

Short Communication

X-Ray Crystal Structure Determination and Spectroscopic Characterization of *trans*-Diamminedihydroxoplatinum(II) Dihydrate

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The reaction pattern of *cis*- and *trans*-[PtCl₂(NH₃)₂] with biologically important compounds, e.g. nucleic acid constituents, is very complicated because of solvolysis of the dichloro species.¹ In aqueous solution, in particular, the hydrolysis products of both isomers play an important role in the complexation.^{2,3} Therefore, establishment of different binding modes of Pt(II) is much more convenient with the aqua derivatives than with the dichloro species.⁴ Using Ag⁺ ions both chloro ligands can be easily replaced by water molecules in the case of *cis*-[PtCl₂(NH₃)₂], while far more forcing conditions are required for the *trans* isomer.⁵ There are few reports of the isolation of Pt(II) compounds with terminal aqua or hydroxo groups. Concentration of acidic aqueous solutions of both mono-⁶ and bifunctional Pt(II)⁷ amines has given species in which the vacant coordination sites are occupied by anions present in solution. On the other hand, under neutral conditions hydroxo-bridged oligomers have been obtained.⁸ Only a few examples of complexes with one terminal aqua or hydroxo group have been reported.^{9,10}

Recently, we have shown that carefully controlled hydrolysis of *trans*-[PtCl₂(NH₃)₂] in the presence of 1.2 equiv. of base gives *trans*-[PtCl(OH)(NH₃)₂]·H₂O in a moderate yield,¹⁰ whereas prolonged treatment of the dichloro compound in the presence of 2.2 equiv. of base yields the corresponding dihydroxo derivative, which can be isolated in a 60% yield as a dihydrate.³ In this paper we report the first crystal structure determination of *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O and its characterisation by IR and [¹H, ¹⁵N] NMR spectroscopies.

Results and discussion

Spectroscopic characterisation. The IR spectrum of *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O shows three broad absorptions centered at about 3300, 1600 and 850 cm⁻¹ typical of the stretching, bending and rotational modes of lattice water, respectively.¹¹ The rather high frequency for the rotational mode may be attributed to extensive hydrogen bonding in the lattice (*vide infra*). The broad band at about 1150 cm⁻¹ may be assigned to the PtOH bending mode, which is expected to appear below 1200 cm⁻¹.¹¹ For example, in [Pt(OH)₆]²⁻ this mode absorbs at 1065 cm⁻¹.¹² The strong band at 525 cm⁻¹ and the weak one at 496 cm⁻¹ are probably due to the ν(Pt–N) and ν(Pt–O) modes, although their unambiguous assignments are difficult. TG analyses (using a Mettler TA 1 thermo-analyzer) show that the compound loses about 11% of its weight between 40 and 90°C, which corresponds to the removal of two molecules of water per formula unit. The IR spectrum of the dried substance shows no absorption for lattice water, whereas the skeletal modes remain practically unaffected and absorb at 530 and 498 cm⁻¹. The PtOH bending mode appears to shift from 1150 to 1053 cm⁻¹ (broad), which may be attributed to changes in hydrogen-bonding interactions by the OH groups due to the loss of water of crystallization. In addition, the dried substance shows strong bands at 1580 and 922 cm⁻¹ typical of NH₃ asymmetric deformation and NH₃ rocking vibrations, respectively.¹¹ Accordingly, these findings are fully consistent with the formulation that the OH group is bound to Pt^{II} rather than H₂O.

It is worth noting that *trans*-[PtCl(OH)(NH₃)₂]·H₂O, whose structure has been confirmed by X-ray crystallography,¹⁰ behaves very similarly. According to TG analy-

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Table 1. Crystallographic data for *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O^a

Formula	H ₁₂ N ₂ O ₄ Pt
Formula weight	299.20
Crystal dimensions/mm	0.16×0.22×0.20
Crystal system and space group	Monoclinic, <i>P2₁/a</i>
Z	4
Cell constant determination	24 reflections (49.2 < 2θ < 49.9°)
a/Å	9.5811(6)
b/Å	4.4350(6)
c/Å	15.5616(6)
β/°	106.922(4)
V/Å ³	632.62
D _{calc} /g cm ⁻³	3.141
Mo K _α radiation	λ = 0.71069 Å
μ/cm ⁻¹	223.48
θ _{max}	27.5°
h, k, l range	12, 6, ±20
Absorption correction	PSI-scan and DIFABS (trans.factors: 0.81–1.33) Decay (1.03% decline) Secondary extinction (coefficient: 1.5531 × 10 ⁻⁶)
No. of reflections collected	1735
No. of unique reflections	1691
R _{int}	0.059
No. of observed reflections	544 [I > 3.00 σ(I)]
No. of variables	68
R	0.031
R _w	0.048
Δρ _{max} /Δρ _{min}	2.04/–1.30

^a Hydrogen atom parameters were not refined.

sis it loses about 5% of its weight between 65 and 100°C, which corresponds to the removal of approximately one water molecule per formula unit. This treatment is accompanied by the disappearance of the absorptions of lattice water, while bands at 548 and 503 cm⁻¹ assigned to skeletal modes are only slightly shifted to 532 and 500 cm⁻¹. In addition, the dried substance shows two bands at 1613 and 905 cm⁻¹ which may be assigned to NH₃ asymmetric deformation and NH₃ rocking vibrations, respectively.¹¹ As observed for the dihydroxo species, these bands are not resolved for the hydrate. For *trans*-[PtCl(OH)(NH₃)₂]·H₂O the broad band at 1134 cm⁻¹ may be assigned to the PtOH bending mode, whereas several bands appear at 1100–950 cm⁻¹ after removal of lattice water, although it is not clear which one of these represents this vibration. Thus, *trans*-[PtCl(OH)(NH₃)₂]·H₂O and *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O have very similar IR spectroscopic properties, consistent with the presence of OH ligands.

Trans-[Pt(OH)₂(¹⁵NH₃)₂]·2H₂O was prepared by hydrolyzing the ¹⁵N-labelled dichloro species⁵ under basic conditions. A 10 mM solution of this complex in 90% H₂O/10% D₂O gave rise to a [¹H, ¹⁵N] cross-peak at –64.1, 3.81 ppm in the 2D HMQC [¹H, ¹⁵N] NMR spectrum at 298 K, recorded as previously described.^{13,14} (¹H shifts are referenced to TSP, and ¹⁵N shifts to external 1.5 M NH₄Cl in 1 M HCl.) ¹⁹⁵Pt satellites were observed with ¹J(¹⁹⁵Pt, ¹⁵N) 305 Hz and ²J(¹⁹⁵Pt, ¹H) 68 Hz. These shifts and couplings are consistent with the

presence of *trans* ammine and *trans* hydroxo ligands.⁵ Two minor cross-peaks (accounting for <2% of the total intensity) at –64.1, 3.84 ppm and –59.1, 4.11 ppm are assignable to *trans*-[PtCl(OH)(NH₃)₂], and either *trans*-[Pt(OH)(NH₃)₂]₂(μ-OH)⁺ or *trans*-[PtCl(NH₃)₂]₂(μ-OH)⁺, respectively.⁵

X-Ray diffraction study. All data were collected on a Rigaku AFC5S diffractometer at 23°C. Crystals suitable for X-ray structure determination were obtained by dissolving the dihydroxo compound in the minimum amount of 0.005 M NaOH solution, and allowing the solvent to evaporate slowly over dry DMF in a sealed system at room temperature. Long, pale-yellow prisms of *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O appeared after 4 days. An appropriately sized piece of crystal was cut and sealed in a

Table 2. Atomic coordinates and equivalent temperature factors, B_{eq}, for *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O.

Atom	x	y	z	B _{eq} ^a
Pt(1)	0.000	0.000	0.500	1.42(7)
Pt(2)	0.000	0.000	0.000	1.28(7)
O(1)	–0.214(2)	0.088(4)	0.450(1)	1.4(6)
O(2)	0.173(2)	–0.061(3)	–0.046(1)	1.2(7)
O(3)	–0.289(2)	0.319(6)	0.294(1)	5(1)
O(4)	0.076(2)	–0.276(7)	–0.207(1)	5(1)
N(1)	0.013(2)	0.270(5)	0.610(1)	1.8(9)
N(2)	0.091(2)	–0.262(6)	0.111(1)	2(1)

$$^a B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

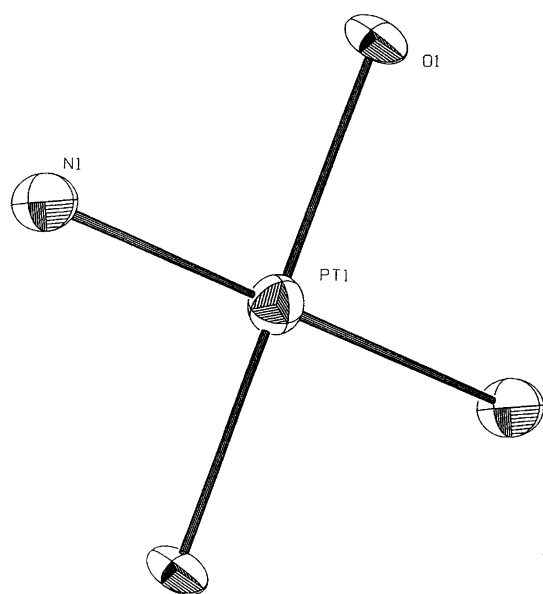


Fig. 1. View of one of two independent molecules of *trans*-[Pt(OH)₂(NH₃)₂].

Table 3. Selected bond distances (in Å) and angles (in °) for *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O.

Pt(1)–O(1)	2.01(1)	O(1)–Pt(1)–N(1)	90.9(7)
Pt(1)–N(1)	2.07(2)	O(1)–Pt(1)–N(1)	89.1(7)
Pt(2)–O(2)	2.01(2)	O(2)–Pt(2)–N(2)	91.9(7)
Pt(2)–N(2)	2.05(2)	O(2)–Pt(2)–N(2)	88.1(7)

capillary to prevent decomposition due to the loss of water of crystallization. The structure was solved by stan-

dard Patterson and difference Fourier methods and refined by full-matrix least-squares calculations employing MSC (Texsan) program package.¹⁵ Crystal data, details on data collection and refinements are given in Table 1 and atomic parameters in Table 2.

The Pt coordination spheres in both crystallographically-independent molecules of *trans*-[Pt(OH)₂(NH₃)₂] are approximately square-planar with N–Pt–O angles between 88.1(7) and 91.9(7)° (Fig. 1). Selected interatomic distances and angles are given in Table 3. Although the X-ray data obtained do not permit unambiguous determination of the hydrogen atoms, the spectroscopic data and TG analysis strongly support the formulation presented above. The Pt–N distances of 2.05(2) and 2.07(2) Å are within the expected range, and close to those reported for *trans*-[PtCl(OH)(NH₃)₂]·H₂O, viz. 2.024(7) and 2.048(7) Å.¹⁰ Interestingly, the Pt–O bond lengths of 2.01(1) Å are very similar to the Pt–O distances found in *trans*-[PtCl(OH)(NH₃)₂]·H₂O [1.989(7) Å]¹⁰ and in *cis*-[Pt(NO₃)₂(NH₃)₂] [1.99(1) and 2.03(1) Å].⁷ Differences in the *trans* influences of these ligands are therefore not detectable from the Pt–O bond lengths; an analogous situation has been found in the case of Pt–Cl distances when the *trans* donors are S, Cl or O.¹⁰ By contrast, comparison of the rate parameters for the hydrolysis of *trans*-[PtCl₂(NH₃)₂] ($k_1 = 1.05 \times 10^{-3} \text{ s}^{-1}$) and *trans*-[PtCl(OH)(NH₃)₂] ($k_{2,\text{OH}} = 2.0 \times 10^{-5} \text{ s}^{-1}$) reveals a considerable *trans* effect Cl⁻ > OH⁻.³

The packing of *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O is affected by extensive hydrogen bonding between the OH groups and water molecules (Fig. 2). A strong hydrogen bond connects the OH group to a water molecule [O(1)···O(3) = 2.54(2) Å, O(2)···O(4) = 2.59(2) Å], and water molecules are connected by medium strength H-bonds to each other [O(3)···O(4') = 2.72(2) Å,

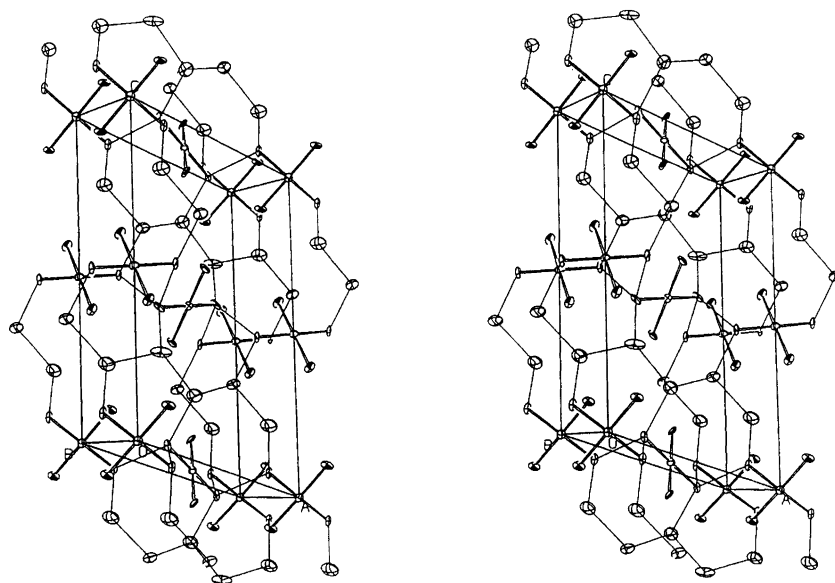


Fig. 2. Proposed hydrogen bonding (thin lines) between the oxygen atoms in *trans*-[Pt(OH)₂(NH₃)₂]·2H₂O.

$O(3)\cdots O(4^{II}) = 2.76(2) \text{ \AA}$.[†] There may be weak intermolecular H-bonds between coordinated OH groups [$O(1)\cdots O(1^{III}) = 2.91(2) \text{ \AA}$, $O(2)\cdots O(2^{IV}) = 2.82(2) \text{ \AA}$, and, in addition, the OH groups may form weak intermolecular H-bonds to the ammine groups [$O(1)\cdots N(1^V) = 3.08(2) \text{ \AA}$, $O(2)\cdots N(2^{IV}) = 3.03(2) \text{ \AA}$]. Other $O\cdots N$ distances are all above 3.2 \AA . The proposed H-bond network of the oxygen atoms closely resembles that found in *trans*-[PtCl(OH)(NH₃)₂] \cdot H₂O.¹⁰ In addition, both of these cases give strong support to the earlier suggestion⁶ of the importance of hydrogen bonding and hydration to the existence of Pt^{II}-OH bonds in the solid state.

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[†] Symmetry relations are defined by roman numerals:
^I $-1/2 - x, 1/2 + y, -z$; ^{II} $-x, -y, -z$; ^{III} $-1/2 - x; 1/2 + y, 1 - z$;
^{IV} $1/2 - x, 1/2 + y, -z$; ^V $-1/2 - x, 1/2 - y, 1 - z$.