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Synthesis of Ammonium Trichloromonoammineplatinate(II) Improved through Control of Temperature

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In the reaction of *cis*-$[PtCl_2(NH_3)_2]$ with HCl, the impact of temperature on the progress of the reaction was found to be critical, and an unexpected temperature effect was discovered. As a result of these findings the side reactions could be avoided, and the reaction between *cis*-$[PtCl_2(NH_3)_2]$ and HCl could be carried on to completion, with production solely of $NH_4[PtCl_3NH_3]$. The crystal structure of $NH_4[PtCl_3NH_3]\cdot H_2O$ is described.

The trichloroammineplatinate(II) complex has historically been important in the development of coordination chemistry, and it is of current interest as a precursor for several platinum complexes of medical significance. The complex has played an important role in theoretical studies on the *trans* effect of four-coordinate planar d^8 platinum(II) complexes.[1] The reaction kinetics and stability of the complex have also been of interest.[2,3] The discovery of the antitumour activity of *cis*-$[PtCl_2(NH_3)_2]$ (Cisplatin) has inspired further studies on the square-planar coordination complexes of platinum(II). Even $[PtCl_3NH_3]^-$ itself has been reported to show antitumour activity.[4] $K[PtCl_3NH_3]$ and analogous monoamine complexes are important precursors for the mixed-amine platinum complexes, which exhibit some new and desirable properties relative to the *cis*-diammine complex, i.e. liposolubility[5] and higher antitumour activity.[6–8] The binding modes to DNA, the primary target of the platinum anticancer drugs, have been studied for several mixed-amine complexes.[9,10] $K[PtCl_3NH_3]$ has also been used as the starting material in the synthesis of the diamine bridged dinuclear[11,12] and trinuclear[13] bis(platinum) complexes, a class of promising anticancer agents, which are active also in some Cisplatin-resistant cell lines.

$K[PtCl_3NH_3]$ has never been synthesized in more than relatively low yield, in spite of various attempts to improve the traditional methods and develop new ones. Traditionally, the trichloroammineplatinate(II) complex has been prepared by refluxing *cis*-$[PtCl_2(NH_3)_2]$ and HCl with platinum metal catalyst in an aqueous medium.[2] An optimized version of this method achieving 60% yield has recently been published.[11] A comparable method with 46% yield involves refluxing *cis*-$[PtCl_2(NH_3)_2]$ with KCl in glacial acetic acid.[3] Warming of $K_2[PtCl_4]$ with NH_3 in $HCONMe_2$ has given 30% yield.[14] Other modifications have involved changing the counter-ion or the solvent or both. For instance, $[Ph_4P][PtCl_3NH_3]$ has been prepared from *cis*-$[PtCl_2(NH_3)_2]$ in $MeCONMe_2$ with 74% yield.[15] The complex can also be prepared from the iodo-bridged dimer $[PtI_2NH_3]_2$ by hydrolytic cleavage followed by precipitation with KCl. This method gives 50% yield.[16] An alternative route to the mixed-amine complexes, via a direct reaction of the iodo-bridged dimer $[PtI_2Am]_2$ (Am = alkylamine) with an appropriate amine or ammine, has often provided a more economical and versatile method than the reaction of the monoammine complex with an amine.[8,17,18]

In the work described here we investigated the reaction between *cis*-$[PtCl_2(NH_3)_2]$ and HCl as part of a study on the formation of one-dimensional compounds with linear chains of platinum units containing alternating oxidation states. The conditions favouring the formation of side-products were studied with the purpose of identifying the ideal conditions for the formation of $NH_4[PtCl_3NH_3]$. Detailed information is given for a synthesis that gives 90–95% yield. The crystal structure of $NH_4[PtCl_3NH_3]\cdot H_2O$ is also reported and compared with the analogous $K[PtCl_3NH_3]\cdot H_2O$.[19]

Experimental

Preparation of $NH_4[PtCl_3NH_3]$. *cis*-$[PtCl_2(NH_3)_2]$ was prepared from $K_2[PtCl_4]$ via $K_2[PtI_4]$ according to the method of Dhara.[20] 1 g (3.33 mmol) of *cis*-$[PtCl_2(NH_3)_2]$ was refluxed with 10 cm^3 of conc. HCl and 20 cm^3 of water to give $NH_4[PtCl_3NH_3]$.[21] The solid *cis*-$[PtCl_2(NH_3)_2]$ deposited on the walls of the condenser

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during the refluxing, and it was occasionally flushed back by stopping the water circulation in the condenser for short periods. All the *cis*-$[PtCl_2(NH_3)_2]$ was dissolved within 1 h, forming a bright yellow solution. Within 2 h the solution had begun to turn orange, and the colour deepened when the refluxing proceeded. The refluxing time was varied between 5 and 9 h. Pt(II) did not oxidize to Pt(IV) during the reaction but only when the solution was stored below 10°C for several weeks, and thus no precaution against oxidation was needed.

Isolation of products. The reaction mixture was concentrated to one quarter of its initial volume and stored at room temperature for a few days. The unreacted *cis*-$[PtCl_2(NH_3)_2]$ was removed as shiny yellow needles. The solution was then concentrated to a very small volume, and the bulk product was allowed to crystallize at room temperature. Various conditions were tested for the concentration steps. When the reaction was carried out for 9 h under constant refluxing and the concentration steps were carefully made below 50°C, avoiding sudden changes in the temperature, the yield of $NH_4[PtCl_3NH_3]\cdot H_2O$ was 90–95%. The bulk product was crystalline, and no crystals of the side-products were observed.

Identification of products. All crystals were collected and dried in air. The crystals of $NH_4[PtCl_3NH_3]\cdot H_2O$ were very fragile, and if dried in a desiccator above silica gel or in air after being washed with ethanol, they easily lost water with disruption of the crystal structure. If they were isolated without further purification, however, they were stable in air. Since all the products crystallized easily when the solution was evaporated to dryness, they could be identified by X-ray diffraction methods. $(NH_4)_2[PtCl_4]$ and $(NH_4)_2[PtCl_6]$ were obtained as side-products. These compounds, with previously defined structures, were identified by unit-cell determinations. Owing to the distinct colours and shapes of the crystals, the individual products were easily distinguished from each other with an optical microscope.

Table 1. Crystal data and details of data collection for $NH[PtCl_3NH_3]\cdot H_2O$.

Formula	$NH_4[PtCl_3NH_3]\cdot H_2O$
Formula weight/g mol^{-1}	336.45
Space group	Orthorhombic $Cmc2_1$
Z	4
a/Å	4.6925(9)
b/Å	21.583(5)
c/Å	8.148(1)
V/Å^3	825.2(3)
T/K	298
Density/g cm^{-3}	2.86
Crystal size/mm	0.075×0.075×0.05
$\lambda(MoK_\alpha)$Å	0.71069
$\mu(MoK_\alpha)$/mm^{-1}	18.8
Diffractometer	Syntex $P2_1$
Data collection mode	ω
2Θ limits/°	3.0–60.0
Scan speed/°min^{-1}	1.0–10.0
$(\sin\Theta/\lambda)_{max}$/Å^{-1}	0.7033
Total no. of collected reflections	669
No. of reflections used in refinement, $I > 3\sigma(I)$	641
No. of parameters	33
R	0.035
R_w[a]	0.036
$F(000)$/e A^{-3}	640
Min/max transmission factors	0.41/1.00
S	2.525
$(\Delta/\sigma)_{max}$/e Å^{-3}	0.037
$\Delta\rho_{max}$/e Å^{-3}	1.3
$\Delta\rho_{min}$/e Å^{-3}	−1.2

[a] $R_w = \Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$.

Structure determination. The structure of $NH_4[PtCl_3NH_3]\cdot H_2O$ was determined by single-crystal X-ray diffraction methods. Table 1 gives the crystal data and details of the data collection. The intensities were corrected for absorption through the ψ-scan technique. The crystal was stable, and the standard reflections showed no significant variation in the intensities during the data collection. The data were corrected for Lorentz and polarization factors, and for dispersion. The structure was solved by Patterson methods using the SHELXS-86 program package.[22] In the final refinement, anisotropic thermal parameters were used for Pt and Cl atoms and isotropic parameters for N and O atoms. The refinements were carried out with the XTAL 3.0 program.[23] The neutral-atom scattering factors were those included in the program, and the corrections for anomalous dispersion for all the non-H atoms were taken from Ref. 24.

Absences of $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ reflections in the diffraction data indicated two possible

Table 2. Positional and thermal parameters (×10^2 Å^2) for $NH_4[PtCl_3NH_3]\cdot H_2O$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{iso}
Pt	0.0000	0.33972(3)	0.250[a]	3.39(3)	3.08(3)	3.17(3)	0.1(2)	
Cl(1)	0.0000	0.4476(2)	0.244(3)	6.2(3)	3.6(2)	3.8(5)	−1.5(6)	
Cl(2)	0.0000	0.3358(6)	0.530(2)	10(1)	3.7(7)	5(1)	2.3(6)	
Cl(3)	0.0000	0.3374(7)	−0.031(2)	8(1)	7(1)	2.6(7)	1.5(5)	
N(1)	0.0000	0.2446(7)	0.269(5)					4.5(4)
O	0.0000	0.0739(9)	0.118(2)					5.2(4)
N(2)	0.0000	0.046(1)	0.457(3)					5.0(5)

[a] The z-coordinate for the position of the Pt atom has not been refined.

space groups: orthorhombic *Cmcm* and *Cmc*2_1. The refinement in centrosymmetric space group *Cmcm* resulted in a significant residual electron density maximum near the non-coordinated N and O atoms, with $R = 0.044$. In space group *Cmc*2_1 the maxima were absent, giving discrete positions for both N and O atoms. This solution gave $R = 0.036$. The non-coordinated N and O atoms could not be distinguished with certainty. The choice of the position of the NH_4 ion was based on the position of the K ion in the analogous potassium compound.[19] The positional and thermal parameters are given in Table 2.

Results and discussion

Identification of products. The main product, $NH_4[PtCl_3NH_3]\cdot H_2O$, crystallized as long and thin plates with the colour varying from yellow–orange to orange depending on the thickness. $K[PtCl_3NH_3]\cdot H_2O$ has been reported to appear in a red or yellow form depending on the purity of the crystal.[25] One of the side-products were obtained as bright yellow prismatic crystals with dull apices and holes on the crystal faces, the other as deep red rods. The axis of 9.899(1) Å measured for the first crystal is close to that reported in the literature (9.858 Å) for cubic $(NH_4)_2[PtCl_6]$.[26] The unusual appearance of the prismatic crystals with the holes has been described as typical for this compound.[27] The unit-cell dimensions of the deep red rod were $a = 7.160(1)$ and $c = 4.292(1)$ Å, corresponding to the literature values of 7.1525(9) and 4.2979(5) Å reported for tetragonal $(NH_4)_2[PtCl_4]$.[28]

Formation of the products

$[PtCl_4]^{2-}$

Substitution of chloride for the ammine ligand in the trichloroammineplatinate(II) ion is very difficult and did not occur during 9 h reflux in 4 M HCl. However, if the refluxing was interrupted, and the reaction mixture containing the trichloro species was cooled to room temperature, the reaction mixture rapidly turned red when it was reheated to reflux temperature. This unexpected behaviour was observed repeatedly even in the concentration process when the solution was heated from room temperature to 50–60 °C. From the red solutions formed in these experiments, deep red crystals of $(NH_4)_2[PtCl_4]$ were obtained among the crystals of the main product. The side reaction is not in itself surprising, but this kind of temperature effect has not been mentioned before. Although no explanation for the effect is offered, the effect supplied us with the means to improve the yield of $NH_4[PtCl_3NH_3]$. The traditional synthesis via the reaction between *cis*-$[PtCl_2(NH_3)_2]$ and HCl in the presence of the platinum metal catalyst yields a mixture of the main product and $[PtCl_4]^{2-}$ with a significant amount of unreacted *cis*-$[PtCl_2(NH_3)_2]$.[11,25] The $[PtCl_4]^{2-}$ can be removed by precipitating the highly insoluble complex $[Pt(NH_3)_4][PtCl_4]$[25] or by an anion-exchange method.[11]

Spectroscopic techniques may provide the tools to investigate the species involved in the cooled solution. Since the purpose of the present work was to improve the yield of the $NH_4[PtCl_3NH_3]$, spectroscopic monitoring of the progress of the reaction was not carried out. Identification of the crystalline products was unambiguous, and spectroscopic monitoring was not expected to give additional information about the composition of the bulk product.

$[PtCl_6]^{2-}$

When the concentrated orange reaction mixture remaining after the removal of *cis*-$PtCl_2(NH_3)_2$ was stored below 10 °C in an open vessel for several weeks, bright yellow prismatic crystals of $(NH_4)_2[PtCl_6]$ were obtained. All the crystals were homogeneous in colour, shape and size. Oxidation did not occur when the solution was stored in air at room temperature. Fanwick and Martin[24] have described the oxidation in $K[PtCl_3NH_3]$ water solution when the mixture was stored in air, and on the basis of elemental analysis, gave the formula $KPtCl_5NH_3\cdot H_2O$ for the precipitated oxidized product.

Ideal conditions for the formation of $NH_4[PtCl_3NH_3]$. The amount of unreacted starting material decreased significantly with increasing reaction time. A reaction time of 9 h was optimal, and in the best case only 50 mg (5%) of the *cis*-$[PtCl_2(NH_3)_2]$ remained unreacted. The formation of $[PtCl_4]^{2-}$ was avoided when the refluxing was followed by concentration of the reaction mixture in an oil bath at 50 °C before the mixture had cooled below this temperature. After the removal of *cis*-$PtCl_2(NH_3)_2$ the mixture was evaporated to a very small volume either in

Table 3. Selected interatomic distances and bond angles of $NH_4[PtCl_3NH_3]\cdot H_2O$ and $K[PtCl_3NH_3]\cdot H_2O$.

$NH_4[PtCl_3NH_3]\cdot H_2O$		$K[PtCl_3NH_3]\cdot H_2O$[19]	
Distances/Å			
Pt–Cl(1)	2.329(5)		2.317(7)
Pt–Cl(2)	2.28(2)		2.29(3)
Pt–Cl(3)	2.29(2)		2.28(1)
Pt–N(1)	2.06(1)		2.04(2)
N(2)···O	2.83(3)	K···O	2.80(2)
$N(2)\cdots O^{iii}$	2.90(3)	$K\cdots O^{iii}$	2.72(2)
$Cl(2)\cdots O^{ii}$	3.14(2)	$Cl(2)\cdots O^{ii}$	3.05(2)
$N(2)\cdots Cl(1)^{ii}$	3.31(2)	$K\cdots Cl(1)^{ii}$	3.26(2)
$N(2)\cdots Cl(3)^{ii}$	3.44(2)	$K\cdots Cl(3)^{ii}$	3.4(1)
$N(1)\cdots Cl(3)^{ii}$	3.36(2)	$N(1)\cdots Cl(3)^{ii}$	3.55(3)
$Cl(2)\cdots N(1)^{ii}$	3.51(2)	$Cl(2)\cdots N(1)^{ii}$	3.30(4)
$Cl(1)\cdots N(2)^{i}$	3.61(2)	$Cl(1)\cdots K^{i}$	3.39(1)
$Cl(1)\cdots O^{i}$	3.74(2)	$Cl(1)\cdots O^{i}$	3.56(2)
$Cl(1)\cdots O^{ii}$	3.87(2)		
$Cl(2)\cdots Cl(3)^{iv}$	3.58(2)	$Cl(2)\cdots Cl(3)^{iv}$	3.56(2)
Bond angles/°			
Cl(1)–Pt–Cl(2)	93.4(7)		93.1(6)
Cl(1)–Pt–Cl(3)	90.0(7)		90.6(5)
Cl(2)–Pt–N(1)	84(1)		91.9(9)
Cl(3)–Pt–N(1)	93(1)		84.4(7)

^{i} $1/2+x$, $1/2+y$, z. ^{ii} $1/2+x$, $1/2-y$, $1/2+z$. ^{iii} x, $-y$, $1/2+z$. ^{iv} x, y, $1+z$.

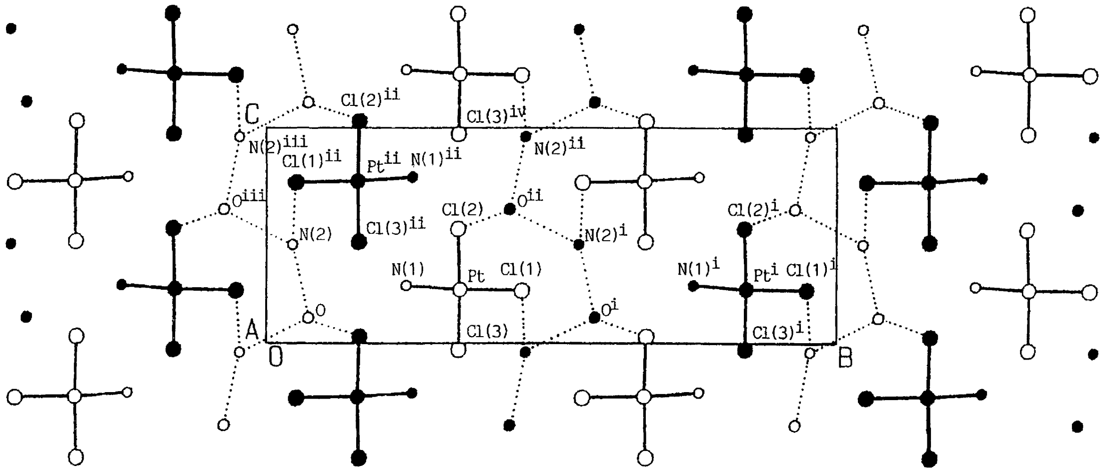

Fig. 1. The packing of $NH_4[PtCl_3NH_3]\cdot H_2O$ viewed down the x-axis. Atoms located in the mirror plane $x=0$ are marked with open circles and atoms in the mirror plane $x=1/2$ with full circles. The atoms in the plane $x=1$ are situated under the open circles. The possible hydrogen bond contacts are illustrated with dotted lines. Symmetry operations: $^{i}1/2+x$, $1/2+y$, z; $^{ii}1/2+x$, $1/2-y$, $1/2+z$; ^{iii}x, $-y$, $1/2+z$; ^{iv}x, y, $1+z$.

an open vessel at 50°C or under reduced pressure with very carefull warming. The temperature of the solution under reduced pressure was kept close to room temperature.

Structure of $NH_4[PtCl_3NH_3]$. The crystal structure of the compound is presented in Fig. 1, showing the packing of the molecules in two layers viewed down the x-axis. The figure also shows the possible hydrogen-bond contacts. The coordination around platinum is square-planar, and all the non-H atoms of the molecule are located in the mirror planes. The distances between the water molecules and the ammonium ions located in the same mirror plane are reasonable for medium-strong hydrogen bonding. The $PtCl_3NH_3$ units are only weakly hydrogen bonded, forming two identical N–H···Cl bonds between the Cl(1) atoms and the ammonium ions and two identical O–H···Cl bonds between the Cl(2) atoms and the water molecule. The packing around the water molecule and the ammonium ion is critical for the stability of the crystal, and removal of water from the lattice ruptures the crystal structure. The N(1)···Cl(2) and N(1)···Cl(3) distances are longer than the sums of the corresponding van der Waals radii, resulting in parallel cavities between the hydrogen-bonded zones. The tendency of the crystals to cleave along the diagonals and to shatter when cut in other directions indicates an aligned orientation of the hydrogen bonds.

The packing of the isostructural $K[PtCl_3NH_3]\cdot H_2O$ is slightly denser than that of the title compound. The unit-cell volumes are 825.2 Å^3 for the title compound and 781.0 Å^3 for the K-analogue. The coordination angles of the N(1) atom differ in the two compounds. Selected interatomic distances and bond angles for

Table 4. Bond distances in compounds $Q[PtCl_3L]\cdot nH_2O$, where Q denotes the cationic counter ion, L the N-donor ligand and Cl^t the chloride *trans* to the N atom of the ligand. Cl′ and Cl″ are *cis* to the N atom of the ligand; *D* is the difference between the *trans* and *cis* Pt–Cl bond lengths.

L[a]	NH_3	NH_3	NH_3	Py	Py	i-Propam	c-Pentam
Q[b]	NH_4^+	K^+	Ph_3PBz^+	Ph_3PBz^+	Et_4N^+	K^+	K^+
n	1	1	0	0	0	0.5	0.5
Pt–Cl^t	2.329(5)	2.317(7)	2.313(5)	2.288(1)	2.305(2)	2.320(3)	2.315(4)
Pt–Cl′	2.28(2)	2.29(4)	2.295(4)	2.298(3)	2.293(2)	2.299(3)	2.311(4)
D	0.05	0.03	0.018	−0.010	0.012	0.021	0.004
Pt–Cl″	2.29(2)	2.28(1)	2.307(4)	2.300(1)	2.299(2)	2.296(2)	2.302(4)
D	0.04	0.04	0.006	−0.012	0.006	0.024	0.013
Pt–N	2.06(2)	2.06(2)	2.03(2)	2.028(6)	2.018(6)	2.03(1)	2.04(1)
Ref.	This work	19	31	31	32	29	30

[a] Py, pyrimidine; i-Propam, isopropylamine; c-Pentam, cyclopentylamine. [b] Ph_3PBz^+, benzyltriphenylphosphonium cation; Et_4N^+, tetraethylenammonium cation.

$NH_4[PtCl_3NH_3]\cdot H_2O$ and $K[PtCl_3NH_3]\cdot H_2O$[19] are compared in Table 3. Compounds $K[PtCl_3(i\text{-}C_3H_7NH_2)]\cdot {}^1/_2H_2O$[29] and $K[PtCl_3(c\text{-}C_5H_9NH_2)]\cdot {}^1/_2H_2O$[30] have monoclinic *C*2/*c* unit-cell symmetries, but the orientation of the molecules in the lattice is similar to that of the title compound.

Trans *effect.* Among the Pt(II) complexes, the bond lengths do not always agree with the polarization theory of the *trans* effect, which predicts the Pt–Cl bond *trans* to the Pt–N bond to be weaker than the *cis* bonds. The trend can be seen in Table 4, which lists the bond lengths and the differences between the *trans* and *cis* bond lengths in trichloroplatinum(II) complexes with various N-donor ligands.

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