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The X-Ray Structure of Bis((*S*,*S*)-2,4-pentanediamine)platinum(II) Ion, $[Pt(SS\text{-}ptn)_2]^{2+}$

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The bis((*S*,*S*)-2,4-pentanediamine)platinum(II) chloride monohydrate crystallizes in the space group $P2_12_12_1$ with four formula units in a unit cell of dimensions $a=12.089(3)$, $b=13.547(3)$, $c=10.697(2)$ Å. The crystal structure has been determined from diffractometer data and refined to R=0.052 for 1903 independent reflections. The Pt atom has a square planar coordination by four N atoms, the average value of the Pt–N distance being 2.05 Å. The complex has a pseudo two-fold axis which is perpendicular to the coordination plane defined by the four N atoms. The 6-membered chelate ring is of a chair conformation and one methyl group is axial with respect to the chelate ring, while the other is equatorial. From a comparison of the circular dichroism spectra of the diammine-(*S*,*S*)-2,4-pentanediamineplatinum(II) and the bis((*S*,*S*)-2,4-pentanediamine)platinum(II) ions, the effect of the (*S*,*S*)-2,4-pentanediamine on the rotatory strength of the Pt(II) complex has been found to be not additive.

The (*S*,*S*)-2,4-pentanediamine (*SS*-ptn) can coordinate to a metal ion yielding the 6-membered chelate ring with a skew or chair conformation, and it has been utilized in the studies of circular dichroism (CD) exhibited by the Co(III) complexes with 6-membered rings. In the crystal structure analyses made for some octahedral Co(III) chelates, the *RR*-ptn ring has been found usually to be of the λ skew conformation,[1] although a recent CD study for $[Co(NH_3)_{2n}(RR\text{-}ptn)_{3-n}]^{3+}$ (n=0, 1, or 2) gave evidence for interconversion between the λ skew and the chair conformations in solution.[2] Appleton and Hall concluded, on the basis of the PMR study on Pt(II) chelates, that the *SS*-(or *RR*-)ptn ring in the planar complexes preferentially assumes the chair conformation.[3] The present work is an attempt to confirm their view and to study the structural parameters of the *SS*-ptn ring.

Experimental

Preparations of Complexes. *SS*-ptn·2HCl was purchased from Tokyo Kasei Co., Ltd. and used for the preparation of the complexes without further purification. $PtCl_2$(*SS*-ptn) was prepared by the method of Appleton and Hall[4] using the *SS*-ptn instead of *rac*-ptn.

$[Pt(NH_3)_2$(SS-ptn)$]Cl_2$: The $PtCl_2$(*SS*-ptn) was suspended in water and concentrated aqueous ammonia added to the suspension at 80 °C until the dichloro complex was completely dissolved. The resulting solution was rotary evaporated. The colorless crystals were obtained by recrystallization from water-1-propanol.

Found: C, 14.75; H, 5.12; N, 13.84%. Calcd for $[Pt(NH_3)_2(C_5H_{14}N_2)]Cl_2$: C, 14.92; H, 4.97; N, 13.93%.

$[Pt$(SS-ptn)$_2]Cl_2\cdot H_2O$: $K_2[PtCl_4]$ (1.27 g) and *SS*-ptn·2HCl (1.50 g) were dissolved in water. The solution was heated to 80 °C with stirring and then KOH solution (0.96 g in 10 ml of water) was added dropwise. The resulting solution was rotary evaporated to dryness. The separation of the Pt(II) complex from the residue was effected by extraction with methanol, the process being repeated two times to complete separation and the crystals were recrystallized from water-1-propanol.

Found: C, 24.75; H, 6.24; N, 11.59%. Calcd for $[Pt(C_5H_{14}N_2)_2]Cl_2\cdot H_2O$: C, 24.59; H, 6.15; N, 11.48%.

Spectral Measurements. Electronic spectrum was measured in aqueous solution on a Hitachi EPS-3T Recording Spectrometer. The CD spectrum in aqueous solution was obtained using a JASCO J-20 Automatic Recording Spectrometer. The FT ^{13}C NMR spectra were obtained in D_2O at 15.04 MHz with broad band proton decoupling and off-resonance proton decoupling on a JEOL JNM-FX-60 Spectrometer. Dioxane was used as an internal reference but the chemical shifts are given based on the TMS scale. In every ^{13}C NMR spectrum 4096 data points were taken over a 1-kHz spectral width. All measurements were conducted at room temperature.

Measurement of X-Ray Data of $[Pt$(SS-ptn)$_2]Cl_2\cdot H_2O$. *Crystal Data*: $C_{10}Cl_2H_{30}N_4OPt$, *F.W.*=488.1, orthorhombic, $a=12.089(3)$, $b=13.547(3)$, $c=10.697(2)$ Å, $D_m=1.85$, $D_c=1.85$ g/cm^3, $Z=4$, space group $P2_12_12_1$, $\mu(\text{Mo } K\alpha)=87.3$ cm^{-1}. The space group and the approximate unit cell dimensions were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. The unit cell dimensions were refined by the least-squares analysis of 15 θ values measured on a Philips PW1100 four circle diffractometer, Mo $K\alpha$ radiation being employed.

Data Collection: Diffraction intensities were measured by ω-2θ scan method on the diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The crystal size was 0.28×0.26×0.25 mm. The scan speed and scan width in ω were 0.017° s^{-1} and $(0.8+0.2\tan\theta)°$, respectively. Background was counted for 20 s at each end of the scan range. A total of 1903 independent reflections for which $I_t-2\sqrt{I_t}>I_b$ were collected in the $2\theta \geq 55°$ range (I_t=intensity at the top of peak; I_b=mean background intensity obtained from preliminary background measurements for 5 s on both sides of the peak). A spherical absorption correction (r=0.13 mm) was applied. During the data collection no appreciable variations were observed in the intensities of three standard reflections (200,020,002) monitored every 2 h.

Structure Determination and Refinement. The crystal structure of $[Pt(SS\text{-}ptn)_2]Cl_2\cdot H_2O$ was solved by the Patterson and Fourier method. The positional and thermal parameters were refined by a block-diagonal least-squares method, the minimized function being $\sum w(F_o-|F_c|)^2$. The weighting scheme, $w=1.0$ for $F_o\leq 100.0$ and $w=(100.0/F_o)^2$ for $F_o>100.0$, were found to be optimum conditions to make the average values of $w|\Delta F_o|^2$ relatively constnat over ranges of F_o. The final R value was 0.052. In the final cycle of the refinement all parameter shifts were less than 0.2σ. Positional and thermal parameters are listed in Table 1.

Atomic scattering factors of Pt^0, Cl$^-$, N, C, O were taken from Ref. 5. Anomalous dispersion corrections were made for Pt^0 and Cl$^-$. The absolute crystal structure was determined on the basis of the configuration (*S*) of asymmetric carbon atoms. The observed and calculated structure factors are preserved at the Chemical Society of Japan (Docu-

Table 1. Positional and thermal parameters

	x	y	z	B/Å^2		x	y	z	B/Å^2
Pt	0.15536(4)	0.24402(3)	0.20000(4)	a)	C(3)	0.406(2)	0.244(1)	0.057(2)	4.1(3)
Cl(1)	0.3336(5)	0.4345(3)	0.6707(7)	a)	C(4)	0.356(2)	0.345(1)	0.089(2)	4.1(3)
Cl(2)	0.2726(6)	0.0639(3)	0.8223(5)	a)	C(5)	0.391(2)	0.380(2)	0.222(2)	5.0(4)
N(1)	0.256(1)	0.134(1)	0.133(1)	3.1(2)	C'(1)	−0.020(2)	0.456(1)	0.440(2)	4.3(4)
N(2)	0.230(1)	0.339(1)	0.079(1)	2.8(2)	C'(2)	0.056(1)	0.368(1)	0.410(2)	3.1(3)
N'(1)	0.056(1)	0.355(1)	0.266(1)	3.1(2)	C'(3)	0.013(2)	0.277(1)	0.470(2)	3.8(3)
N'(2)	0.080(1)	0.147(1)	0.321(1)	2.8(2)	C'(4)	0.081(1)	0.184(1)	0.459(2)	3.2(3)
C(1)	0.448(2)	0.065(1)	0.111(2)	4.8(4)	C'(5)	0.202(2)	0.195(2)	0.501(2)	5.2(4)
C(2)	0.378(1)	0.157(1)	0.147(2)	3.4(3)	O$_w$	0.188(2)	0.284(1)	−0.176(2)	6.6(4)

a) Anisotropic temperature factors (×10^4) in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	37.9(3)	33.1(2)	48.3(4)	−3.9(6)	−5.1(6)	−1.4(6)
Cl(1)	64(4)	49(2)	225(9)	5(5)	−6(10)	−6(7)
Cl(2)	114(5)	54(2)	87(4)	35(6)	−13(8)	−17(5)

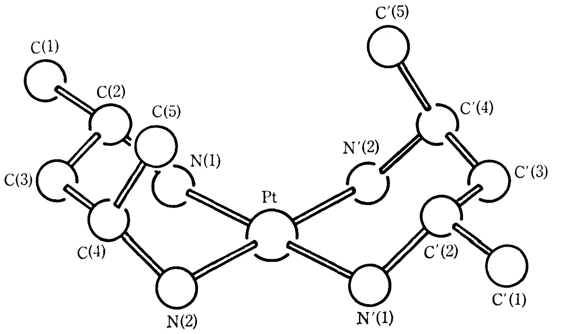

Fig. 1. The structure of [Pt(*SS*-ptn)$_2$]$^{2+}$.

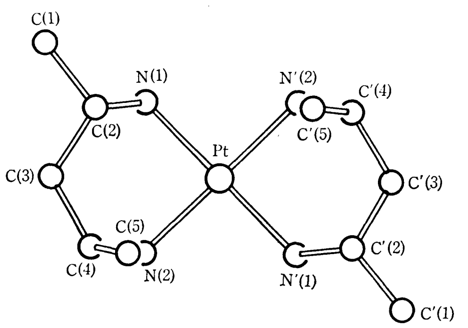

Fig. 2. The projection of complex on the coordination plane.

ment No. 7909). All computations were conducted on a FACOM 270-30 computer of Osaka City University, using RSSFR-5, HBLS-IV, and DAPH programs in the UNICS.[6]

Results and Discussion

The perspective drawing and projection of the complex are shown in Figs. 1 and 2, respectively. The complex has a pseudo two-fold axis which runs through Pt and is perpendicular to the coordination plane defined by N(1), N(2), N'(1), and N'(2). The disposition of these atoms is completely planar (±0.005 Å) and the Pt atom lies on the plane, the deviation being 0.003 Å.

Table 2. Bond lengths (l/Å) and bond angles (ϕ/°)

Pt-N(1)	2.05(1)	C(1)-C(2)	1.56(3)
Pt-N(2)	2.04(1)	C(2)-C(3)	1.55(3)
Pt-N'(1)	2.05(1)	C(3)-C(4)	1.53(3)
Pt-N'(2)	2.06(1)	C(4)-C(5)	1.56(3)
N(1)-C(2)	1.52(2)	C'(1)-C'(2)	1.53(3)
N(2)-C(4)	1.53(2)	C'(2)-C'(3)	1.48(3)
N'(1)-C'(2)	1.55(2)	C'(3)-C'(4)	1.52(3)
N'(2)-C'(4)	1.56(2)	C'(4)-C'(5)	1.54(3)
N(1)-Pt-N(2)	88.6(5)	N'(1)-Pt-N'(2)	89.5(5)
Pt-N(1)-C(2)	113(1)	Pt-N'(1)-C'(2)	115(1)
Pt-N(2)-C(4)	115(1)	Pt-N'(2)-C'(4)	113(1)
N(1)-C(2)-C(1)	110(1)	N'(1)-C'(2)-C'(1)	107(1)
N(1)-C(2)-C(3)	108(1)	N'(1)-C'(2)-C'(3)	110(1)
N(2)-C(4)-C(3)	110(1)	N'(2)-C'(4)-C'(3)	109(1)
N(2)-C(4)-C(5)	110(2)	N'(2)-C'(4)-C'(5)	109(1)
C(1)-C(2)-C(3)	110(2)	C'(1)-C'(2)-C'(3)	110(1)
C(2)-C(3)-C(4)	117(2)	C'(2)-C'(3)-C'(4)	118(2)
C(3)-C(4)-C(5)	112(2)	C'(3)-C'(4)-C'(5)	114(2)

Each chelate ring is of a chair conformation. One methyl group is equatorial with respect to the chelate ring, while the other is axial. The interplanar angle between the coordination plane and the mean plane of N(1), C(2), C(4), and N(2) is 130°, whereas that between the coordination plane and [N'(1), C'(2), C'(4), N'(2)] plane is 133°. These values are generally smaller than those (136.3—158.6°) of the 6-membered ring of tn (=1,3-propanediamine) with a chair conformation in octahedral complexes.[7] The larger interplanar angle in the octahedral complexes could be ascribed to interligand interactions within the complex, while the smaller interplanar angle in the present complex indicates that the extent of the interaction is smaller in spite of the presence of the methyl substituents in the ring. The Pt···C(5) and Pt···C'(5) distances are 3.40 and 3.34 Å, respectively. Bond lengths and angles are given in Table 2.

In the chelate ring the N–Pt–N coordination angle is significantly greater than those (81.9—87.4°) in the 5-membered ring,[8] but slightly less than 90°. The Pt–N–C bond angles are small compared with

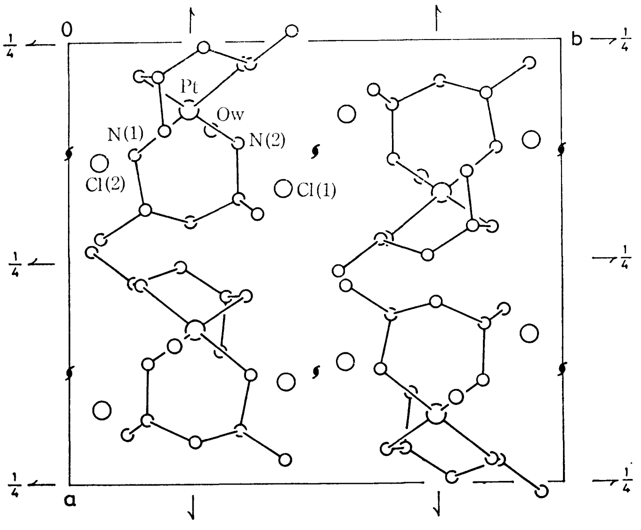

Fig. 3. The crystal structure viewed down the c axis.

Table 3. Possible hydrogen bonds

$X\text{-}H^{a)}\cdots Y$	$X\cdots Y(l/\text{Å})$	$H\cdots Y(l/\text{Å})$	$X\text{-}HY(\phi°)$
$N(1)\text{-}H\cdots Cl(2^{I})$	3.46(2)	2.50	156
$N(1)\text{-}H\cdots Cl(2^{II})$	3.38(2)	2.37	168
$N(2)\text{-}H\cdots O_w{}^{b)}$	2.87(2)	1.84	174
$N(2)\text{-}H\cdots Cl(1^{III})$	3.31(2)	2.31	164
$N'(1)\text{-}H\cdots Cl(1^{III})$	3.31(2)	2.29	168
$N'(2)\text{-}H\cdots Cl(2^{II})$	3.37(2)	2.35	173
$N'(2)\text{-}H\cdots Cl(1^{IV})$	3.18(2)	2.26	148
$O_w\text{-}H\cdots Cl(1^{I})^{b)}$	3.15(2)		
$O_w\text{-}H\cdots Cl(2^{I})^{b)}$	3·16(2)		

Roman numeral superscripts refer to the atoms in the following equivalent positions:

I $x, y, -1+z$ II $(1/2)-x, -y, -(1/2)+z$
III $(1/2)-x, 1-y, -(1/2)+z$
IV $-(1/2)+x, (1/2)-y, 1-z$

a) The positions of amino H atoms have been calculated on the assumption that the N-H distance is 1.03 Å. b) $N(2)\cdots O_w\cdots Cl(1^{I})=103(1)°$, $N(2)\cdots O_w\cdots Cl(2^{I})=101(1)°$, $Cl(1^{I})\cdots O_w\cdots Cl(2^{I})=115(1)°$.

those (116.5—121.3°) in the octahedral tn complexes.[7] This is also in harmony with the smaller inter-ligand interaction in the planar complex, since the decrease in the interplanar angle is related to the decrease in the Pt-N-C angle. Both of C(2)-C(3)-C(4) angle and its primed analogue are significantly larger than those (111.3—116.0°) in the tn complexes[7] and this is thought due to steric repulsion between the axial methyl group and C(2)-H(axial) segment.

The crystal structure viewed down the c axis is shown in Fig. 3. Except for the axial H atom bonded to N′(1) all remaining amino H atoms participate in $N\text{-}H\cdots Cl^-$ or $N\text{-}H\cdots O(H_2O)$ hydrogen bonding, the data of which are given in Table 3.

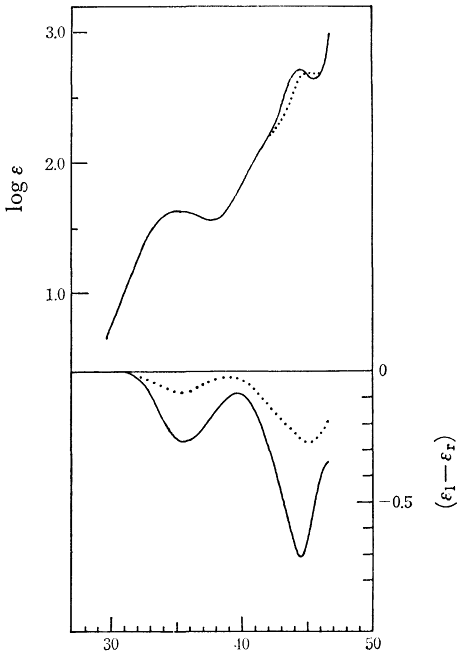

Fig. 4. The absorption (top) and CD (bottom) spectra of $[Pt(NH_3)_2(SS\text{-ptn})]Cl_2$ (······) and $[Pt(SS\text{-ptn})_2]Cl_2\cdot H_2O$ (——) in aqueous solution.

In the ^{13}C NMR spectrum of $[Pt(NH_3)_2(SS\text{-ptn})]Cl_2$ three signals, each of which is accompanied with satellites due to paltinum coupling, appear at 46.6 ($^2J_{Pt\text{-}C}=25$ Hz), 40.6 ($^3J_{Pt\text{-}C}=21$ Hz), and 21.9 ppm ($^3J_{Pt\text{-}C}=31$ Hz). These signals have been assigned to the resonances due to CH, CH_2, and CH_3 carbons, respectively, on the basis of the spectrum with off-resonance proton decoupling. The corresponding resonances appeared at 46.8, 40.7, and 21.8 ppm in $[Pt(SS\text{-ptn})_2]Cl_2\cdot H_2O$. Appleton and Hall reported that the Pt—SS-ptn chelate ring makes rapid chair-to-chair interconversion in solution.[3] The feature of ^{13}C NMR spectrum is compatible with this conclusion, since five carbon signals should be observed if the chelate ring is fixed in the chair conformation. According to the conformational analysis of the planar $Mb_2(tn)$ type complex (b=a monodentate ligand), the interconversion occurs *via* a skew intermediate.[9] However, the intermediate conformer is small in population at room temperature, as the free energy difference (ΔG) between the skew and chair conformers has been estimated to be 1.6 kcal/mol.[9] In $Mb_2(SS\text{-ptn})$ both methyl groups are equatorial in the δ skew conformer, whereas they are axial in the λ one. Conformational analysis of $[CoCl_4(S(\text{or } R\text{-})\text{-}1,3\text{-butanediamine})]^-$ showed that in the case of the skew ring the chelate ring with axial methyl group has greater atom overcrowding than that with equatorial one.[10] This may also be the case for planar $Mb_2(SS\text{-ptn})$. The ΔG(chair, δ skew) value in $Mb_2(SS\text{-ptn})$ may not be very different from that in $Mb_2(tn)$ but the ΔG(chair, λ skew) may be larger in magnitude than the ΔG(chair, δ skew).

Figure 4 shows the absorption and CD spectra of $[Pt(NH_3)_2(SS\text{-ptn})]Cl_2$ and $[Pt(SS\text{-ptn})_2]Cl_2\cdot H_2O$ in aqueous solution. The absorption spectra are very similar to those of the corresponding 1,2-propanediamine complexes.[11] Since the populations of the skew conformers are small as inferred from the free energy differences, the CD spectrum of the diammine complex can be regarded as virtually arising from the vicinal effect due to the *S* asymmetric carbons.

The effect of the *SS*-ptn ligand on the CD spectra of $[Pt(NH_3)_2(SS\text{-ptn})]^{2+}$ and $[Pt(SS\text{-ptn})_2]^{2+}$ is not additive as seen in Fig. 4, indicating that the vicinal effect of the asymmetric carbons is not the only source of the CD of bis(*SS*-ptn) complex. In general the asymmetry factors responsible for the optical activity of the Pt(II) chelates of *SS*-ptn are the chirality of the asymmetric carbon in the chelate ring and the chelate ring in the skew conformation. The non-additivity suggests that the CD spectrum of the bis-chelate comprises the conformational contribution from the conformers with skew ring.

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