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Facile Isolation and Crystal Structure Determination of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$

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A substitution-inert OH group has facilitated the isolation of the first hydrolysis product of *trans*-diamminedichloroplatinum(II); the crystal structure of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$ has been determined.

Binding of *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ to DNA involves the substitution of the labile chloro ligands by nitrogen atoms of nucleobases.[1] In both cases hydrolysis of the first chloro ligand appears to be the rate-limiting step in the complexation.[2] The chemotherapeutic inactivity of the *trans* isomer, a long-standing puzzle, may well result from different properties of the first hydrolysis products. Although the binding properties[3] and basic aqueous chemistry[3,4] of *cis*-$[PtCl(NH_3)_2(H_2O)]^+$ are relatively well characterized, far less is known about the corresponding *trans* isomer.[5] This may, in part, be attributed to general experimental difficulties in preparing the aqua derivatives of *trans*-$[PtCl_2(NH_3)_2]$, as outlined recently by Appleton *et al.*[5] Apart from these solution studies there seems to be no information on the preparative isolation and structural characterization in the solid state of the first hydrolysis products in the literature, in spite of their fundamental role in the aqueous chemistry of both isomers.

In this paper we report the first preparative isolation and crystal structure determination of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$. We have shown previously that a hydroxo group bound to Pt^{II} is inert toward substitution reactions relative to a co-ordinated aqua ligand.[6] In addition, the rate of hydrolysis of the first chloro ligand in *trans*-$[PtCl_2(NH_3)_2]$ is expected to be much more rapid than that of the second, because the *trans* effect of Cl^- is greater than H_2O or OH^-.[7] Accordingly, upon carefully controlled hydrolysis of *trans*-$[PtCl_2(NH_3)_2]$ under basic conditions the compound *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$ was isolated in moderate yield (50%),† and was recrystallized from the minimum amount of 5 mmol dm^{-3} NaOH solution to give crystals (pale yellow-green prisms) suitable for X-ray analysis. The selected crystal was sealed in a capillary to avoid decomposition due to the loss of water of crystallization.‡

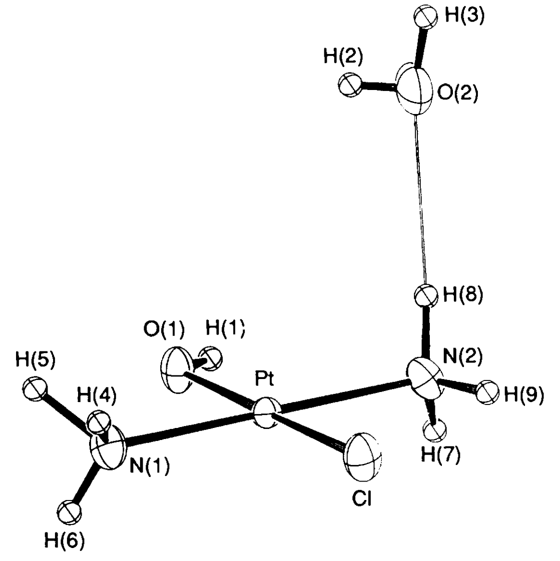

Fig. 1 Molecular structure of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$. Selected intramolecular distances (Å) and angles (°): Pt–Cl 2.302(3), Pt–O(1) 1.989(7), Pt–N(1) 2.024(7), Pt–N(2) 2.048(7); Cl–Pt–O(1) 177.3(2), Cl–Pt–N(1) 90.1(3), Cl–Pt–N(2) 90.4(2), O(1)–Pt–N(1) 88.0(3), O(1)–Pt–N(2) 91.4(3), N(1)–Pt–N(2) 179.5(3). The positions of the hydrogen atoms were found from the electron-density maps, except for those of N(2), which were obtained from the idealized geometry

The molecular structure of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$ shows that the platinum atom has an almost idealized square-planar geometry (Fig. 1). The angles N(1)–Pt–N(2) and Cl–Pt–O(1) are 179.5(3) and 177.3(2)°, respectively, and the other four angles around Pt^{II} range from 88.0(3) to 91.4(3)°. The Pt–O bond length of 1.989(7) Å is comparable to those of 1.99(1) and 2.03(1) Å found for the nitrate oxygens in *cis*-$[Pt(NO_3)_2(NH_3)_2]$,[9] and to the Pt–O bond length of 2.03(1) Å in the OH-bridged dimer $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2][NO_3]_2$.[10] The Pt–N distances of 2.024(7) and 2.048(7) Å are within the expected range, and are close to that reported earlier for *trans*-$[PtCl_2(NH_3)_2]$, *viz.* 2.05(4) Å.[11] Interestingly, the Pt–Cl bond length of 2.302(3) Å is very similar to those found in *trans*-$[PtCl_2(NH_3)_2]$[2.32(1) Å],[11] and in *trans*-$[PtCl(NH_3)_2(Me_2SO\text{-}S)]^+$ [2.307(5) Å].[12] Although the *trans* influence of the relevant ligands decreases in the order $Me_2SO > Cl^- > OH^-$,[7] it seems to have no major effect on the Pt–Cl bond length.

The packing of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$ is affected by extensive hydrogen bonding (Fig. 2), the importance of which has been suggested earlier for the crystallization of aqua derivatives of Pt^{II}.[13] A relatively strong hydrogen bond

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† After the addition of 1.2 equivalents of NaOH to the aqueous solution of *trans*-$[PtCl_2(NH_3)_2]$ (1 mmol in 100 cm^3) the mixture was stirred under nitrogen in the dark for 80 min at 55–65 °C. The removal of hydrolysed Cl^- ions with $AgClO_4$ prior to the concentration of the reaction mixture facilitated the isolation of *trans*-$[PtCl(OH)(NH_3)_2]\cdot H_2O$ (Found: H, 3.15; Cl, 12.2; N, 9.10. $H_9ClN_2O_2Pt$ requires H, 3.05; Cl, 11.8; N, 9.35%), which dissolves readily in water, acid and in alkali.

‡ Crystal data. $H_9ClN_2O_2Pt$, $M = 299.63$, crystal size 0.18 × 0.22 × 0.32 mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.0340(9)$, $b = 4.3598(6)$, $c = 17.421(2)$ Å, $\beta = 93.41(1)°$, $U = 609.1(1)$ Å^3, $Z = 4$, $D_c = 3.267$ g cm^{-3}. Data were collected at 23 °C [1166 reflections with $I > 3.00\sigma(I)$] on a Rigaku 5S diffractometer using Mo-Kα radiation ($\lambda = 0.710\,69$ Å); $2\theta_{max} = 55°$. The structure was solved by the Patterson method and refined to $R = 0.028$ and $R' = 0.034$ using the TEXSAN-TEXRAY[8] system $\{R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, where $w = 1/\sigma^2(F)\}$. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

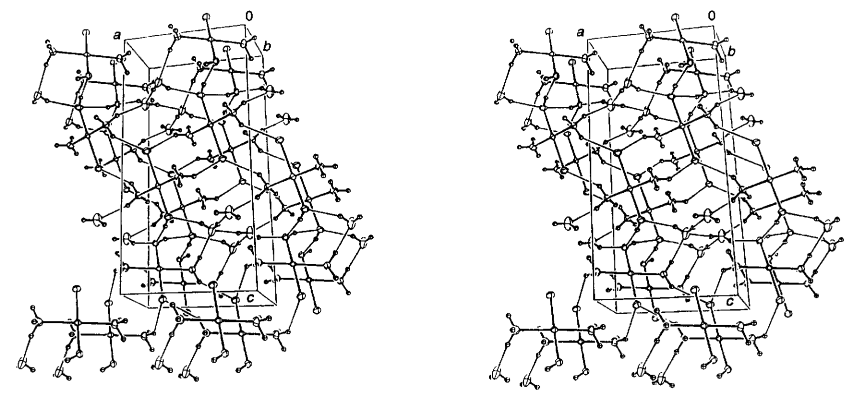

Fig. 2 Packing of *trans*-[PtCl(OH)(NH$_3$)$_2$]·H$_2$O. Thin lines represent proposed H bonds

connects the water molecule to the OH group [O(2) ··· O(1$^{\mathrm{I}}$) 2.68(1) Å, O(2)–H(2) ··· O(1$^{\mathrm{I}}$) 155.8°].* In addition, the OH groups of the neighbouring molecules form medium hydrogen bonds to each other [O(1) ··· O(1$^{\mathrm{II}}$) 2.878(8) Å, O(1)–H(1) ··· O(1$^{\mathrm{II}}$) 165.1°], whereas the water molecules are adjoined by quite strong hydrogen bonds [O(2) ··· O(2$^{\mathrm{III}}$) 2.784(9) Å, O(2)–H(3) ··· O(2$^{\mathrm{III}}$) 172.7°]. The ammine groups are hydrogen bonded to the Cl atom and to the oxygen atom of the water molecule [N(2) ··· Cl$^{\mathrm{IV}}$ 3.401(8) Å, N(2) ··· O(2) 3.21(1) Å, and N(1) ··· Cl$^{\mathrm{V}}$ 3.378(9) Å]. By contrast, the N(1) ··· O(2$^{\mathrm{I}}$) contact of 3.38(1) Å seems insignificant. In particular, the inclusion of the latter would give the oxygen atom of the water molecule a formal co-ordination number of five, which is unrealistic.

This convenient method for the isolation of *trans*-[PtCl(OH)(NH$_3$)$_2$]·H$_2$O is of great help in the quantitative study of the reactions of *trans*-[PtCl$_2$(NH$_3$)$_2$]. By employing the hydrolysis product as a starting material the important intermediate *trans*-[PtCl(NH$_3$)$_2$(H$_2$O)]$^+$ can be generated *in situ* under acidic conditions without the strong intervening influence of Cl$^-$ ion.[14] In addition, preliminary results indicate that an analogous method is also applicable to the isolation of the corresponding diaqua derivative.

Acknowledgements

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* Symmetry relations defined by roman numerals. I $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; II $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; IV $2 - x, 1 - y, 2 - z$; V $1 - x, 1 - y, 2 - z$.