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The Crystal Structures of Monoclinic and Triclinic Forms of Bis[(*R*)-1,2-propanediame]platinum(II) Chloride Dihydrate

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Synopsis. The crystal structures of monoclinic and triclinic forms of $[Pt(R\text{-pn})_2]Cl_2 \cdot 2H_2O$ have been determined from diffractometer data. Despite the difference in crystal systems, the complex cations in the two kinds of crystals have essentially the same structure. The disposition of the CH_3 groups is *trans*. One of the chelate rings is of the λ conformation, with an equatorial CH_3 group, while the other has the δ conformation, with an axial CH_3 group.

The bis[(*R*)-1,2-propanediamine]platinum(II) ion ($[Pt(R\text{-pn})_2]^{2+}$) may exist in *trans* and *cis* isomers. The 100 MHz PMR spectrum of $[Pt(R\text{-pn})_2]Cl_2$ shows one methyl doublet at 1.35 ppm, indicating either that the compound comprises only one isomer or that methyl signals due to the *trans* and *cis* isomers are virtually superimposed in the 100 MHz spectrum.[1] The X-ray structure analysis of the title compound has disclosed that the compound contains only the *trans* isomer.

Experimental

$[Pt(R\text{-pn})_2Cl_2 \cdot 2H_2O$ was prepared in two different ways. i) $[Pt(Cl)_2(R\text{-pn})]$ was treated with an excess of *R*-pn; subsequent recrystallization from water yielded predominantly monoclinic crystals, with a small amount of triclinic crystals. ii) The reaction of $PtCl_2$ with an excess of *R*-pn in water gave a compound with the same formula as that obtained in i), but in this case the quantity of triclinic crystals was larger than that of monoclinic ones. Both the monoclinic and triclinic crystals gave satisfactory analyses.

Crystal Data: 1) Monoclinic form (**1**), $a=5.181(2)$, $b=21.142(11)$, $c=6.776(2)$ Å, $\beta=96.50(3)°$, $D_m=2.02$, $D_c=2.03$ g cm^{-3}, $Z=2$, space group $P2_1$, $\mu(\text{Mo } K\alpha)=103.6$ cm^{-1}: 2) Triclinic form (**2**), $a=10.688(9)$, $b=6.786(4)$, $c=5.174(3)$Å, $\alpha=96.27(6)°$, $\beta=96.54(6)°$, $\gamma=86.19(4)°$, $D_m=2.02$, $D_c=2.02$ g cm^{-3}, $Z=1$, space group P1, $\mu(\text{Mo } K\alpha)=103.1$ cm^{-1}.

The intensities were measured on an automated diffractometer by means of the ω-2θ scan method, with graphite-monochromated Mo $K\alpha$ radiation. Crystal size: $0.20 \times 0.20 \times 0.25$ mm for **1**, $r=0.07$ mm for **2** (ground spherically); scan speed: 0.017° s^{-1} for **1** and **2**; scan range: $(0.8+0.2 \tan \theta)°$ for **1**, $(1.0+0.2 \tan \theta)°$ for **2**; background measurement at each end of the scan range: 20 s for **1** and **2**; maximum 2θ value: 55° for **1**, 50° for **2**; number of reflections with $F_0^2 > 3\sigma(F^2_0)$: 1576 for **1**, 1691 for **2**.

The refinement of the structures were performed by means of the block-diagonal least-squares method. The function minimized was $\sum w(F_0-|F_c|)^2$. The convergence was attained with $R=0.033$ ($R_w=0.042$) for **1** and $R=0.039$ ($R_w=0.048$) for **2**. w for **1**: $w=0.7$ for $F_0<13.0$, $w=1.0$ for $13.0 \leq F_0 \leq 32.0$, $w=(32.0/F_0)^2$ for $F_0>32.0$. w for **2**: $w=0.7$ for $F_0<17.0$, $w=1.0$ for $17.0 \leq F_0 \leq 40.0$, $w=(40.0/F_0)^2$ for $F_0>40.0$. No attempt was made to locate the H atoms. The atomic scatterings factors, with corrections for anomalous scattering of Pt^0 and Cl^-, were taken from Ref. 2. The F_0-F_c tables are deposited as Document No. 8015 at the Chemical Society of Japan. The atomic coordinates are listed in Table 1. All the computations were performed by using programs in UNICS[3] on a FACOM 230-60 computer at this University.

Results and Discussion

The crystal structures of **1** and **2** are shown in Fig. 1. Both the monoclinic and triclinic crystals comprise only the *trans* isomer with substantially identical

Table 1. Positional and thermal parameters

Atom	Monoclinic form (1)				Triclinic form (2)			
	10^4x	10^4y	10^4z	B/Å^2	10^4x	10^4y	10^4z	B/Å^2
Pt	1423.6(6)	0	4261.6(5)	a)	0	0	0	a)
Cl(1)	8010(6)	−796(2)	8870(5)	a)	−1639(5)	−4416(7)	−6953(9)	a)
Cl(2)	4776(6)	819(2)	−299(5)	a)	1562(5)	4474(7)	−2991(9)	a)
N(1)	2944(20)	−489(5)	2039(15)	2.7(2)	−1027(14)	2241(22)	−1691(29)	3.0(3)
N(2)	2477(21)	−796(5)	5875(15)	2.7(2)	−1600(14)	−1469(22)	−1402(29)	3.1(3)
N(3)	−190(20)	479(5)	6449(15)	2.5(2)	937(13)	−2289(20)	1853(26)	2.6(2)
N(4)	237(20)	776(5)	2611(15)	2.5(2)	1529(13)	1523(21)	1562(27)	2.8(2)
C(1)	4249(31)	−1075(7)	2858(24)	3.6(2)	−2145(20)	1649(32)	−3285(42)	4.0(4)
C(2)	2755(28)	−1331(7)	4470(21)	3.3(2)	−2670(20)	−26(30)	−1982(40)	3.8(4)
C(3)	3934(35)	−1914(10)	5518(27)	4.6(3)	−3765(24)	−912(37)	−3531(49)	5.1(5)
C(4)	−1939(26)	983(6)	5482(20)	2.9(2)	1971(17)	−1407(26)	3799(34)	3.9(3)
C(5)	−622(27)	1293(7)	3831(20)	3.0(2)	2578(17)	141(27)	2571(36)	3.1(3)
C(6)	1687(31)	1708(8)	4657(25)	4.0(3)	3397(21)	−687(33)	482(43)	4.3(4)
O(1)	4144(36)	−2718(9)	676(24)	7.1(4)	4561(20)	4158(33)	−3413(43)	7.0(5)
O(2)	−828(40)	−2218(10)	452(29)	7.9(4)	5613(23)	4081(37)	1789(48)	8.2(6)

a) Anisotropic thermal parameters ($\times 10^4$) 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 these parameters:

	Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
1	Pt	163(1)	14.8(1)	89.2(6)	−4(1)	22(1)	−2(1)
	Cl(1)	245(10)	24.9(8)	168(6)	−20(5)	63(13)	19(4)
	Cl(2)	229(10)	22.4(8)	149(6)	−22(5)	51(12)	13(4)
2	Pt	75.5(4)	86.3(8)	215(2)	−27(1)	63(1)	−10(2)
	Cl(1)	102(5)	166(9)	308(17)	−62(11)	93(14)	10(20)
	Cl(2)	96(5)	168(9)	310(17)	−56(11)	72(14)	32(20)

Table 2. Selected bond distances (l), bond angles (ϕ), and torsion angles (τ)

Bond lengths (l/Å)	**1**	**2**	Bond angles (ϕ/°)	**1**	**2**
Pt–N(1)	2.06(1)	2.03(2)	N(1)–Pt–N(2)	82.9(4)	80.9(7)
Pt–N(2)	2.05(1)	2.06(2)	N(3)–Pt–N(4)	82.9(4)	83.6(6)
Pt–N(3)	2.05(1)	2.06(2)			
Pt–N(4)	2.04(1)	2.03(2)			

N–H···Cl hydrogen bonds

N–H[a]···Cl			N···Cl (l/Å)		H···Cl (l/Å)		N–H···Cl (ϕ/°)	
	1[b]	**2**[b]	**1**	**2**	**1**	**2**	**1**	**2**
N(1)–H···Cl(2)	I	I	3.38(1)	3.41(2)	2.52	2.54	144	145
N(1)–H···Cl(1)	III	IV	3.21(1)	3.24(2)	2.22	2.25	173	174
N(2)–H···Cl(1)	I	I	3.32(1)	3.31(2)	2.34	2.34	167	166
N(2)–H···Cl(1)	II	V	3.25(1)	3.22(2)	2.28	2.25	162	162
N(3)–H···Cl(1)	II	V	3.34(1)	3.34(2)	2.41	2.41	155	155
N(3)–H···Cl(2)	IV	III	3.27(1)	3.25(1)	2.30	2.28	163	163
N(4)–H···Cl(2)	I	I	3.24(1)	3.26(2)	2.31	2.33	153	155

Torsion angles (τ/°)

	1	**2**		**1**	**2**
N(1)–C(1)–C(2)–N(2)	52	49	N(3)–C(4)–C(5)–N(4)	50	52
N(1)–C(1)–C(2)–C(3)	3	5	N(3)–C(4)–C(5)–C(6)	71	72
Pt–N(2)–C(2)–C(3)	9	13	Pt–N(4)–C(5)–C(6)	93	87

a) The coordinates of H atoms were calculated on the assumption of N–H=1.00 Å. b) Roman numerals denote the following equivalent positions for Cl^- ions: **1** I x, y, z; II $-1+x, y, z$; III $-1+x, y, -1+z$; IV $x, y, -1+z$ **2** I x, y, z; II $x, y, 1+z$; III $x, -1+y, z$; IV $x, 1+y, 1+z$; V $x, y, 1+z$.

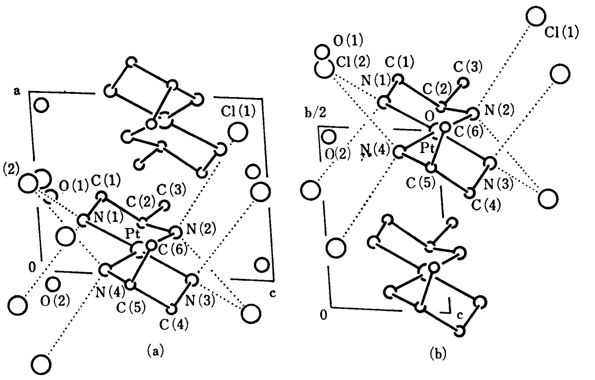

Fig. 1. The crystal structures of the monoclinic form (a) and the triclinic form (b).
The dotted lines indicate N–H···Cl hydrogen bonds.

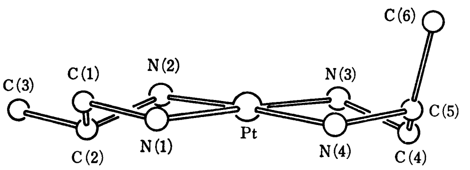

Fig. 2. The structure of $[Pt(R\text{-pn})_2]^{2+}$ ion.

structures. Moreover, the environments of the complex ions in the two structures have a close resemblance to one another. Furthermore, the two-dimensional crystal structure parallel to (010) in **1** is similar to that parallel to (100) in **2**, though the three-dimensional structures are different from each other in the stacking modes along the axes perpendicular to the respective planes. Such circumstances are reflected in the interrelation between the unit-cell dimensions of the two kinds of crystals; the a, b, c, and β in **1** are very close in magnitude to c, $2a$, b, and α in **2**. All the amino H atoms are involved in N–H···Cl hydrogen bonds, which are rather weak in view of the N···Cl distances.

One chelate ring has a λ conformation, with an equatorial CH_3 group, while in the other the conformation is δ, with an axial CH_3 group (Fig. 2). There have been two conflicting views regarding the behavior of the 5-membered chelate ring composed of Pd(II) or Pt(II) with the pn ligand. The observed coupling constants among the CH_2 and CH protons have been shown to be consistent with theoretical ones obtained from the conformationally fixed ring model with an equatorial CH_3 group.[1] On the other hand, the ^1H–^1H[4] and ^{195}Pt–^{13}C coupling constants,[5] as well as the circular dichroism intensity,[6] have been utilized to estimate the abandance ratio of the λ conformer to the δ conformer in the Pt(or Pd)-pn ring on the assumption that a rapid $\lambda \leftrightarrow \delta$ inversion takes place in the chelate ring. The λ: δ ratios were estimated to be 50: 50 and 70: 30 from the analyses of the ^1H–^1H and ^{195}Pt–^{13}C coupling constants respectively, and 3: 1, from that of the CD data, indicating the presence of a considerable amount of the axial CH_3 conformer in solution. Although the structure in a solid is not always held in solution, the axial CH_3 ring found in this work is indicative of the flexibility of the Pt-pn ring. From the point of view of the inverting ring model, the $\lambda\delta$ conformer is favorable in entropy term by $RT \ln 2$ over the $\lambda\lambda$ or $\delta\delta$ conformer. Provided that there exists no significant difference between the strain energies of the λ and δ rings, and that the two rings in the bis chelate are inverted independently from each other, the $\lambda\delta$ conformer is the most abundant species in solution. The finding that both kinds of crystals contain only the $\lambda\delta$ conformer implies that the assumption is not far from the real situation, although the conformation is largely dependent on the crystal packing.

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References

1) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 3184 (1969).

2) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 71, 148.

3) "The Universal Crystallographic Computation Program System," The Crystallographic Society of Japan (1969).

4) C. J. Hawkins and R. M. Peachey, *Aust. J. Chem.*, **29**, 33 (1976).

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

6) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience (1971), Chap. 5.