resolution of $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$ is effected by using silver di-μ-(+)-tartrato(4−)-bis(antimonate(III)) ($Ag_2[Sb_2(+)\text{-tart}_2]$) as the resolving agent. X-Ray structure analysis of the less soluble diastereoisomeric salt, $(+)_{350}$-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})][Sb_2(+)\text{-tart}_2]\cdot H_2O$, revealed that the asymmetric secondary nitrogen is of the *R* configuration. The crystal is orthorhombic, with a $P2_12_12_1$ space group, $a=19.302(7)$ Å, $b=14.791(4)$ Å, $c=7.925(2)$ Å, and $Z=4$. The structure was determined from counter intensity data and refined to *R* 0.049 using the least-squares method for 1955 independent non-zero reflections. The Pt atom has a square-planar coordination with 4 N atoms and both the $N\text{–}CH_3$ and $C\text{–}CH_3$ groups are equatorial with respect to the chelate ring. The circular dichroism spectrum of *R*-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})](ClO_4)_2$, which was obtained from the less soluble di-μ-(+)-tartrato(4−)-bis(antimonate(III)) salt, is presented and discussed on the basis of the distribution of the possible conformers, the relative abundances of which were infered from ^{13}C NMR data.

Since Ito *et al.* studied the circular dichroism (CD) of a number of Pt(II) and Pd(II) complexes,[1] few studies have been made on this subject. Recently, Bosnich and Sullivan have reported the CD and stereochemistries of several Pt(II) chelates of *N*-substituted diamines,[2] and the absolute configuration of $(-)_{280}$-dichloro-((*S*)-1-*N*-methyl-1,2-propanediamine)platinum(II) has been determined by Ball *et al.*[3] Yokoho *et al.* and Matsumoto *et al.* attempted the resolution of dissymmetric Pt(II) complexes into enantiomeric forms in order to work out the CD-structure relationship for these complexes.[4,5] In the course of the present study, the optical resolution of the *N*-racemic $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$ was successful with the final result being the isolation of the $(-)_{260}$-enantiomer in perchlorate form. This paper deals with the absolute configuration and the CD spectrum of the title complex.

Experimental

Preparations of Compounds. (*S*)-1-*N*-methyl-1,2-propanediamine (N^1-Me-(*S*)-pn) was prepared following the method of Saburi *et al.*[6] $[Pt(NH_3)_2(\text{rac-pn})](ClO_4)_2$ and $[Pt(NH_3)_2(\text{rac-chxn})]Cl_2$ were obtained using similar methods to those described in Ref. 1 (pn=1,2-propanediamine; chxn=1,2-cyclohexanediamine).

$(-)_{260}$-$[Pt(NH_3)_2(Meen)](ClO_4)_2$ (Meen=*N*-methylethylenediamine): $(-)_{260}$-$[Pt(NH_3)_2(Meen)]Cl_2$ was obtained following the method of Goddard and Basolo.[7] This chloride was then converted to a perchlorate using $AgClO_4$ in a perchloric acid solution. The resulting perchlorate was washed with methanol and recrystallized from acetone–ethanol acidified slightly with perchloric acid.

Found: C, 7.20; H, 3.14; N, 11.07%. Calcd for $[Pt(NH_3)_2(CH_3NH(CH_2)_2NH_2)](ClO_4)_2$: C, 7.18; H, 3.21; N, 11.16%.

$(+)_{350}$-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})][Sb_2(+)\text{-tart}_2]\cdot H_2O$ ($[Sb_2(+)\text{-tart}_2]^{2-}$=di-μ-(+)-tartrato(4−)-bis(antimonate(III))ion): $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$ was prepared using a method similar to that reported by Bosnich and Sullivan.[2] A solution of $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$ (1.15 g in 20 ml of water) was added dropwise to the solution of $Ag_2[Sb_2(+)\text{-tart}_2]$ (2.12 g in 500 ml of water) and the mixture was stirred at 60 °C for 2 h in the dark. AgCl was then filtered off and the filtrate was rotary evaporated to *ca.* 50 ml. Colorless crystals were separated out and they were then recrystallized from hot water containing a drop of perchloric acid.

Found: C, 16.50; H, 2.84; N, 6.29%. Calcd for $[Pt(NH_3)_2(CH_3NHCH_2CH(CH_3)NH_2)][Sb_2(C_4H_2O_6)_2]H_2O$: C, 16.54; H, 2.76; N, 6.43%.

$(-)_{260}$-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})](ClO_4)_2$: Conversion of the preceding salt to the perchlorate was carefully carried out in acidic media, since the rate of racemization of the assymmetric secondary nitrogen is known to be very slow at low pH values.[8] The di-μ-(+)-tartrato(4−)-bis(antimonate(III)) salt (0.40 g) was dissolved in 100 ml of water acidified with a drop of perchloric acid. This solution was passed through an anion-exchange column in the perchlorate form (Dowex 1-X8, 50—100 mesh) at a speed of one drop every 5 s. The effluent was rotary evaporated to near dryness. The residue was dissolved in a minimum amount of acetone and then *ca.* 15 ml of 1-propanol was added. Colorless plate-like crystals were obtained and these were recrystallized three times from acetone acidified slightly with perchloric acid.

Found: C, 9.53; H, 3.52; N, 10.92%. Calcd for $[Pt(NH_3)_2(CH_3NHCH_2CH(CH_3)NH_2)](ClO_4)_2$: C, 9.30; H, 3.49; N, 10.85%.

Spectral Measurements. The FT ^{13}C NMR spectra were recorded at 15.04 MHz with broad-band proton decoupling on a JEOL JNM-FX60 Spectrometer, dioxane being used as an internal reference (the values of chemical shifts given in the text have been converted to the TMS scale). The signal from the solvent, D_2O, was used as an internal lock. Usually, 4096 data points were taken over a 1-kHz spectral width. Electronic spectra were obtained with a Hitachi EPS-3T Recording Spectrometer. A JASCO J-20 Automatic Recording Spectrometer was employed for the CD spectra. All measurements were performed at room temperature. In the case of $(-)_{260}$-$[Pt(NH_3)_2(N\text{-}^1\text{Me-}(S)\text{-pn})](ClO_4)_2$, the solutions were acidified slightly with DCl (NMR) or with $HClO_4$ (CD) in order to prevent the active complex ion from racemizing.

X-Ray Data Measurement. The crystallographic data for $(+)_{350}$-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})][Sb_2(+)\text{-tart}_2]\cdot H_2O$ are as follows: $M=870.6$, orthorhombic, space group $P2_12_12_1$, $a=19.302(7)$ Å, $b=14.791(4)$ Å, $c=7.925(2)$ Å, $Z=4$, $D_m=2.55\ \text{g cm}^{-3}$, $D_c=2.56\ \text{g cm}^{-3}$, $\mu(\text{Mo}K\alpha)=87.6\ \text{cm}^{-1}$. The space group was determined from oscillation and Weissenberg photographs. The unit cell dimensions were obtained by a least-squares analysis of 29 θ values measured on a Phillips diffractometer using Mo*Kα* radiation.

The intensities were measured using the ω-2θ scan method on a Phillips PW1100 four-circle diffractometer employing a graphite monochromator and Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) with a crystal of dimensions $0.14\times0.16\times0.18$ mm^3. A scan speed of 0.017° s^{-1}, a scan width of $(0.8+0.2\tan\theta)°$, and two 20 s background counts were employed. Three standard reflections (800, 060, 004) monitored every 4 h throughout the period of data collection, showed no significant intensity variations. A total of 1955 intensity peaks with $I_t-2\sqrt{I_t}>I_b$ were measured in the $6°\leq2\theta\leq55°$ range (I_t is the intensity (counts/s) measured at the top of the peak, and I_b is the mean background intensity (counts/s) obtained from preliminary background measurements for 5 s on each side of the peak). A spherical absorption correction ($r=0.08$ mm) was applied.

Structure Determination and Refinement. The crystal structure was solved by the heavy-atom technique, and the positional and thermal parameters were refined by the least-squares method, the function minimized being $\sum w\Delta F^2$. In the final stage of refinement, the weighting scheme, $w=0.8$ for $F_o<32.3$, $w=1$ for $32.3\leq F_o\leq161.3$, and $w=(161.3/F_o)^2$ for $F_o>161.3$, was used to render $\sum w\Delta F^2$ approximately constant over the entire ranges of F_o and $(\sin\theta/\lambda)$. All parameter shifts in the final cycle refinement were $<0.2\sigma$. The final R value was 0.049. The atomic scattering factors for neutral Pt, Sb, O, N, and C were taken from Ref. 9. The real and imaginary parts of the anomalous dispersion corrections were applied for Pt and Sb atoms.

The atomic coordinates given in Table 1 correspond to the absolute crystal structure which was determined on the basis of the known configuration of the $[\mathrm{Sb_2}(+)\text{-tart}_2]^{2-}$ ion. The observed and calculated structure factors are available at the Chemical Society of Japan (Document No. 7713). The computer programs used are as follows: RSSFR-4, HBLS-4, and DAPH, all of which were adapted to the FACOM 270-30 computer of Osaka City University.

Results and Discussion

X-Ray Structure. The absolute configuration of $(-)_{260}$-$[\mathrm{Pt(NH_3)_2}(N^1\text{-Me-}(S)\text{-pn})]^{2+}$ is shown in Fig. 1. The bond lengths and angles are given in Table 2 along with selected interatomic distances. The Pt atom has a square-planar coordination of four nitrogen atoms. The secondary nitrogen atom has R absolute configuration and the N–$\mathrm{CH_3}$ group is equatorial. The C–$\mathrm{CH_3}$ group is also disposed equatorially, imposing a δ conformation on the chelate ring. The Pt–N bond lengths range from 2.03 to 2.07 Å with an average value of 2.05 Å, wheras the N–Pt–N bond angle in the chelate ring is 84.1°. These values are comparable to those found in $(+)_{350}$-$[\mathrm{Pt(NH_3)_2(Me_3en)}][\mathrm{Sb_2}(+)\text{-tart}_2]\cdot\mathrm{H_2O}$ (2.07 Å, 84.4°),[4] $(+)_{350}$-$[\mathrm{Pt}(R\text{-pn})(\mathrm{Me_2en})][\mathrm{Sb_2}(+)\text{-tart}_2]\cdot2\mathrm{H_2O}$ (2.06 Å, 84.2°),[5] and $[\mathrm{Pt(en)_2}][(+)$-

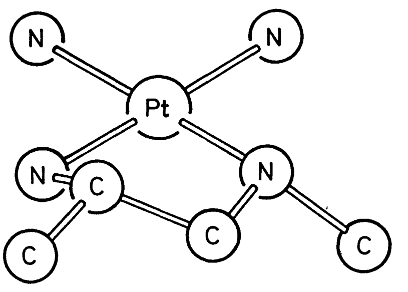

Fig. 1. The absolute configuration of $(-)_{260}$-$[\mathrm{Pt(NH_3)_2}$-$(N^1\text{-Me-}(S)\text{-pn})]^{2+}$.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS WITH THEIR e. s. d. VALUES IN PARENTHESIS

	x	y	z	B/Å^2		x	y	z	B/Å^2
Pt	0.21359(4)	0.19812(5)	0.23194(10)	a)	C(10)	0.430(1)	0.227(2)	−0.027(3)	2.4(4)
N(1)	0.197(1)	0.263(1)	0.009(2)	2.3(3)	C(11)	0.427(1)	0.180(1)	−0.198(3)	2.4(4)
N(2)	0.182(1)	0.318(1)	0.337(2)	2.3(3)	C(12)	0.353(1)	0.148(1)	−0.227(3)	2.7(4)
N(3)	0.251(1)	0.086(1)	0.111(2)	2.3(3)	O(1)	0.536(1)	−0.059(1)	−0.133(2)	3.5(3)
N(4)	0.231(1)	0.131(1)	0.457(2)	2.3(3)	O(2)	0.577(1)	−0.132(1)	0.095(2)	3.6(4)
C(1)	0.179(2)	0.423(2)	−0.103(4)	4.8(6)	O(3)	0.408(1)	−0.050(1)	−0.019(2)	2.6(3)
C(2)	0.203(1)	0.366(2)	0.044(3)	2.8(4)	O(4)	0.494(1)	0.040(1)	0.253(3)	2.7(3)
C(3)	0.160(1)	0.382(2)	0.205(3)	3.4(5)	O(5)	0.367(1)	0.055(1)	0.353(2)	3.0(3)
C(4)	0.123(1)	0.311(2)	0.465(4)	4.0(5)	O(6)	0.342(1)	−0.088(1)	0.320(2)	3.4(3)
Sb(1)	0.44149(8)	−0.01609(10)	−0.24774(20)	a)	O(7)	0.529(1)	0.214(1)	0.159(2)	3.3(3)
Sb(2)	0.45037(9)	0.15363(12)	0.30975(20)	a)	O(8)	0.544(1)	0.284(1)	−0.091(3)	4.1(4)
C(5)	0.528(1)	−0.094(2)	0.016(3)	2.7(4)	O(9)	0.398(1)	0.174(1)	0.098(2)	2.7(3)
C(6)	0.455(1)	−0.092(2)	0.089(3)	2.4(4)	O(10)	0.474(1)	0.108(1)	−0.203(2)	2.9(3)
C(7)	0.458(1)	−0.043(1)	0.264(3)	2.6(4)	O(11)	0.345(1)	0.062(1)	−0.241(2)	2.6(3)
C(8)	0.383(1)	−0.023(2)	0.317(3)	2.7(4)	O(12)	0.306(1)	0.203(1)	−0.237(2)	2.7(3)
C(9)	0.508(1)	0.244(2)	0.012(4)	3.1(4)	O$_w$(13)	0.297(1)	0.356(1)	0.553(2)	3.8(4)

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	80(1)	268(3)	755(9)	12(5)	23(9)	−56(13)
Sb(1)	192(4)	328(6)	842(21)	26(8)	34(19)	−120(26)
Sb(2)	195(4)	436(8)	1031(25)	108(11)	−252(17)	−345(25)

TABLE 2. INTERATOMIC DISTANCES (l/Å) AND BOND ANGLES (ϕ/°)

Pt-N(1)	2.03(2)	N(1)-Pt-N(2)	84.1(8)
Pt-N(2)	2.05(2)	N(1)-Pt-N(3)	91.7(8)
Pt-N(3)	2.04(2)	N(2)-Pt-N(4)	96.4(7)
Pt-N(4)	2.07(2)	N(3)-Pt-N(4)	87.7(8)
N(1)-C(2)	1.56(3)	Pt-N(1)-C(2)	107(1)
N(2)-C(3)	1.47(3)	Pt-N(2)-C(3)	111(1)
N(2)-C(4)	1.54(4)	Pt-N(2)-C(4)	115(2)
C(1)-C(2)	1.52(4)	C(3)-N(2)-C(4)	107(2)
C(2)-C(3)	1.55(4)	N(1)-C(2)-C(1)	113(2)
		N(1)-C(2)-C(3)	105(2)
		C(1)-C(2)-C(3)	112(2)
		N(2)-C(3)-C(2)	109(2)

Interatomic distances (l/Å) concerning possible hydrogen bonds

Atom		l/Å of	Position[a)] of	
A	B	A···B	A	B
N(2)	O_w(13)	2.85(3)	1	1
O_w(13)	O(2)	2.71(3)	1	2
O_w(13)	O(12)	2.81(3)	1	3

a) The numbers refer to the following equivalent positions: 1; x, y, z, 2; $1-x$, $(1/2)+y$, $(1/2)-z$, 3; x, y, $1+z$.

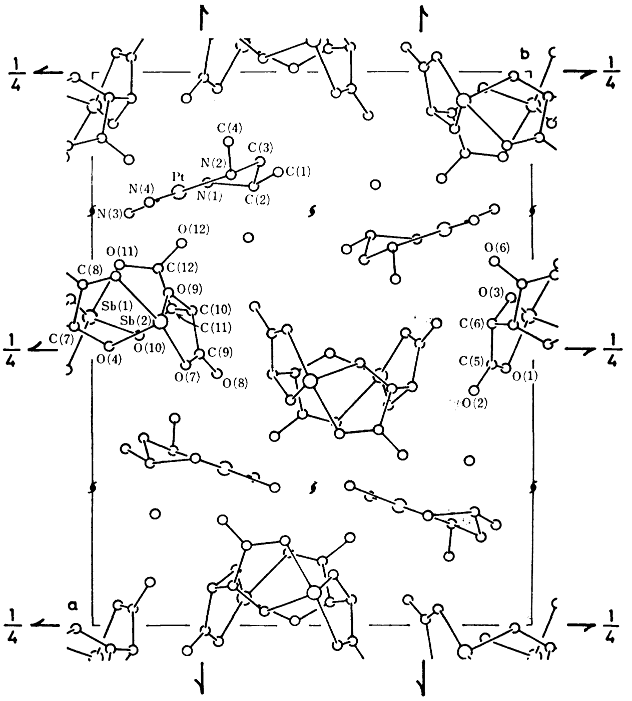

Fig. 2. The crystal structure of $(+)_{350}$-$[Pt(NH_3)_2(N^1$-Me-(S)-pn)]·$[Sb_2(+)$-tart$_2]$·H_2O viewed down the c axis. The atoms denoted as O(1), O(2), O(3), O(6), C(5), and C(6) are related with the corresponding ones in Table 1 by a unit translation in y.

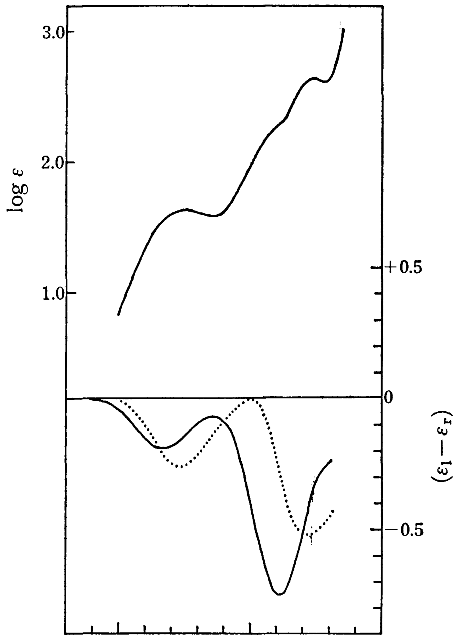

Fig. 3. The absorption (top) and CD (bottom) spectra of $(-)_{260}$-$[Pt(NH_3)_2(N^1$-Me-(S)-pn)]$(ClO_4)_2$: ——, and the CD spectrum of rac-$[Pt(NH_3)_2(N^1$-Me-(S)-pn)]Cl_2: ······.

tart] (2.043 Å, 83.2°),[10)] but the Pt–N bond length appears to be slightly longer than that in $(-)_{280}$-[Pt-$Cl_2(N^1$-Me-(S)-pn)] (2.021 Å, 83.1°).[3)] The torsional angle in the N(1)–C(2)–C(3)–N(2) fragment is 52°. The equation for the plane defined by the four nitrogen atoms is

$$-0.936X-0.350Y-0.020Z=-4.961,$$

and the deviations of the atoms from this plane are as follows: 0.04 for Pt, 0.04 for N(1), −0.04 for N(2), −0.04 for N(3), 0.04 for N(4), −0.45 for C(1), −0.62 for C(2), 0.05 for C(3), and 1.06 Å for C(4). (The X, Y, and Z coordinates in Å refer to the crystallographic axes.)

Every complex cation is surrounded tetrahedrally by four $[Sb_2(+)$-tart$_2]^{2-}$ anions at (x,y,z), $((1/2)-x, -y, (1/2)+z)$, $(-(1/2)+x, (1/2)-y, -z)$, and $(1-x, (1/2)+y, (1/2)-z)$. The $[Sb_2(+)$-tart$_2]^{2-}$ anion selects the N(S) and N(S), N′(S)-C(R) isomers yielding the least soluble diasteroisomeric salts $(+)_{350}$-$[Pt(NH_3)_2(Me_3$-en)]$[Sb_2(+)$-tart$_2]$·H_2O[4)] and $(+)_{350}$-[Pt(R-pn)(Me_2-en)]$[Sb_2(+)$-tart$_2]$·$2H_2O$,[5)] respectively. In the present case, however, the N(R)–C(S) isomer is preferred by the same anion as the counter ion for the less soluble diastereoisomeric salt, $(+)_{350}$-$[Pt(NH_3)_2(N^1$-Me-(S)-pn)]$[Sb_2(+)$-tart$_2]$·H_2O. The geometry and dimensions of the $[Sb_2(+)$-tart$_2]^{2-}$ anion agree well with those for $K_2[Sb_2(+)$-tart$_2]$·$3H_2O$.[11)]

CD Spectrum. The absorption and CD spectra of R-$[Pt(NH_3)_2(N^1$-Me-(S)-pn)]$(ClO_4)_2$ are shown in Fig. 3, in which the CD spectrum of the racemic compound is also given. The N(R) isomer is stable with respect to racemization in a 0.01 M perchloric acid solution; actually no appreciable change in the CD curve was observed over a period of 24 h. The electronic spectrum of this complex bears a close resemblance to that of $[Pt(R$-pn$)_2]Cl_2$, and accordingly, the peak at 35000 cm^{-1}, on the basis of D_{4h} symmetry, can be assigned to ${}^1A_{1g}\rightarrow{}^3A_{2g}$, ${}^3E_g$ and those at 41500 (shoulder) and 44500 cm^{-1} to ${}^1A_{2g}$ and ${}^1E_g$ transitions.[1] The CD spectra are different from each other, showing marked influence of the vicinal effect of the asymmetric nitrogen.

The optical activity due to the chelate ring of N^1-Me-(S)-pn may arise from (i) the vicinal effect of the chiral secondary nitrogen, (ii) the conformational effect of the chelate ring, and (iii) the vicinal effect of the asymmetric carbon. Bosnich and Sullivan have shown that the first and the resultant of the remaining two effects are additive in the rotational strength for R- and/or S-$[PtCl_2(N^1\text{-Me-}(S)\text{-pn})]$.[2] Such additivity can be anticipated to be valid in the CD of the R-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]^{2+}$ considered here. The CD curve of the racemic N^1-Me-(S)-pn complex was subtracted from that of the N(R) isomer. The resulting curve (the dotted line in Fig. 4) should be regarded as representing the CD due to the vicinal effect of the R asymmetric nitrogen. It is noteworthy that this curve agrees well with the CD of $(-)_{260}$-$[Pt(NH_3)_2(Meen)](ClO_4)_2$ (Fig. 4). The CD band at 31000 cm^{-1} may be assigned to the ${}^3A_{2g}$ transition.[1]

According to the ${}^{13}C$ NMR studies of Bagger[12] and Erickson *et al.*,[13] rapid ring inversion ($\delta\leftrightarrow\lambda$) occurs in the 5-membered chelate ring composed of the Pt(II) and N-substituted 1,2-diaminopropane. The present ${}^{13}C$ NMR data for C-methyl carbons in some relevant complexes are given in Table 3. The β-carbon resonances in $[Pt(NH_3)_2(rac\text{-chxn})]Cl_2$ and the C-methyl carbon resonances in $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]X_2$ and $[Pt(NH_3)_2(rac\text{-pn})]Cl_2$ were readily identified by comparison with the corresponding resonances in complexes of the $[Pt(bipy)(diamine)]Cl_2$ type.[13] Each of these signals is accompanied by two ${}^{195}Pt$ satellites. The ${}^3J_{Pt-C}$ value obtained from the spacing of the satellites is the weighted average of the coupling constants of the conformer with the equatorial C–CH_3 group and that with the axial group; ring inversion changes the equatorial C–CH_3 into an axial one or *vise versa*. Following Erickson *et al.*, the coupling constants ${}^3J_{Pt-C}$ of 0 and 50 Hz were assigned to the axial and equatorial conformers, respectively.[13] The mol fractions of the equatorial conformer calculated from the observed ${}^3J_{Pt-C}$ values are listed in the last column of Table 3.

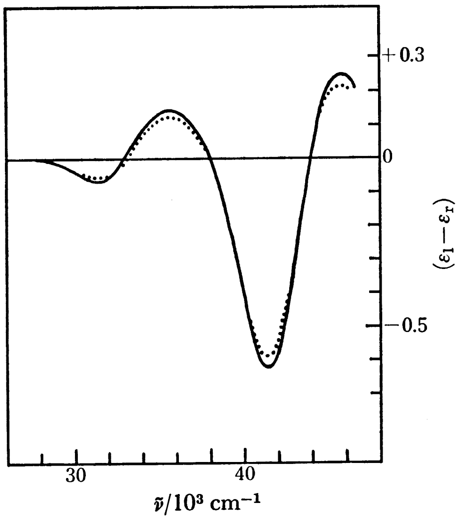

Fig. 4. The calculated curve of [Δε(R-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})](ClO_4)_2$) − Δε-($rac$$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$)]: ······, and the CD spectrum of $(-)_{260}$-$[Pt(NH_3)_2(Me\text{-en})](ClO_4)_2$: ——.

The four possible conformers (I—IV) in $[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]^{2+}$ are illustrated in Fig. 5. The resonances at 16.3 and 16.7 ppm in the racemic N^1-Me-(S)-pn complex are attributable to the N(R) and the N(S) isomer, respectively. The relative abundances of the equatorial and axial C–CH_3 conformers for each of the N(R) and N(S) isomers indicate that the equatorial conformer is more stable than the axial. The I : II abundance ratio (86 : 14) is greater than that of III : IV (70 : 30), which reflects a greater conformational energy difference between I and II than between III and IV.

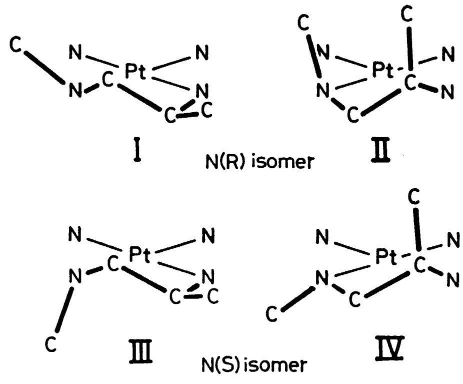

Fig. 5. The four possible conformers in R- and S-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]^{2+}$.

TABLE 3. ${}^{13}C$ CHEMICAL SHIFTS AND COUPLING CONSTANTS (${}^3J_{Pt-C}$) OF C-METHYL CARBONS

	${}^{13}C$ chemical shift (δ/ppm)	${}^3J_{Pt-C}$ (J/Hz)	n_{eq}[a]
R-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})](ClO_4)_2$	16.3	43	0.86
rac-$[Pt(NH_3)_2(N^1\text{-Me-}(S)\text{-pn})]Cl_2$	16.3 16.7	43 35	0.86 0.70
$[Pt(NH_3)_2(rac\text{-pn})](ClO_4)_2$	16.8	38	0.76[b]
$[Pt(NH_3)_2(rac\text{-chxn})]Cl_2$	33.3	52[d]	1
$[Pt(NH_3)_2(R,R\text{-bn})]Cl_2$[c]		50[d]	1

a) The mol fraction of the equatorial C–CH_3 conformer. b) Making use of the CD data presented in Ref. 1, Hawkins predicted that the ratio of n_{eq} to n_{ax} is of the order of 3 : 1 (Ref. 14, p. 204). c) Ref. 12; R,R-bn: (2R,3R)-2,3-butanediamine. d) These were utilized to check the appropriateness of the ${}^3J_{Pt-C}$ values assigned to the equatorial C–CH_3 conformer.

The chelate ring of the pn or its derivative has been thought to preferentially assume the conformation with equatorial C–CH$_3$ even for the planar complex.[14] However, in case there is a significant amount of axial conformers in the system, the CD of the Pt(II) chelate of the pn or its analogue must be reconsidered with the relative populations of the δ and λ conformers being taken into account.

As described above, the additivity found by Bosnich and Sullivan for the CD of R- and S-[PtCl$_2$(N^1-Me-(S)-pn)] is probably applicable to the case of R-[Pt(NH$_3$)$_2$(N^1-Me-(S)-pn)]$^{2+}$. Thus, the CD curves for the conformers I and II can be represented by $x\Delta\varepsilon[\mathrm{V_N}(R)]+x\Delta\varepsilon[\mathrm{eq}]$ and $(1-x)\Delta\varepsilon[\mathrm{V_N}(R)]+(1-x)\Delta\varepsilon[\mathrm{ax}]$ respectively, where $\Delta\varepsilon[\mathrm{V_N}(R)]$ is the CD arising from the vicinal effect of N(R)–CH$_3$, $\Delta\varepsilon[\mathrm{eq}]$ and $\Delta\varepsilon[\mathrm{ax}]$ denote, respectively, the CD due to the (S)-pn ring with equatorial C–CH$_3$ and that with axial C–CH$_3$, and x is the mol fraction of conformer I. A calculation gives $(1/2)(x+y)\Delta\varepsilon[\mathrm{eq}]+[1-(1/2)(x+y)]\Delta\varepsilon[\mathrm{ax}]$ for the CD of the racemic compound and $\Delta\varepsilon[\mathrm{V_N}(R)]+(1/2)(x-y)\cdot(\Delta\varepsilon[\mathrm{eq}]-\Delta\varepsilon[\mathrm{ax}])$ for that of the calculated curve in Fig. 4 (y=the mol fraction of conformer III). The chelate ring of the (S)-pn has two asymmetry factors: the chirality of the chelate ring conformation and the asymmetric carbon atom. For the Co(III) complex in which one bidentate ligand has two asymmetric centers, it has been demonstrated that the two centers act additively for the CD of the complex.[15] Although the situation is somewhat different, the conformational and vicinal effects are expected to be nearly additive for the rotational strength induced by the (S)-pn ring. Then $\Delta\varepsilon[\mathrm{eq}]$ and $\Delta\varepsilon[\mathrm{ax}]$ may be written as $\Delta\varepsilon[\mathrm{eq}]\simeq\Delta\varepsilon[\delta]+\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{eq}}]$ and $\Delta\varepsilon[\mathrm{ax}]\simeq\Delta\varepsilon[\lambda]+\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]$, where $\Delta\varepsilon[\delta(\text{or }\lambda)]$ is the CD due to the conformational effect of the δ(or λ) chelate ring and $\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{eq}}]$ or $\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]$ is the CD ascribed to the vicinal effect of the equatorial or axial C(S)–CH$_3$.[16] However, $\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{eq}}]$ is known to be small[17] and hence, $\Delta\varepsilon[\mathrm{eq}]\simeq\Delta\varepsilon[\delta]$. Thus, the calculated curve can be approximated by

$$\Delta\varepsilon[\mathrm{V_N}(R)]+(x-y)\Delta\varepsilon[\delta]-(1/2)(x-y)\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}].$$

Since x=0.86 and y=0.70 (Table 3), this formula becomes

$$\Delta\varepsilon[\mathrm{V_N}(R)]+0.16\Delta\varepsilon[\delta]-0.08\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}].$$

The CD of [Pt(NH$_3$)$_2$(S,S-chxn)]Cl$_2$ shows two negative bands with intensities $\Delta\varepsilon(^3\mathrm{E_g})=-0.40$ (35000 cm^{-1}) and $\Delta\varepsilon(^1\mathrm{E_g})=-0.86$ (45000 cm^{-1}), and that of [Pt(NH$_3$)$_2$(S-pn)]Cl$_2$ has two minima with $\Delta\varepsilon(^3\mathrm{E_g})=-0.22$ (35200 cm^{-1}) and $\Delta\varepsilon(^1\mathrm{E_g})=-0.51$ (44800 cm^{-1}).[1,18] The CD curve of the former compound can be considered to display an approximate δ conformational effect, $\Delta\varepsilon[\delta](\simeq\Delta\varepsilon[\delta]+2\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{eq}})])$, whereas that of the latter compound may be approximated by $(2x-1)\Delta\varepsilon[\delta]+(1-x)\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]$ which becomes $0.52\Delta\varepsilon[\delta]+0.24\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]$ upon the substitution of 0.76 for x (Table 3; x=the mol fraction of the equatorial conformer). If the $\Delta\varepsilon$ value of the latter CD curve is divided by 0.52, we obtain $\Delta\varepsilon[\delta]+0.46\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]$, which gives a curve with two extrema of $\Delta\varepsilon(^3\mathrm{E_g})=-0.42$ (35200 cm^{-1}) and $\Delta\varepsilon(^1\mathrm{E_g})=-0.98$ (44800 cm^{-1}). These $\Delta\varepsilon$ value are in agreement with the corresponding ones for the S,S-chxn complex. This indicates that the vicinal effect is small compared with the conformational effect: $0.46|\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]|\simeq(1/2)|\Delta\varepsilon[\mathrm{V_C}(S)_{\mathrm{ax}}]|\ll|\Delta\varepsilon[\delta]|$. Therefore, the calculated curve can be taken as representing

$$\Delta\varepsilon[\mathrm{V_N}(R)]+0.16\Delta\varepsilon[\delta].$$

The secondary nitrogen in $(-)_{260}$-[Pt(NH$_3$)$_2$(Me-en)]$^{2+}$ is sure to be of R configuration from a comparison of the Cotton effect for this complex with that for $(+)_{260}$-[Pt(NH$_3$)$_2$(Me$_3$en)]SbCl$_5$, the absolute configuration of which was determined by the X-ray method[19] (Me$_3$en= N,N,N'-trimethylethylenediamine). The N–CH$_3$ group in the R-Meen complex is considered to favor the equatorial disposition in view of the steric interaction with solvent molecules (and/or with some anions in the solution) which may be located at the axial positions of the complex cation. This disposition of the N–CH$_3$ imposes a δ conformation on the chelate ring in contrast to the λ conformation induced by the axial N–CH$_3$. Accordingly, the CD curve of the R-Meen complex is presumably represented by the formula

$$\Delta\varepsilon[\mathrm{V_N}(R)]+z\Delta\varepsilon[\delta]$$

(z=the difference between the mol fraction for the equatorial N–CH$_3$ conformer and that of the axial conformer, which is greater than zero in this case). Although the good agreement between the calculated curve and the CD spectrum of the R-Meen complex is accidental, this agreement supports the fact that the δ conformational effect is partly responsible for the calculated curve,[20] and moreover, this curve receives little contribution from the vicinal effect of the asymmetric carbon.

As mentioned above, $\Delta\varepsilon[\delta]$ may be very similar to the CD of [Pt(NH$_3$)$_2$(S,S-chxn)]$^{2+}$ and, hence, may have relatively intense $^3\mathrm{E_g}$ and $^1\mathrm{E_g}$ CD bands. If the curves shown in Fig. 4 are corrected for the δ conformational contribution, the intensities of the $^3\mathrm{E_g}$ and $^1\mathrm{E_g}$ components due to the N(R) vicinal effect will have some, not insignificant enhancement. However, the signs of the Cotton effects are taken to be those characteristic of the N(R)–CH$_3$ group.

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References

1) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967).

2) B. Bosnich and E. A. Sullivan, *Inorg. Chem.*, **14**, 2768 (1975).

3) R. G. Ball, N. J. Bowman, and N. C. Payne, *Inorg. Chem.*, **15**, 1704 (1976).

4) K. Yokoho, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **49**, 1864 (1976).

5) K. Matsumoto, S. Ooi, M. Sakuma, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **49**, 2129 (1976).

6) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).

7) J. B. Goddard and F. Basolo, *Inorg. Chem.*, **8**, 2223 (1969).

8) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **90**, 2293 (1968).

9) "International Tables for X-Ray Crystallography," Vol. 3 Kynoch Press, Birmingham (1962), pp. 202, 215.

10) W. A. Freeman, *Inorg. Chem.*, **9**, 2235 (1976).

11) M. E. Gress and R. A. Jacobson, *Inorg. Chim. Acta*, **8**, 209 (1974).

12) S. Bagger, *Acta Chem. Scand.*, **A28**, 467 (1974).

13) L. E. Erickson, J. E. Sarneski, and C. N. Reilley, *Inorg. Chem.*, **14**, 3007 (1975).

14) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience (1971), Chap. 6.

15) N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, *Chem. Lett.*, **1972**, 543.

16) No differentiation was made here between $\Delta\varepsilon[V_N(R)_{eq}]$ and $\Delta\varepsilon[V_N(R)_{ax}]$, and it was assumed that $\Delta\varepsilon[V_N(R)_{eq}] = \Delta\varepsilon[V_N(R)_{ax}] = \Delta\varepsilon[V_N(R)]$, since the positional change of the N–CH_3 group on the equatorial↔axial interconversion is small compared with the case of the C–CH_3 group.

17) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972); Ref. 14, p. 202; Ref. 6.

18) The CD data for $[Pt(NH_3)_2(R\text{-pn})]Cl_2$ and $[Pt(NH_3)_2(R,R\text{-chxn})]Cl_2$ are given in Ref. 1. In the text, however, the inverted CD's of these compounds were used as those of the *S*- and *S*,*S*-analogues.

19) K. Yokoho, K. Matsumoto, S. Ooi, and H. Kuroya, Proceedings of the 25th symposium of coordination chemistry (1975), p. 73.

20) In Ref. 2, it was concluded that the N–CH_3 in *R*-$[Pt(NH_3)_2(Meen)]^{2+}$ is predominantly in the equatorial disposition. However, the fair agreement between the two curves in Fig. 4 suggests that $z \simeq 0.16$ and that the abundance ratio of the equatorial N–CH_3 conformer to the axial conformer is about 58 : 42.