The Absolute Configuration and Circular Dichroism of $(+)_{240}^{CD}$-[(2*S*,7*S*)-2,7-Dimethyl-3,6-diazaoctane-1,8-diamine]platinum(II) Chloride Dihydrate

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The title compound was synthesized and characterized by means of absorption, circular dichroism, and its NMR spectra as well as X-ray structure analysis. The crystals are monoclinic, with a $P2_1$ space group, $a=9.175(3)$, $b=12.423(5)$, $c=7.434(3)$ Å, $\beta=108.1(4)°$, and $Z=2$. The structure was determined from the diffractometer data and refined by a least-squares method to $R=0.041$ for 1732 observed reflections. The Pt atom has an essentially planar coordination with 4 N atoms. The disposition of the four donor atoms is not rectangular, but trapezoidal; it is, moreover, slightly tetrahedral. The quadridentate ligand forms three 5-membered chelate rings with the Pt atom. The two terminal rings are of a δ asymmetric envelope conformation, while the middle ring has a λ symmetric skew conformation. Both of the secondary N atoms possess a *R* configuration. The complex ion has a pseudo-two-fold axis by which the two terminal rings are related to each other. The circular dichroism spectrum reflects mainly the conformations of the 5-membered chelate rings. The features of the absorption and circular dichroism spectra are discussed on the basis of the geometry of the PtN_4 chromophore.

This work has been undertaken as a part of the investigation into the interrelation between structure and circular dichroism (CD) in the Pt(II) complexes. For the title complex there are three possible isomers, as is shown in Fig. 1, where *RR*, *RS*, and *SS* denote the configurations of the asymmetric nitrogens in each isomer. The information from the PMR spectrum is that the synthesized compound is not a mixture of these isomers, but contains either the *RR*- or the *SS*-isomer. The CD spectrum suggests that the compound consists of the *RR*-isomer, but this is not decisive. Therefore, a single-crystal structure analysis has been performed on the title complex.

Experimental

Preparation of the Compound. The (2*S*,7*S*)-2,7-dimethyl-3,6-diazaoctane-1,8-diamine (=3*S*,8*S*-dimetrien, NH_2CH_2-C*H(CH_3)NH(CH_2)$_2$NHC*H(CH_3)CH_2NH_2) hydrochloride was prepared according to the method described in the literature.[1]

$K_2[PtCl_4]$ (3.8 g) and 3*S*,8*S*-dimetrien·4HCl (2.0 g) were dissolved in 50 cm^3 of water. The solution was heated at 80 °C, and then a KOH solution (1.4 g in 10 cm^3 of water) was added, drop by drop. The precipitate was washed with water and found by analysis to be [Pt(dimetrien)]-[$PtCl_4$].

Found: C, 13.59; H, 3.13; N, 8.01%. Calcd for [Pt-($C_8H_{22}N_4$)][$PtCl_4$]: C, 13.60; H, 3.12; N, 7.93%.

The Magnus-type salt (2.0 g) was dissolved in 2 dm^3 of an aqueous $HClO_4$ solution (pH≈3). The resulting solution was passed through an anion-exchange column (Dowex 1X-8) in the chloride form, and the effluent was rotary-evaporated. The single crystals of [Pt(3*S*,8*S*-dimetrien)]Cl_2·$2H_2O$ were subsequently obtained by recrystallization from water-acetone.

Found: C, 20.23; H, 5.57; N, 12.07%. Calcd for [Pt-($C_8H_{22}N_4$)]Cl_2·$2H_2O$: C, 20.16; H, 5.46; N, 11.76%.

Spectral Measurements. The PMR spectrum was recorded at 60 MHz on a JEOL-C-60HL Spectrometer, using DSS as the internal reference. The FT ^{13}C NMR spectrum was obtained at 15.04 MHz with broad-band proton decoupling. Dioxane was used as the internal reference. The values of the chemical shifts in the text have been converted to the TMS scale. The absorption spectrum was measured using a Hitachi EPS-3T Spectrophotometer, while the CD spectrum was recorded on a JASCO J-20 Automatic Recording Spectrometer. In order to protect the asymmetric nitrogens from inversion, samples were dissolved in a 0.01 M DCl solution in the NMR measurements, whereas a 0.03 M HCl solution was used in the absorption and CD measurements.

X-Ray Data Measurement. Crystal Data: C_8Cl_2-$H_{26}N_4O_2Pt$, *F.W.*=476.1, Monoclinic, $a=9.175(3)$, $b=12.423(5)$, $c=7.434(3)$ Å, $\beta=108.1(4)°$, $U=805.4(5)$ Å^3, $D_m=1.93$, $D_c=1.96$ g/cm^3, $Z=2$, μ(Mo $K\alpha$)=94.8 cm^{-1}. The Laue symmetry and approximate unit-cell dimensions were determined from Weissenberg and precission photographs. The unit-cell dimensions were refined by a least-squares analysis of 28 θ values measured on a Philips PW1100 diffractometer.

Data Collection: A unique data set in the $2\theta \leq 55°$ range was collected by a conventional ω-2θ scan method using graphite-monochromated Mo $K\alpha$ radiation. The crystal size was 0.16×0.17×0.19 mm. The scan speed and scan width in ω were 0.017° s^{-1} and (1.0+0.2 tan θ)° respectively. The background was counted for 20 s at each end of the scan range. No significant variations were found in the intensities of three standard reflections menitored every 3 h. A total of 1732 intensities with $I_t - 2\sqrt{I_t} > I_b$ were collected and used for the structure analysis (I_t, intensity at the peak of reflection; I_b, mean background count obtained from preliminary background measurements for 5 s at each side of the peak). Intensity data were corrected for the Lp factors.[2] A spherical absorption correction ($r=0.085$ mm) was applied.

Structure Determination and Refinement. The crystal structure was solved by the heavy atom method. The positional and thermal parameters were refined by a block-diagonal least-squares method. The minimized function was $\sum w(F_o - |F_c|)^2$. The weighting scheme, $w=1.0$ for $F_o \leq 96.0$ and $w=(96.0/F_o)^2$ for $F_o > 96.0$, was found to be optimum in order to make $w\Delta F_o^2$ relatively constant over the ranges of F_o. The final *R* value was 0.041. In the final cycle of refinement all the parameter shifts were less than 0.2σ. The positional and thermal parameters are listed in Table 1.

The atomic scattering factors for all atoms were taken from Ref. 3, with corrections for anomalous scattering for Pt^0 and Cl^-. The absolute crystal structure was determined on the basis of the configuration (*S*) of asymmetric carbons.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS, WITH e.s.d. VALUES IN PARENTHESES

	x	y	z	B/Å^2		x	y	z	B/Å^2
Pt	0.25071(4)	0.0	0.13658(4)	a)	C(3)	0.327(2)	0.196(1)	0.339(2)	3.2(2)
Cl(1)	0.5369(5)	−0.5526(4)	0.2806(5)	a)	C(4)	0.156(2)	0.177(1)	0.316(2)	3.5(3)
Cl(2)	−0.0842(5)	−0.2292(4)	0.2125(6)	a)	C(5)	−0.060(2)	0.066(1)	0.086(2)	3.2(2)
N(1)	0.441(1)	−0.087(1)	0.138(2)	3.0(2)	C(6)	−0.070(1)	−0.007(2)	−0.087(2)	3.1(2)
N(2)	0.400(1)	0.088(1)	0.334(1)	2.6(2)	C(7)	0.677(2)	0.131(2)	0.466(2)	4.2(3)
N(3)	0.096(1)	0.116(1)	0.132(1)	2.5(2)	C(8)	−0.187(2)	0.152(2)	0.038(3)	4.2(3)
N(4)	0.068(1)	−0.077(1)	−0.047(2)	3.0(2)	O_w(1)	0.575(1)	−0.305(1)	0.183(2)	4.4(2)
C(1)	0.581(2)	−0.037(1)	0.286(2)	3.3(2)	O_w(2)	−0.100(2)	0.397(2)	0.407(3)	7.5(4)
C(2)	0.551(2)	0.086(1)	0.302(2)	3.5(3)					

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

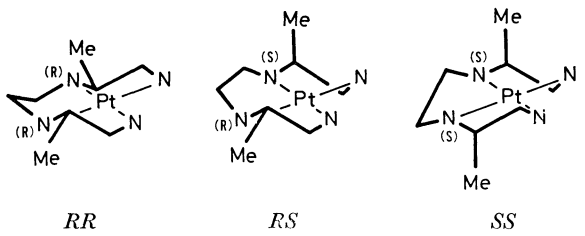
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	75.9(4)	36.9(2)	90.5(7)	14(1)	70(1)	16(1)
Cl(1)	173(6)	67(3)	154(7)	−20(7)	151(10)	−33(7)
Cl(2)	160(6)	70(3)	204(8)	−63(7)	186(11)	−74(8)

The observed and calculated structure factors are available at the Chemical Society of Japan (Document No. 7916). All the computations were carried out using programs in the UNICS.[4]

Results and Discussion

As is illustrated in Fig. 1, the complex ion may exist in three isomers. In the *RR*-isomer two terminal rings assume a δ conformation, while the middle ring is of a λ conformation, both methyl groups being equatorial with respect to the chelate ring. The *SS*-isomer has a δ middle ring and two λ terminal rings with axial methyl groups. In the *RS*-isomer the middle ring has an envelope conformation, but one of the terminal rings is of a λ conformation and the other is of a δ one. Of the two methyl groups, one is axial, whereas the other is equatorial. Although the *RR*-isomer with equatorial methyl groups seems to be the most probable of the three, the *RS*- and *SS*-isomers should not be left out of account, since, in the planar complex, the methyl group is not always constrained in the equatorial disposition.[5] The *RR*- and *SS*-isomers have a two-fold axis, but the *RS*-isomer has no symmetry.

The PMR spectrum showed one prominent methyl doublet at 1.19 ppm, while four carbon signals appeared at 12.73, 54.94, 56.76, and 61.24 ppm in the ^{13}C NMR spectrum. These observations indicate that the prepared compound is not a mixture of the isomers, but is, rather composed of either the *RR*- or the *SS*-isomer. Since the CD spectrum did not offer data decisive for distinguishing between these isomers, an X-ray structure analysis was performed.



RR *RS* *SS*

Fig. 1. Possible isomers for $(+)^{CD}_{240}$-[Pt(3*S*,8*S*-dimetrien)]$^{2+}$.

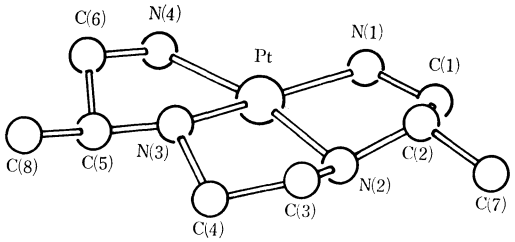


Fig. 2. Structure of $(+)^{CD}_{240}$-[Pt(3*S*,8*S*-dimetrien)]$^{2+}$.

Figure 2 shows a perspective drawing of the complex ion. This structure corresponds to the *RR*-isomer. The ion has an approximate two-fold axis which runs through the Pt atom and bisects the N(1)–Pt–N(4) bond angle. The molecular parameters (Table 2) related by this axis are in good agreement, within the limit of experimental error. In each of the three 5-membered rings, the middle ring is of a symmetric λ skew conformation, while the two terminal rings have an asymmetric δ envelope conformation.

The projection of the complex ion is shown in Fig. 3. The disposition of the 4 N atoms is not square or rectangular, but trapezoidal. Moreover, these atoms are disposed in a slightly tetrahedral configuration around the Pt atom, as may be seen in Fig. 3, where the deviations of atoms from the coordination plane defined by N(1)–N(4) are given in parentheses. Such a trapezoidal disposition of four ligators is usual in the metal chelates of triethylenetetramine (=trien) and its substituted derivatives.[6,7] Although the N(1)–Pt–N(4) angle is considerably larger than 90°, it is comparable to the corresponding angle (104°) in [Pd(trien)] $(PF_6)_2 \cdot KPF_6$.[8] An examination of the scaled model of the complex ion indicates that the slightly tetrahedral disposition of the 4 N atoms results from the conformation of the 3*S*,8*S*-dimetrien ligand, in which both C(*S*)–CH_3 groups are constrained equa-

Table 2. Bond lengths and angles

Bond lengths (l)	l/Å		l/Å
Pt-N(1)	2.05 (1)	Pt-N(4)	2.04 (1)
Pt-N(2)	1.99 (1)	Pt-N(3)	2.02 (1)
N(1)-C(1)	1.54 (2)	N(4)-C(6)	1.49 (3)
N(2)-C(2)	1.48 (2)	N(3)-C(5)	1.50 (2)
N(2)-C(3)	1.50 (2)	N(3)-C(4)	1.50 (2)
C(1)-C(2)	1.57 (2)	C(5)-C(6)	1.56 (3)
C(2)-C(7)	1.50 (3)	C(5)-C(8)	1.54 (3)
C(3)-C(4)	1.54 (2)		
Bond angles (ϕ)			
	ϕ/°		ϕ/°
N(1)-Pt-N(2)	84.1 (5)	N(3)-Pt-N(4)	84.2 (5)
N(2)-Pt-N(3)	86.3 (5)	N(1)-Pt-N(4)	106.2 (5)
Pt-N(1)-C(1)	108 (1)	Pt-N(4)-C(6)	109 (1)
Pt-N(2)-C(2)	110 (1)	Pt-N(3)-C(5)	109 (1)
Pt-N(2)-C(3)	107 (1)	Pt-N(3)-C(4)	107 (1)
C(2)-N(2)-C(3)	118 (1)	C(5)-N(3)-C(4)	118 (1)
N(1)-C(1)-C(2)	109 (1)	N(4)-C(6)-C(5)	110 (2)
N(2)-C(2)-C(1)	103 (1)	N(3)-C(5)-C(6)	104 (1)
N(2)-C(2)-C(7)	113 (1)	N(3)-C(5)-C(8)	111 (1)
C(1)-C(2)-C(7)	108 (1)	C(6)-C(5)-C(8)	112 (1)
N(2)-C(3)-C(4)	108 (1)	N(3)-C(4)-C(3)	104 (1)

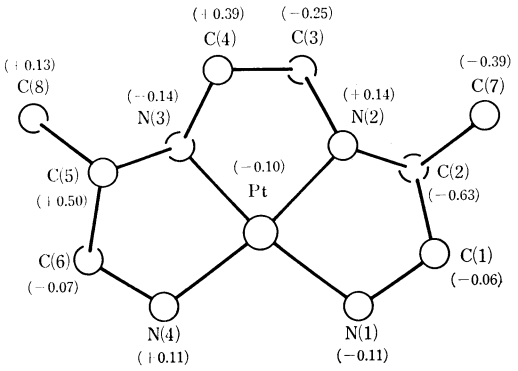


Fig. 3. Projection of $(+)^{CD}_{240}$-[Pt(3*S*,8*S*-dimetrien)]$^{2+}$ on the coordination plane defined by four nitrogen atoms. The deviations (Å) of atoms from the plane are given in parentheses.

torially. Such a disposition seems to be characteristic of the *RR*-isomer. This view is supported by the similar configuration of the 4 N atoms in $(-)_{589}$-*trans*-[Co$(NO_2)_2$(3*S*,8*S*-dimetrien)]ClO_4,[6] in which the dimetrien ligand has the same conformation as the present complex ion.

The Pt–N(secondary) distance seems to be shorter than the Pt–N(primary) distance. Such a tendency was also found in the Pd–N(secondary) and Pd–N(primary) bond lengths in the Pd(II) chelate of trien cited above for comparison. The C(2)–N(2)–C(3) and C(4)–N(3)–C(5) bond angles are significantly larger than the tetrahedral angle. This may be caused by the planar coordination of the quadridentate ligand. The other bond lengths and angles are normal.

Figure 4 shows the crystal structure viewed along the b axis. All amino H atoms participate in the

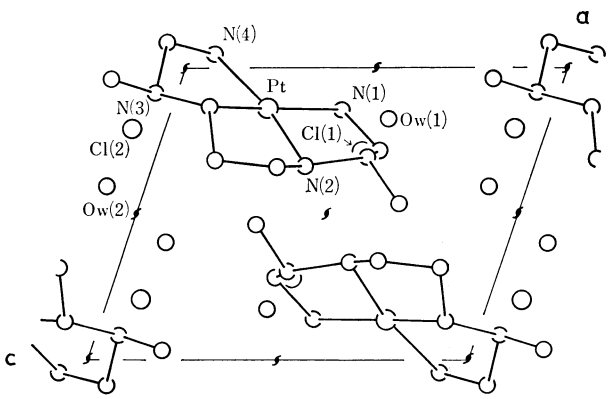


Fig. 4. Crystal structure viewed down the b axis.

Table 3. Possible hydrogen bonds

A	B	A···B (l/Å)	H···B (l/Å)	N-H···B (ϕ/°)
N(1)-H[a]	Cl(1^{III})	3.21 (1)	2.19	170
N(1)-H	O_w(1^{I})	2.95 (2)	2.18	131
N(2)-H	Cl(1^{III})	3.25 (1)	2.25	164
N(3)-H	Cl(2^{IV})	3.18 (1)	2.16	168
N(4)-H	Cl(2^{I})	3.30 (1)	2.41	145
N(4)-H	O_w(2^{V})	2.81 (3)	1.79	168
Cl(1)	O_w(1^{I})	3.20 (2)		
Cl(1)	O_w(2^{VII})	3.23 (2)		
Cl(2)	O_w(1^{VI})	3.21 (2)		
Cl(2)	O_w(2^{VIII})	3.22 (2)		

Roman-numeral superscripts refer to atoms in the following equivalent positions:
I x, y, z; II $1+x$, $(1/2)+y$, z; III $1+x$, $(1/2)+y$, $1+z$; IV x, $(1/2)+y$, z; V x, $-(1/2)+y$, z; VI $-1+x$, y, z; VII $1+x$, $-1+y$, z; VIII x, $-(1/2)+y$, $1+z$

a) The positions of the H atoms in the NH_2 groups were calculated on the assumption that the N-H distance is 1.03 Å.

N–H···Cl^- or N–H···O(H_2O) hydrogen bonding, the data of which are presented in Table 3.

The absorption and CD spectra are presented in Fig. 5. The electronic spectrum shows three bands, at 35000, 41000, and 44200 cm^{-1}. The peak positions are very similar to those in [Pt$(NH_3)_2$ (*RR*-chxn or *R*-pn)]Cl_2 and in [Pt(*RR*-chxn or *R*-pn)$_2$]Cl_2;[9] hence these peaks can be assigned to the $^1A_1 \rightarrow {}^3A_2$ and ^3E, $^1A_1 \rightarrow {}^1A_2$, and $^1A_1 \rightarrow {}^1E$ transitions (D_4 symmetry), respectively (*RR*-chxn = (1*R*,2*R*)-1,2-cyclohexanediamine; *R*-pn = (*R*)-1,2-propanediamine). However, the absorption is generally more intense than those in the chxn and pn complexes. Similarly, the absorption intensity in [Pd(trien)]$^{2+}$ was found to be about three times as intense as that in [Pd(*R*-pn)$_2$]$^{2+}$.[8] The disposition of the 4 N donor atoms is rectangular in [Pt(*R*-pn)$_2$]$^{2+}$;[5] this may also be the case in [Pd(*R*-pn)$_2$]$^{2+}$ and in the Pt(II) chelates of chxn, whereas the disposition is trapezoidal in the 3*S*,8*S*-dimetrien and trien complexes. The PtN_4 and PdN_4 chromophores in the last two complexes lack a center of symmetry, which may be responsible for the enhancement of the absorp-

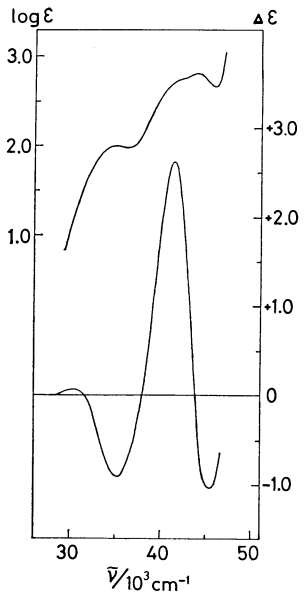


Fig. 5. Absorption (top) and CD (bottom) spectra of $(+)^{CD}_{240}$-[Pt(3*S*,8*S*-dimetrien)]$Cl_2 \cdot 2H_2O$

tion intensity. The enhancement is largest in the $^1A_1 \rightarrow {}^1A_2$ ($d_{xy} \rightarrow d_{x^2-y^2}$) transition. This is compatible with the interpretation of the intensity enhancement, because the electronic transition within the coordination plane should be the most sensitive to the disposition of donor atoms in the plane.

The d→d optical activity of the present complex could be regarded as composed of the contributions from the vicinal effects of the dissymmetric 5-membered rings and that of the asymmetric secondary nitrogen. The second effect may be small in magnitude, since the local effective symmetry around the secondary nitrogen can be taken as C_s. Then, the *RR*-isomer can be anticipated to show a CD pattern similar to that of $[Pt(NH_3)_2(SS\text{-chxn})]^{2+}$,[9] with one δ ring. Indeed, the CD signs of the ^3E and ^1E bands in the present complex are the same as those in the *SS*-chxn complex, but there is a remarkable difference between the CD spectra of these complexes; the $^1A_2$ CD band which appears at 41000 cm^{-1} in the former complex (Fig. 5) is not found in the latter complex. Similarly, the $^1A_2$ band is not observed in the CD spectra of $[Pt(NH_3)_2(S\text{-pn})]^{2+}$ and $[Pt(SS\text{-chxn or } S\text{-pn})_2]^{2+}$.[9] As has been described above, the increase in the electric-dipole transition moment is largest for the $^1A_2$ transition; this is responsible for the emergence of the intense $^1A_2$ CD band in the former. The CD sign of this band is compatible with that of the $^1A_2$ band in *trans*-$[CoCl_2(3S,8S\text{-dimetrien})]^+$.[10] The intensities of the other CD bands are also larger than those in $[Pt(NH_3)_2(SS\text{-chxn})]^{2+}$; this increase is mainly attributable to the increase in the transition moments.

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