

Tetraammineplatinum(II) Bis[trichloro(2,6-dimethylpyridine)platinate(II)]

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Abstract. $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{C}_7\text{H}_9\text{N})\text{Cl}_3]_2$, $2\text{C}_7\text{H}_9\text{Cl}_3\text{N}-\text{Pt}^-(\text{NH}_3)_4\text{Pt}^{2+}$, $M_r = 1080.39$, triclinic, $P\bar{1}$, $a = 7.531(5)$, $b = 7.925(5)$, $c = 12.867(9)$ Å, $\alpha = 76.71(5)$, $\beta = 85.74(6)$, $\gamma = 68.47(5)^\circ$, $Z = 1$, $V = 695.2(8)$ Å³, $D_x = 2.580$, $D_m = 2.57(1)$ Mg m⁻³ (floatation); $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 16.421$ mm⁻¹ and $T = 295$ K. Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to $R = 0.032$ and $R_w = 0.034$. The Pt atom in the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion is located on a centre of symmetry. The coordination around the Pt atoms is planar. The crystal is stabilized by hydrogen bonds between the ammine groups and the Cl atoms.

Introduction. The complex salt $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(2,6\text{-lut})\text{Cl}_3]_2$ (lut = lutidine = dimethylpyridine) was synthesized from the reaction between $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ and $\text{K}[\text{Pt}(2,6\text{-lut})\text{Cl}_3]$ in 1:2 proportion in water. $\text{K}[\text{Pt}(2,6\text{-lut})\text{Cl}_3]$ was prepared by the method described by Kong & Rochon (1978). The crystals of $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(2,6\text{-lut})\text{Cl}_3]_2$ were recrystallized from water.

A set of precession photographs indicated that the crystals belong to the triclinic system, with space group $P\bar{1}$ or $P\bar{1}$. Since there are one $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and two $[\text{Pt}(2,6\text{-lut})\text{Cl}_3]^-$ ions per unit cell, the $P\bar{1}$ space group would imply that the Pt atom in the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion is on a centre of symmetry.

The intensity data were collected from a small plate with approximate dimensions $0.36 \times 0.33 \times 0.12$ mm on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. 4060 independent reflections were measured in the region of $2\theta < 60^\circ$ by the $2\theta/\theta$ scan technique at a variable speed (24 to 1° min⁻¹). Most reflections were measured at a speed of 1° min⁻¹. The background to scan time ratio was 0.40. The 3115 reflections which had intensities greater than $2.5\sigma(I)$ were considered as observed. The standard deviation, $\sigma(I)$, was calculated as previously described (Melanson, Hubert & Rochon, 1975). An absorption correction based on the equations of the crystal faces was applied to all the observations. The transmission factors varied from 0.026 to 0.162. The data were then corrected for the Lorentz and polarization effects. The atomic scattering factors used were from Cromer &

Waber (1965) except for those of H (Stewart, Davidson & Simpson, 1965). The anomalous-dispersion terms (Cromer & Liberman, 1970) of Pt and Cl were included in the calculations.

The three-dimensional Patterson map clearly indicated the space group $P\bar{1}$. The Pt atom in the $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion was located on the centre of symmetry at the origin. The position of the second independent Pt atom was then easily located. The positions of all the other atoms, except those of H, were obtained by structure factor and Fourier map calculations. An isotropic secondary-extinction correction (Coppens & Hamilton, 1970) was included in the calculations. Individual weights $w = 1/\sigma^2(F)$ (Stout & Jensen, 1968) were finally applied. The three H atoms on the pyridine ring were fixed at their calculated positions ($\text{C}-\text{H} = 0.95$ Å) and assigned isotropic temperature factors $B = 6$ Å². The other H atoms on the methyl and ammine groups could not be located. The refinement of the scale factor, the coordinates and anisotropic temperature factors of all non-hydrogen atoms converged to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.032$ and a weighted $R_w = [\sum w(|F_o| - |F_c|)^2 /$

Table 1. Refined coordinates and U_{eq} values ($\times 10^4$)

Estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^* (Å ²)
Pt(1)	0	0	0	302
Pt(2)	3423.8 (4)	3361.8 (3)	2250.3 (2)	300
Cl(1)	191.6 (27)	4698.3 (24)	1903.4 (15)	435
Cl(2)	6608.7 (26)	1914.7 (25)	2714.0 (14)	459
Cl(3)	3954.9 (31)	2630.3 (26)	590.4 (15)	504
N(1)	1978 (9)	880 (7)	-913 (5)	624
N(2)	-1298 (9)	2604 (7)	319 (5)	629
N(3)	2952 (8)	4127 (7)	3672 (4)	506
C(1)	3309 (15)	7113 (11)	2700 (7)	638
C(2)	2937 (11)	5829 (9)	3734 (7)	458
C(3)	2654 (12)	6351 (10)	4713 (7)	500
C(4)	2318 (12)	5247 (12)	5595 (6)	505
C(5)	2273 (12)	3562 (12)	5547 (6)	488
C(6)	2653 (10)	2983 (8)	4540 (5)	349
C(7)	2529 (12)	1207 (9)	4428 (6)	497

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12} \cos \gamma + 2U_{13} \cos \beta + 2U_{23} \cos \alpha).$$

$\sum w(|F_o|)^2)^{1/2} = 0.034$. The refined parameters are given in Table 1.* The calculations were carried out with a Cyber 73 computer and the programs used have been described previously (Melanson & Rochon, 1975).

Discussion. A labelled diagram of the ions is shown in Fig. 1. The bond lengths and angles are given in Table 2. The Pt atom in [Pt(NH₃)₄]²⁺ is located at the origin on a centre of symmetry. The coordination around the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34832 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

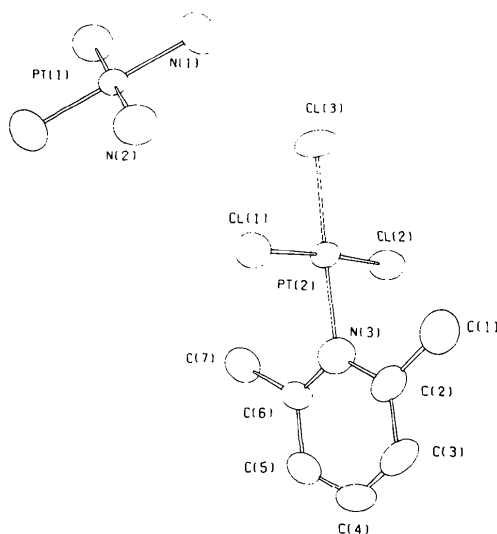


Fig. 1. Labelled diagram of the two ions, [Pt(NH₃)₄]²⁺ and [Pt(2,6-lutidine)Cl₃]⁻.

Table 2. Bond distances (Å) and bond angles (°)

Pt(1)—N(1)	2.052 (7)	N(1)—Pt(1)—N(2)	89.7 (2)
Pt(1)—N(2)	2.057 (5)	N(1)—Pt(1)—N(2)'	90.3 (2)
Pt(2)—Cl(1)	2.302 (2)	Cl(1)—Pt(2)—Cl(2)	175.9 (1)
Pt(2)—Cl(2)	2.303 (2)	Cl(1)—Pt(2)—Cl(3)	90.5 (1)
Pt(2)—Cl(3)	2.309 (2)	Cl(1)—Pt(2)—N(3)	89.1 (2)
Pt(2)—N(3)	2.024 (5)	Cl(2)—Pt(2)—Cl(3)	92.2 (1)
N(3)—C(2)	1.366 (9)	Cl(2)—Pt(2)—N(3)	88.3 (2)
N(3)—C(6)	1.329 (9)	Cl(3)—Pt(2)—N(3)	177.3 (2)
C(2)—C(3)	1.392 (11)	Pt(2)—N(3)—C(2)	119.6 (5)
C(3)—C(4)	1.335 (12)	Pt(2)—N(3)—C(6)	120.2 (5)
C(4)—C(5)	1.364 (13)	C(2)—N(3)—C(6)	120.2 (6)
C(5)—C(6)	1.447 (10)	N(3)—C(2)—C(1)	118.3 (7)
C(1)—C(2)	1.554 (12)	N(3)—C(2)—C(3)	120.0 (7)
C(6)—C(7)	1.485 (10)	C(1)—C(2)—C(3)	121.7 (7)
		C(2)—C(3)—C(4)	121.3 (8)
		C(3)—C(4)—C(5)	119.8 (8)
		C(4)—C(5)—C(6)	118.9 (8)
		N(3)—C(6)—C(5)	119.8 (7)
		N(3)—C(6)—C(7)	118.7 (6)
		C(5)—C(6)—C(7)	121.2 (7)

two independent Pt atoms is square planar. In [Pt(2,6-lut)Cl₃]⁻ the deviations from the weighted coordination plane are: Pt(2) 0.0018 (2), Cl(1) -0.059 (2), Cl(2) -0.059 (2), Cl(3) 0.008 (2) and N(3) 0.092 (6). The angle between the two coordination planes is 82.4°.

The Pt—N bond lengths in [Pt(NH₃)₄]²⁺ (2.052, 2.057 Å) are normal and agree well with the published data on platinum—ammine compounds (Milburn & Truter, 1966; Melanson & Rochon, 1978a). In the [Pt(2,6-lut)Cl₃]⁻ ion the Pt—N distance is slightly shorter (2.024 Å). Similar distances have been reported for platinum—pyridine compounds (Melanson & Rochon, 1977, 1978a,b). In K[Pt(2,6-lut)Cl₃] the Pt—N distance is 2.011 Å (Melanson & Rochon, 1976).

The Pt—Cl bond lengths (2.302, 2.303 and 2.309 Å) are also normal and agree well with the published values. They are almost identical to the distances found in K[Pt(2,6-lut)Cl₃] (2.301, 2.299 and 2.302 Å) (Melanson & Rochon, 1976).

The bond lengths within the aromatic ring vary from 1.33 to 1.45 Å and the angles are all close to 120°. They are similar to the values found in K[Pt(2,6-lut)Cl₃] (Melanson & Rochon, 1976), in a 1:1 complex of 2,6-lutidine with urea (Lee & Wallwork, 1965) and in other platinum—pyridine complexes (Melanson & Rochon, 1977, 1978b). The 2,6-lutidine ring is planar and lies perpendicular to the Pt coordination plane (88.1°) as shown in Figs. 1 and 2. In K[Pt(2,6-lut)Cl₃] the angle is 81.6°.

Fig. 2 illustrates the packing in the [Pt(NH₃)₄]-[Pt(2,6-lut)Cl₃]₂ crystal. It consists of one row of [Pt(NH₃)₄]²⁺ followed by two layers of [Pt(2,6-lut)Cl₃]⁻ ions, the PtCl₃ moiety being oriented towards the cations. The layers are parallel to the *ac* plane.

The environment of the N atoms in the [Pt(NH₃)₄]²⁺ ion was closely examined for possible hydrogen bonding. Many short intermolecular N...Cl contacts with favourable angles indicate that hydrogen bonding is important in the crystal. Table 3 shows that all the NH₃ groups are involved in hydrogen bonding with the Cl atoms. The N...Cl distances vary from 3.26 to 3.56 Å. N...Cl distances of 3.1–3.52 Å have been suggested for this type of hydrogen bond (Schuster, Zundel & Sandorfy, 1976). All the N—H...Cl angles are favourable for hydrogen bonding (98–107°). The Cl...N...Cl angles, however, indicate that not all the H atoms in the NH₃ groups are involved in hydrogen bonds at the same time.

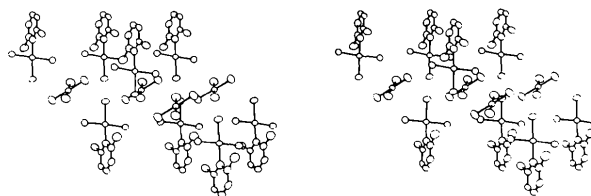


Fig. 2. Stereoscopic view of the packing in the [Pt(NH₃)₄][Pt(2,6-lutidine)Cl₃]₂ crystal.

Table 3. Distances and angles involved in hydrogen bonds

	Transformation (on third atom)	Distance (Å)		Angle (°)
N(1)—H...Cl(1)	-x, 1-y, -z	3.260 (6)	Pt(1)—N(1)...Cl(1)	106.1 (2)
N(1)—H...Cl(2)	1-x, -y, -z	3.416 (6)	Pt(1)—N(1)...Cl(2)	104.1 (2)
N(1)—H...Cl(3)	1-x, -y, -z	3.271 (6)	Pt(1)—N(1)...Cl(3)	107.3 (2)
			Cl(1)...N(1)...Cl(2)	116.0 (2)
			Cl(1)...N(1)...Cl(3)	146.3 (2)
			Cl(2)...N(1)...Cl(3)	59.6 (2)
N(2)—H...Cl(1)	-x, 1-y, -z	3.403 (6)	Pt(1)—N(2)...Cl(1)	101.3 (2)
N(2)—H...Cl(2)	x-1, y, z	3.379 (7)	Pt(1)—N(2)...Cl(2)	105.2 (2)
N(2)—H...Cl(3)	x-1, y, z	3.559 (8)	Pt(1)—N(2)...Cl(3)	97.8 (2)
			Cl(1)...N(2)...Cl(2)	153.6 (2)
			Cl(1)...N(2)...Cl(3)	118.6 (2)
			Cl(2)...N(2)...Cl(3)	57.2 (2)

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Structure of Diaquatetrakis(urea)magnesium Bromide

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Abstract. [Mg{CO(NH₂)₂}₄(H₂O)₂]Br₂, C₄H₂₀MgN₈O₆²⁺.2Br⁻, monoclinic, *P*2₁/*c*, *a* = 8.455 (1), *b* = 11.206 (1), *c* = 9.127 (1) Å, β = 103.52 (2)°, *Z* = 2, *D*_x = 1.818, *D*_m = 1.804 Mg m⁻³. The Mg²⁺ ions are octahedrally coordinated by the O atoms of the four urea and two water molecules. The urea molecules form a pseudotetragonal arrangement with intra-complex hydrogen bonds.

Introduction. Crystals of the title compound were obtained by slow evaporation of an aqueous solution of

magnesium bromide and urea in the molar ratio 1:4. This is probably the same compound as that described as MgBr₂.4urea.H₂O by Suleimankulov, Noguev, Dushenaliyeva & Naumova (1964) in their study of the magnesium bromide–urea–water system.

A crystal ground to a sphere of diameter 0.38 mm was used to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. Variable ω–2θ scans in the θ range 0–27° and graphite-monochromatized Mo *K*α radiation were used. The cell parameters were obtained from a least-squares fit of the setting angles for 15

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