Platinum(IV) Complexes containing a Cationic Amine Ligand: Crystal Structure of [(2-Aminoethyl)ammonium]pentachloroplatinum(IV) Monohydrate †

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The complex [PtCl(dmso)(en)]Cl (dmso = dimethyl sulphoxide, en = 1,2-diaminoethane) reacts with concentrated HCl to give one-end displacement of the diamine and inner-sphere oxidation of Pt^{II} to Pt^{IV} by dmso which is reduced to dimethyl sulphide (dms). The complex $[PtCl_4(dms)(Hen)]Cl$ which is formed reacts further with chloride ion to displace dms and form $[PtCl_5(Hen)]$. The complex $[PtCl_5(Hen)]\cdot H_2O$ crystallizes in the orthorhombic space group $Ccm2_1$ with a = 15.388(8), b = 6.890(5), c = 9.882(6) Å, and Z = 4. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.027 for 543 observed reflections. The structure consists of zwitterionic [(2-aminoethyl)ammonium]pentachloroplatinum(IV) species and water molecules of crystallization; in the complex the metal is octahedrally surrounded by five chlorine atoms (Pt–Cl 2.294—2.306 Å) and a nitrogen atom from the monoprotonated diamine [Pt–N 2.050(4) Å]. The water molecules of crystallization are not involved in hydrogen bonds with either chlorine or nitrogen atoms of the complex.

In recent years there has been increasing interest in complexes containing metals co-ordinated to cationic ligands.[1-5] A few reports have dealt with platinum complexes containing partially protonated polyamine ligands. These were prepared either as precursors for kinetic studies of ring closure (upon deprotonation of the free ends of the amine) or as potential anticancer agents.[6-11]

Pursuing our interest in the preparation of platinum complexes with cationic amine ligands we have isolated two new platinum(IV) species containing a (2-aminoethyl)ammonium ligand (Hen) and the crystal structure of one of these, $[PtCl_5(Hen)]\cdot H_2O$, has been determined by X-ray analysis.

Experimental

Commercial reagent-grade chemicals were used without further purification. The complex *cis*-$[PtCl_2(dmso)_2]$ was prepared from $K_2[PtCl_4]$ and aqueous dimethyl sulphoxide (dmso) by the method of Wayland and co-workers;[12] [PtCl(dmso)(en)]Cl was prepared from the former complex and aqueous 1,2-diaminoethane (en) by the method of Romeo *et al.*[13]

cis-*[(2-Aminoethyl)ammonium]tetrachloro(dimethyl sulphide)platinum*(IV) *Chloride*.—The complex [PtCl(dmso)(en)]Cl (0.2 g) was dissolved in concentrated hydrochloric acid (5 cm^3) to give a yellow solution. This was filtered and placed in a desiccator, containing concentrated sulphuric acid and a beaker of potassium hydroxide pellets, under vacuum. After 2 d at room temperature a yellow residue was left, which was collected and analysed without further purification {Found: C, 9.75; H, 2.90; Cl, 35.95; N, 5.70. $[PtCl_4(dms)(Hen)]Cl$ requires C, 9.70; H, 3.05; Cl, 35.7; N, 5.65%}.

[(2-aminoethyl)ammonium]pentachloroplatinum(IV).—The complex [PtCl(dmso)(en)]Cl (0.2 g) was dissolved in concentrated hydrochloric acid (5 cm^3) and the resulting yellow solution filtered and placed in a desiccator containing concentrated sulphuric acid and a beaker of potassium hydroxide pellets. At normal pressure the solution concentrates slowly (2—3 weeks) and affords large orange crystals of the desired product in about 50% yield. These were collected, washed with ethanol, and air dried. On some occasions, in the first 2—3 d a yellow solid, still containing dimethyl sulphide (dms), precipitated. This was removed and the solution replaced in the desiccator {Found: C, 5.60; H, 2.40; Cl, 38.9; N, 6.05. $[PtCl_5(Hen)]\cdot H_2O$ requires C, 5.30; H, 2.45; Cl, 39.25; N, 6.20%}.

X-*Ray Crystal Structure Determination of* $[PtCl_5(Hen)]\cdot H_2O$.—A yellow prismatic crystal of dimensions *ca.* 0.05 × 0.06 × 0.15 mm was used for data collection. The unit-cell parameters were refined by a least-squares procedure applied to the θ values of 27 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data. $C_2H_{11}Cl_5N_2OPt$, M = 451.48, orthorhombic, space group $Ccm2_1$, a = 15.388(8), b = 6.890(5), c = 9.882(6) Å, U = 1 048(1) $Å^3$, Z = 4, D_c = 2.862 g cm^{-3}, $F(000)$ = 832, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 147.76 cm^{-1}.

The intensity data were collected on the same diffractometer using niobium-filtered Mo-K_α radiation and the θ—2θ scan technique. The intensity of the standard reflection was meas-

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† *Supplementary data available* (No. SUP 23889, 7 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

ured at intervals of 20 reflections as a check of the crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 663 independent reflections was measured (with θ in the range 3—27°), 543 of which, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied in view of the small size of the crystal.

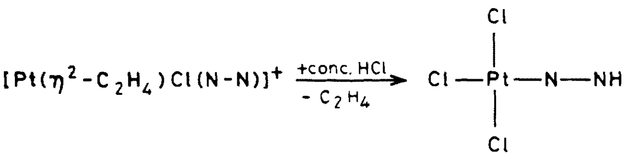
Structure solution and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using the SHELX system of computer programs,[14] with first isotropic and then anisotropic thermal parameters for the Pt and Cl atoms. The hydrogen atoms, except those of the water molecule, were placed at their geometrically calculated positions and included in the final structure-factor calculations with isotropic thermal parameters. The final R and R' $\{= [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.027 and 0.028 respectively (observed reflections only). The atomic scattering factors used, corrected for anomalous dispersion of Pt and Cl, were taken from ref. 15. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 0.3880$ and $g = 0.005$ in the last cycles of refinement.

Final atomic co-ordinates are given in Table 2. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna.

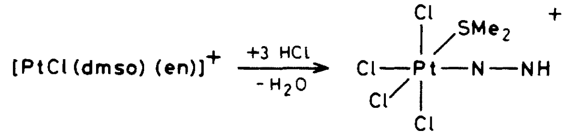
Spectroscopy.—Infrared spectra in the range 4 000—250 cm^{-1} were recorded for KBr pellets on a Perkin-Elmer 457 spectrophotometer; ^{1}H n.m.r. spectra were obtained with a Varian EM 390 spectrometer.

Results and Discussion

Quite recently we prepared some platinum complexes containing (2-dimethylaminoethyl)dimethylammonium and (3-dimethylaminopropyl)dimethylammonium ligands using the reaction procedure outlined in equation (1).[8] The analogous complexes with unsubstituted (2-aminoethyl)ammonium and (3-aminopropyl)ammonium ligands could not, however, be prepared by this procedure since the corresponding precursors, $[Pt(\eta^2\text{-}C_2H_4)Cl(N\text{–}N)]^+$, have not yet been isolated. In an attempt to overcome this difficulty we chose a different substrate, [PtCl(dmso)(en)]Cl (dmso = dimethyl sulphoxide, en = 1,2-diaminoethane), and treated it with concentrated hydrochloric acid. The expectation was that dmso, because of its strong *trans*-labilizing effect,[13] would initially facilitate chelate-ring opening of the diamine and afterwards would be displaced by the excess of chloride. Instead, the reaction led to the formation of a complex which contained a cationic amine ligand, and where the platinum(II) had also been oxidized to Pt^{IV} [equation (2)].



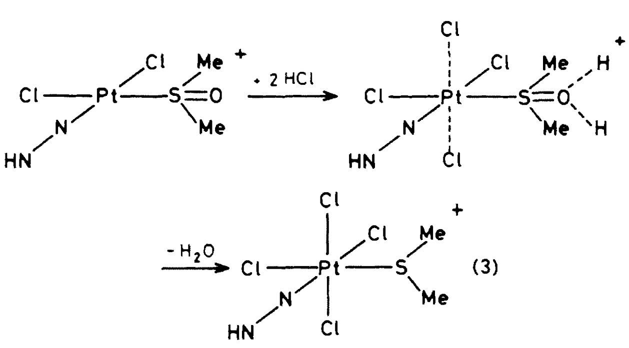
$$[Pt(\eta^2\text{-}C_2H_4)Cl(N\text{-}N)]^+ \xrightarrow[-\,C_2H_4]{+\text{conc. HCl}} Cl\text{—}\overset{Cl}{\underset{Cl}{Pt}}\text{—}N\text{—}NH \quad (1)$$



$$[PtCl(dmso)(en)]^+ \xrightarrow[-H_2O]{+3\ HCl} Cl\text{—}\overset{Cl,\ SMe_2}{\underset{Cl,\ Cl}{Pt}}\text{—}N\text{—}NH^{\ +} \quad (2)$$

The reaction of co-ordinated dimethyl sulphoxide with hydrochloric acid is of interest and has been previously observed. For example Kukushkin *et al.*[16] treated $[PtCl_2(dmso)_2]$ with concentrated HCl with the aim of obtaining $[PtCl_4(dms)_2]$ (dms = dimethyl sulphide). In fact the reaction was more complicated and a definite compound could not be isolated in this way. Braddock *et al.*[17] also observed a redox process in the reaction of *cis*-[PtCl(dmso)(am)$_2$]Cl (am = monoamine) with >1.0 mol dm^{-3} HCl which led to the formation of platinum(IV) complexes containing dimethyl sulphide; but these were neither isolated nor identified.

Thus, the inner-sphere redox process appears to be promoted by two protons reacting with the oxygen of dmso and the two chloride ions entering the co-ordination sphere of platinum [equation (3)]. In equation (3) the starting platinum(II) complex has been written with unidentate 1,2-diaminoethane since the displacement of the nitrogen atom *trans* to dmso in acidic medium is believed to be fast. Upon prolonged reaction the platinum(IV) species underwent displacement of dms by chloride ion and formation of [PtCl$_5$(Hen)]. It is to be noted that the dms is displaced in preference to the unidentate Hen$^+$ group, resembling in this respect the behaviour of the platinum(II) complex $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)]^+$ (Htmen = monoprotonated *N,N,N′,N′*-tetramethylethylenediamine) which, under analogous experimental conditions, underwent C_2H_4 displacement in preference to that of unidentate H-tmen$^+$ [equation (1)].



Using more dilute hydrochloric acid it should be possible, in principle, to suppress the redox process and obtain the desired [PtCl$_3$(Hen)] complex. However, using 1 mol dm^{-3} HCl only dmso displacement by Cl$^-$ took place and the complex [PtCl$_2$(en)] precipitated.

X-*Ray Structure of* [PtCl$_5$(Hen)]·H$_2$O.—The crystal structure consists of zwitterionic [(2-aminoethyl)ammonium]-pentachloroplatinum(IV) species and water molecules of crystallization. A view of the [PtCl$_5$(Hen)] complex with the atomic numbering scheme is given in Figure 1, and the bond distances and angles are given in Table 1.* The platinum atom is octahedrally surrounded by five chlorine atoms and by a nitrogen atom N(1) from the monoprotonated en ligand. The

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* Cl(4) and Cl(5) are not labelled in Figures 1 and 2 because they are related to Cl(1) and Cl(2) by the mirror plane; their corresponding dimensions and atomic co-ordinates are identical to those of Cl(1) and Cl(2) and are thus omitted from Tables 1 and 2.

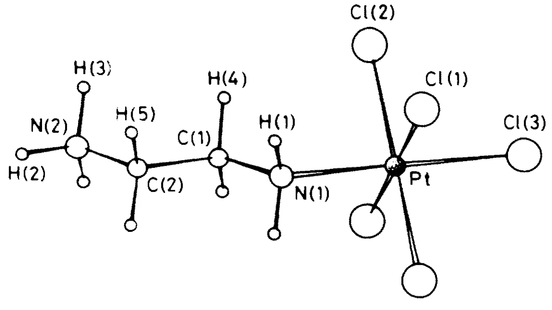

Figure 1. View of the complex $[PtCl_5(Hen)]$ with the atomic numbering scheme

Table 1. Bond distances (Å) and angles (°) for $[PtCl_5(Hen)]{\cdot}H_2O$

Pt-Cl(1)	2.302(2)	N(1)-C(1)	1.420(8)
Pt-Cl(2)	2.306(2)	C(1)-C(2)	1.498(8)
Pt-Cl(3)	2.294(2)	N(2)-C(2)	1.501(7)
Pt-N(1)	2.050(4)		
Cl(1)-Pt-Cl(2)	89.7(2)	Cl(3)-Pt-N(1)	178.1(2)
Cl(1)-Pt-Cl(3)	90.7(2)	Pt-N(1)-C(1)	120.9(4)
Cl(1)-Pt-N(1)	88.0(3)	N(1)-C(1)-N(2)	114.9(4)
Cl(2)-Pt-Cl(3)	89.8(2)	C(1)-C(2)-N(2)	109.7(4)
Cl(2)-Pt-N(1)	91.6(3)		

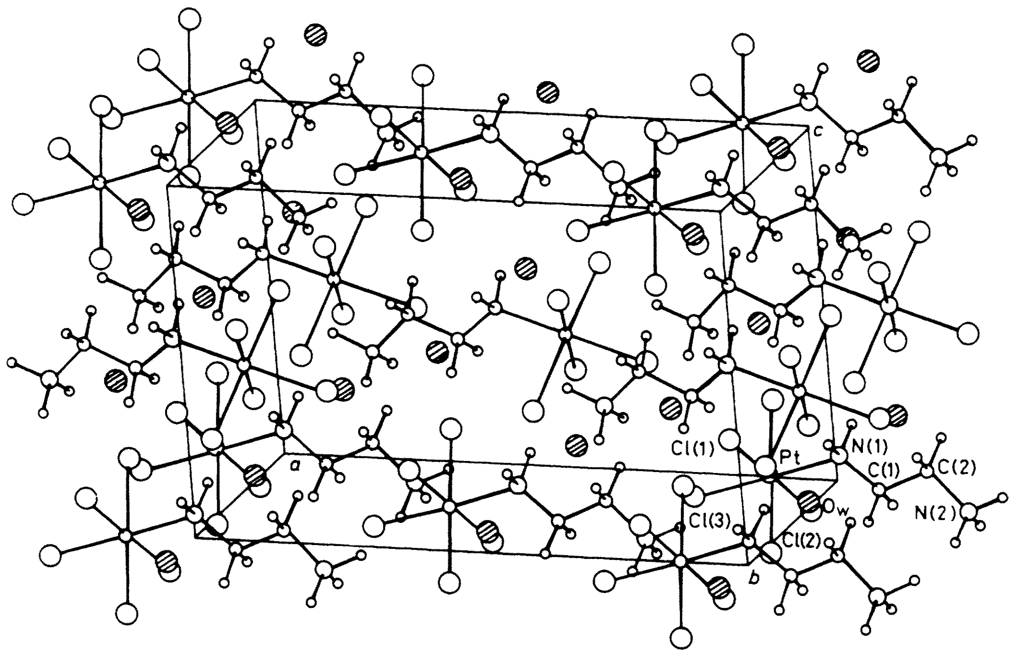

Figure 2. Perspective view of the packing of complexes $[PtCl_5(Hen)]$ and water molecules

complex as a whole has crystallographically imposed *m* symmetry with the metal, Cl(3), and all the non-hydrogen atoms of the Hen^+ ligand lying in the mirror plane. All five Pt-Cl bonds are equal (ranging from 2.294 to 2.306 Å) and are practically identical to those observed in either six-co-ordinated platinum(IV) or four-co-ordinated platinum(II) complexes.[18-20] For instance, in trichloro-9-methyladeniniumplatinum(II), the Pt-Cl distances are in the range 2.297—2.302 Å.[7] Also the present Pt-N distance [2.050(4) Å] falls in the range of values found in complexes of Pt^{IV} and Pt^{II} with amines [*e.g.* 2.053(5) Å for *trans*-diamminebis(pentane-2,4-di-iminato)platinum diperchlorate [21]] in spite of the fact that an adjacent ammonium cation could have been expected to weaken this bond either by an inductive effect transmitted through the organic chain or by a charge interaction through space.

In the Hen^+ ligand the C-N bond distances are different [C(1)-N(1) 1.420(8) and C(2)-N(2) 1.501(7) Å], the longer one being that to the protonated nitrogen. These bonds are perfectly *trans* with respect to the C(1)-C(2) bond because of symmetry restrictions.

The packing of the platinum complexes and water molecules of crystallization is shown in Figure 2 and is determined only by normal van der Waals contacts. It is noteworthy that the water molecules are not involved in hydrogen bonds either with the chlorine atoms or with the nitrogen atoms of the complexes, the shortest contacts $O_w \cdots Cl$, $O_w \cdots N$, and $Cl \cdots N$ ranging from 3.37 to 3.44 Å.

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*
Pt	1 179(1)	0	0
Cl(1)	1 471(3)	2 365(7)	1 582(5)
Cl(2)	876(3)	2 377(7)	−1 573(6)
Cl(3)	2 605(4)	0	−677(8)
O_w	−324(19)	5 000	613(31)
N(1)	−81(17)	0	672(25)
N(2)	−2 354(16)	0	−698(25)
C(1)	−786(22)	0	−255(32)
C(2)	−1 669(22)	0	383(34)

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