

## THE SYNTHESIS AND NMR STUDY ON THE STABILITY OF DIMETHYLMETHOXOPLATINUM(IV) COMPLEXES

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### ABSTRACT

The synthesis of two stable platinum(IV) complexes containing methoxo ligand,  $[Pt(CH_3)_2(OCH_3)(OH)py_2]$  (**1**) and *fac*- $[Pt(CH_3)_2(OCH_3)(H_2O)_3]$  (**2**), has been successfully performed. Complex **1** was prepared by oxidative addition reaction of *cis*- $[Pt(CH_3)_2py_2]$  with dry methanol, and a subsequent reaction of **1** with 70 %  $HClO_4$  in water produced the platinum complex **2**. The stability of complex **2** in acidic aqueous solution was investigated and monitored with  $^1H$  and  $^{195}Pt$  NMR. The platinum complex **2** was found to be quite stable toward hydrolysis and no  $\beta$ -hydride elimination was observed.

**Keywords:** Methoxoplatinum(IV), NMR, complex stability, hydrolysis

### INTRODUCTION

The preparation of new organoplatinum(II) and (IV) complexes is still challenging work which is currently still attracting much attention for platinum chemist. This is not merely due to their uses as anti-tumour agent such as in cisplatin complex, *cis*- $[Pt(NH_3)_2Cl_2]$  and its derivatives and some new class of platinum drugs [1] but they also look closely at the interesting features of some new class of the platinum complexes.

The NMR study for two methoxoplatinum(IV),  $[Pt(CH_3)_2(OCH_3)(OH)(py)_2]$  (**1**) and  $[Pt(CH_3)_2(OCH_3)(H_2O)_3]^+$  (**2**) has been undertaken to find out and understand the behaviour of these complexes and to monitor their stability in acidic solution. This was performed as it is believed that these methoxoplatinum(IV) complexes have interesting and different characteristics to those of platinum(II) alkoxide in particular or metal alkoxide complexes in general [2].

Most transition metal methoxo complexes, as generally known, are susceptible to hydrolysis of the M-OMe bond to give methanol and/or  $\beta$ -hydride elimination to produce a metal hydride plus formaldehyde [3]. Complex **2**, however, was prepared in boiling aqueous perchloric acid solution, and it was stable under the condition used.

Some other platinum(IV) complexes containing methoxo ligand, such as  $[Pt(CH_3)_2(OCH_3)(OH)(bpy)] \cdot H_2O$  [4] and  $[Pt(CH_3)_2(OCH_3)(OH)(ox)_2]^{2-}$  [5] (*bpy* = 2,2'-bipyridil, *ox*<sup>2-</sup> = oxalate), have also been reported as relatively resistant to the decomposition reaction

that normally occurred in metal alkoxide complexes. So it would be interesting to have a new class of metal alkoxide complex which shows different characteristics to those metal alkoxides in general.

### EXPERIMENTAL SECTION

#### General

The  $^1H$  NMR spectra were recorded on a Bruker AC 200 F spectrometer operating at 200 MHz fitted with a 5 mm  $^1H$ ,  $^{13}C$ ,  $^{15}N$ ,  $^{19}F$  Quad Probe. A spectral width of 2,000 Hz - 2,500 Hz was employed together with 16 - 96 scans to obtain the desired F.I.D. A recycle time of 4 s was used with a pulse width of 3.6  $\mu s$  (thus a tilt angle of 45 degrees was used). The number of data points obtained was 16K. All shifts are positive to higher frequency.  $^1H$  shifts are relative to the methyl signal of sodium 3-trimethylsilylpropane-1-sulfonate (TSS) for aqueous solvent and to internal tetramethylsilane (TMS) for non-aqueous solvents.

The  $^{195}Pt$  spectra were recorded at 86.07 MHz on a Bruker AMX 400 spectro-meter fitted with a 5 mm broadband probe. The magnetisation tilt angle was 90°. A recycle time of 0.066 s was used with a pulse width of 23  $\mu s$ . The spectra obtained were both proton coupled and proton decoupled. A Spectral width used was 125,000 Hz. The number of scans used to obtain spectra varied from 1000 to 20,000. The number of data points obtained was 16K.  $^{195}Pt$  shifts relative to a separate sample containing an aqueous solution of  $Na_2[PtCl_6]$  (0.5 g  $ml^{-1}$ ) ( $\delta_{Pt} = 0$ ).

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### Materials

All solvents used were AR Grade. For some solvents (diethyl ether and methanol) were required further purification by standard method, for example, the following procedure has been used to purify diethyl ether: To 1 L of diethyl ether was added 200 g of CaCl<sub>2</sub> anhydrous, it was kept in the dark bottle for overnight, mixed with CaH<sub>2</sub>, and finally distilled under either high purity grade Argon or Nitrogen.

Published methods were used to prepare PtCl<sub>2</sub>(NBD) (NBD = Norbornadiene or bicyclo[2,2,1]hepta-1,3-diene) [6], Pt(CH<sub>3</sub>)<sub>2</sub>(NBD) [7], and *cis*-Pt(CH<sub>3</sub>)<sub>2</sub>py<sub>2</sub> (py = pyridine) [8, 9].

### Preparation of [Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(OH)(py)<sub>2</sub>]

*Cis*-[Pt(CH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] (1 g, 2.611 mmol) was dissolved in 40 mL of dry methanol. The solution was protected from moisture with a drying tube, but not from air, as it has been shown [10] that the analogous reaction of [Pt(CH<sub>3</sub>)<sub>2</sub>(bpy)] (bpy = 2,2'-bipyridil) with methanol proceeds only when dioxygen is present. The solution was allowed to stand for 6 hours or more. The solvent was then removed under high vacuum (reduced pressure) for 3- 4 hours. Further exposure of the sample to high vacuum produced a material whose <sup>1</sup>H NMR spectrum showed no methoxide peak. The oily residue was washed successively with small volume of water, then with acetone, and dried in a vacuum desiccator over calcium chloride for several days. The resultant white solid was dissolved in the minimum volume of dichloromethane and reprecipitated by addition of *n*-hexane, filtered off,

washed with *n*-hexane and dried in a vacuum desiccator. Yield of analytically pure Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(OH)(py)<sub>2</sub> (**1**) was 80 %. (Elemental analysis Found (Calc.) C = 31.3 (31.1); H = 5.8 (5.6); N = 5.7 (5.6)).

### Preparation of [Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup>

[Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(OH)(py)<sub>2</sub>] (1 g, 2.32 mmol) was suspended in 10 mL of H<sub>2</sub>O or D<sub>2</sub>O and 1 mL of 70 % HClO<sub>4</sub> was added. The solid dissolved and the solution was heated at 80° C for 15 minutes, and then filtered. The solution contained [Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> as well as pyridinium salt, Hpy<sup>+</sup>.

### RESULTS AND DISCUSSION

The methoxoplatinum(IV) complex, [Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(OH)(py)<sub>2</sub>] (**1**) was prepared by oxidative addition of dry methanol to *cis*-[Pt(CH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] as shown in Fig 1. Rostovtsev *et al.* [10] have shown that the reaction of [Pt(CH<sub>3</sub>)<sub>2</sub>(N-N)] (N-N = bpy, phen and tmeda) with methanol always involves dioxygen. The mechanism of this reaction is not clear, but they suggested that radical intermediates are involved. It is likely that the reaction of *cis*-[Pt(CH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] with methanol in this work also involves dioxygen

When the methanol used in this preparation reaction contains water molecules, without any further purification, there would be a competition between small portion water present in methanol and methanol itself with *cis*-[Pt(CH<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] and this will lead to a mixture of the product complex **1** and the possible product [Pt(CH<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(py)<sub>2</sub>] (**3**).

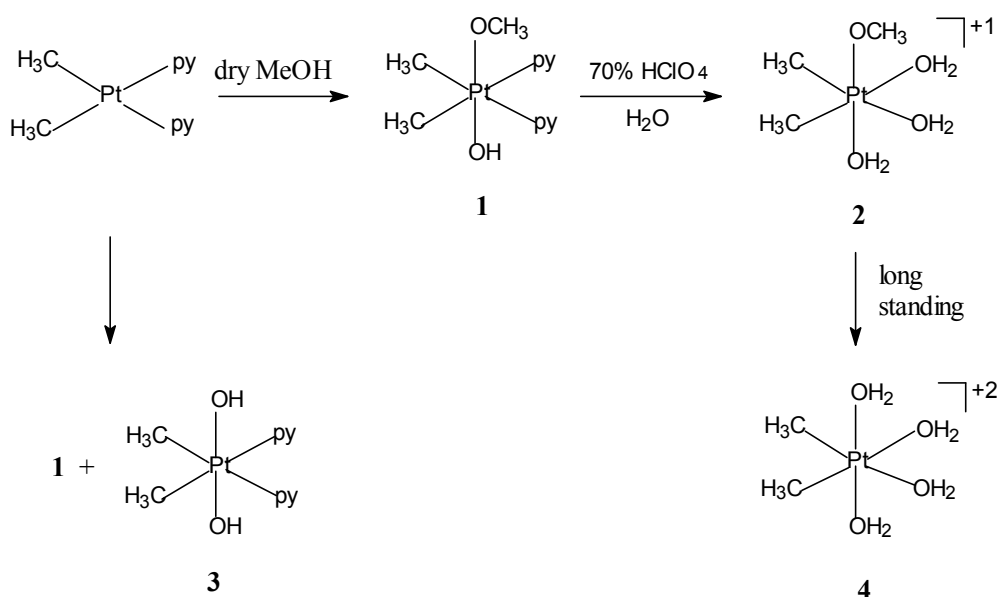
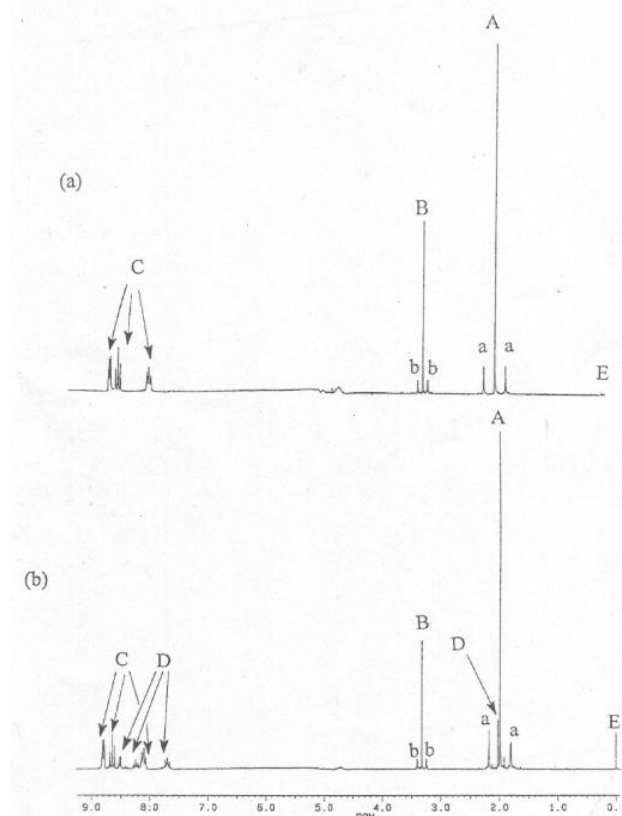


Figure 1 The preparative route of complex 1 and 2

The proton decoupled  $^{195}\text{Pt}$  NMR of **1** shows a singlet peak at  $-806$  p.p.m. relative to  $\text{Na}_2[\text{PtCl}_6]$  as external standard. This peak is similar to that of the product of reaction between  $[\text{Pt}(\text{CH}_3)_2(\text{bpy})]$  and dry methanol,  $[\text{Pt}(\text{CH}_3)_2(\text{OCH}_3)(\text{OH})(\text{bpy})]$ ,  $-803$  p.p.m. Preparation of this compound was previously reported [4]. The complex **2** was obtained by a subsequent reaction of **1** with water and 70% perchloric acid and heating at  $80^\circ\text{C}$  for 15 minutes. The amount of perchloric acid used and temperature control are very important, as they will affect the platinum product obtained.

In the  $^1\text{H}$  N.M.R. spectrum of **2** in  $\text{D}_2\text{O}$  solvent, the methyl groups give a singlet with satellites (**A, a**) at  $2.04$  p.p.m. and  $^2J(\text{Pt} - \text{CH}_3)$   $75.6$  Hz and another singlet with satellites peaks (**B, b**) from methoxide at  $3.2$  p.p.m. and  $^2J(\text{Pt} - \text{CH}_3)$   $30.1$  Hz as well as a set of three pyridinium ion peaks,  $\text{Hpy}^+$  present in the solution mixture.

Figure 2 (a) shows the spectrum when the product **2** was obtained in solution are clearly free from impurities. The  $\delta_{\text{H}}$  from proton N.M.R. of **2**



**Figure 1** 200.13 MHz  $^1\text{H}$  NMR of (a) Freshly and cleanly prepared of solution **1** (b) Solution containing **1** with some impurities; Aa = Pt- $\text{CH}_3$  in **1**, Bb = Pt- $\text{OCH}_3$  in **1**, C = Set of three pyridinium peaks ( $\text{Hpy}^+$ ), D = Impurities, E = Reference (TSS = sodium-3-trimethylsilylpropane sulfonate)

solution depends on the acidity of the solution used and the variation value range is about  $0.1 - 0.2$  p.p.m.

However, in the preparation of **2**, there are often some impurities present as shown in the proton N.M.R. spectra (an example is in Figure 2 (b)). In Figure 2 (b), the impurity peaks labeled **D** correspond to three sets of pyridine peaks and a singlet with satellites from Pt- $\text{CH}_3$ .

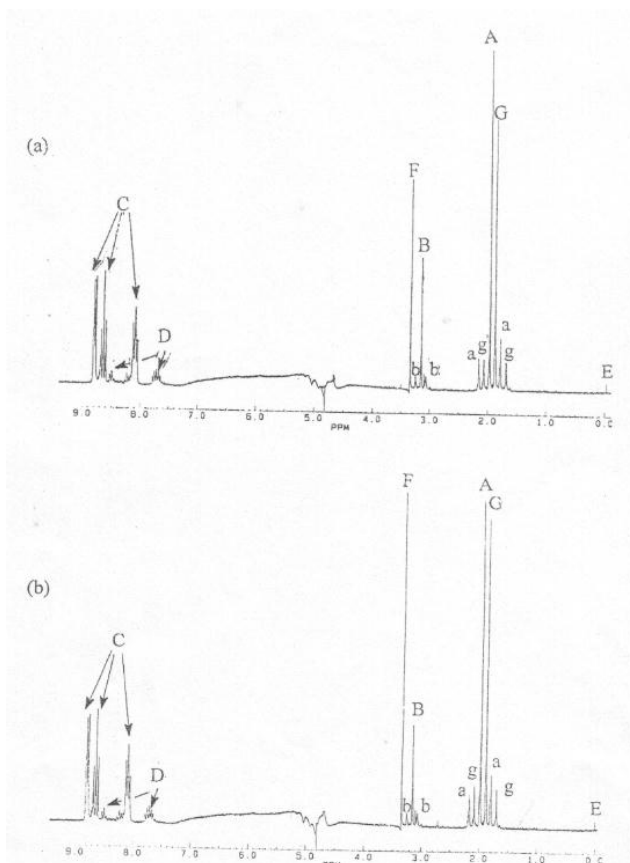
The proton decoupled  $^{195}\text{Pt}$  N.M.R. spectrum of a solution containing **2** gives a sharp singlet peak at  $-556$  p.p.m. relative to  $\text{Na}_2\text{PtCl}_6$  as an external standard. The proton coupled spectrum is a simple septet from Pt- $\text{CH}_3$  coupling confirming that the compound contained two Pt- $\text{CH}_3$  groups, the coupling with the methoxide proton was not resolved. The  $\delta_{\text{Pt}}$  is also dependent on the acidity of solution used in the measurement and the approximate range of this  $\delta_{\text{Pt}}$  is from  $-530$  to  $-556$  p.p.m. The more acidic the solution used, the more negative the value (the lower the frequency).

Part of the interest in complex **2** is its high stability toward both hydrolysis and  $\beta$ -hydride elimination in this acidic aqueous solution. It is, however, not completely inert towards these reactions.

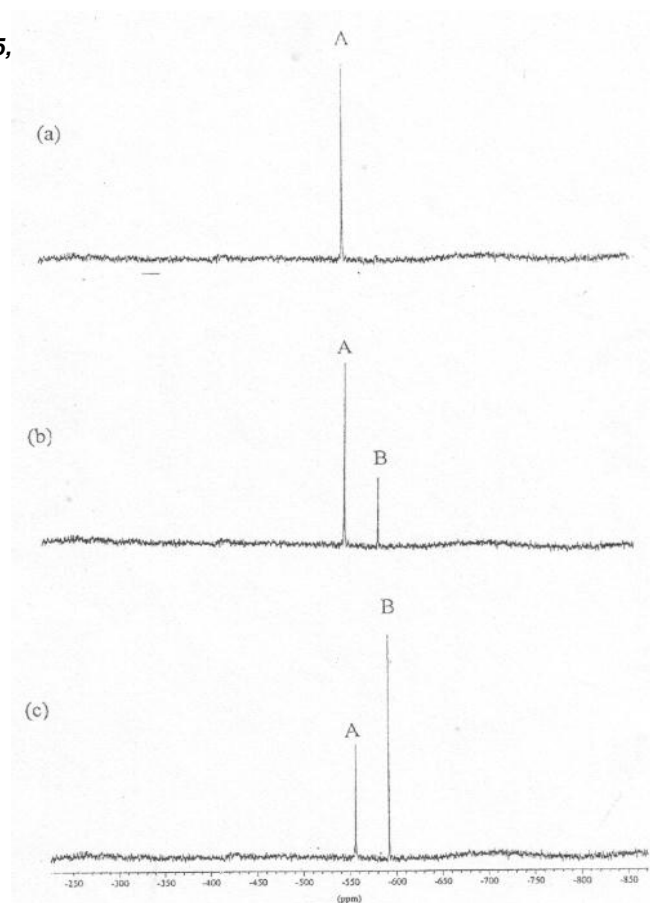
Slow hydrolysis occurs when the solution of **2** is left outside on the bench for long periods (2 months or more), but with exposure to normal laboratory light, no example of  $\beta$ -hydride elimination was observed during the study of this complex.

The slow hydrolysis of **2** has been monitored mainly with  $^1\text{H}$  N.M.R. (Figures 2 (a) and (b)) and  $^{195}\text{Pt}$  N.M.R. (Figure 3). From the  $^1\text{H}$  N.M.R. spectrum, after about three months, another singlet with satellite in methyl region was observed (**G, g** label) i.e. at  $1.98$  p.p.m. and  $^2J(\text{Pt} - \text{CH}_3)$   $75.8$  Hz and this similar to what has been reported by Agnew *et al.*<sup>9</sup> (reported value:  $\delta_{\text{H}}$   $2.04$  p.p.m. and  $^2J(\text{Pt} - \text{CH}_3)$   $75.8$  Hz), and this was accompanied by the appearance of a singlet peak at  $3.33$  p.p.m. which was assigned free methanol (**F**). The intensity of these additional peaks are continued to increase with time as the solution was left on the bench for about six months. This free methanol is derived from the methoxide bound to platinum, which was displaced by water as in Fig 1.

In  $^{195}\text{Pt}$  N.M.R. spectra (Figure 4), an additional peak appears at lower frequency, with  $\delta_{\text{Pt}}$  value of  $-587$  p.p.m. (Figure 4 (b)). With time, the intensity of this additional peak increased and the intensity of the peaks from the parent compound decreased. These spectra strengthen the assignment of the new complex as  $[\text{Pt}(\text{CH}_3)_2(\text{H}_2\text{O})_4]^+$  (**4**) ( $\delta_{\text{Pt}}$  reported by Agnew *et al.* [11],  $-596$  p.p.m.).



**Figure 3** 200.13 MHz  $^1\text{H}$  NMR of solution 1, (a) After being left in the bench for about 3 months, (b) After being left in the bench for about 6 months, Aa = Pt-CH<sub>3</sub> in **1**, Bb = Pt-OCH<sub>3</sub> in **1**, C = Set of three pyridinium peaks (Hpy<sup>+</sup>), D = Impurities, E = Reference (TSS = sodium-3-trimethylsilylpropane sulfonate), F = Free methanol, Gg = Pt-CH<sub>3</sub> in **4**



**Figure 4** 86.017 MHz  $^{195}\text{Pt}$  NMR of solution 2 (a) A freshly prepared; (b) After being left in the bench for 3 months (c) After being left in the bench for 6 months

**Table 1** NMR data of the platinum(IV) complexes

Complex	Solvent	$\delta_{\text{Pt}}$ p.p.m.	$\delta_{\text{H}}$ (Me) p.p.m.	$^2J_{\text{Pt-CH}_3}$ (Hz)	Other parameters (Hz)
[Pt(CH <sub>3</sub> ) <sub>2</sub> (OCH <sub>3</sub> )(OH)(py) <sub>2</sub> ] ( <b>1</b> )	CDCl <sub>3</sub>	-806	1.30	73.2	OCH <sub>3</sub> : $\delta_{\text{H}}$ 3.10 (42.4)
[Pt(CH <sub>3</sub> ) <sub>2</sub> (OCH <sub>3</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup> ( <b>2</b> )	D <sub>2</sub> O	-550	2.02	75.6	OCH <sub>3</sub> : $\delta_{\text{H}}$ 3.20 (30.2)
[Pt(CH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> (py) <sub>2</sub> ] ( <b>3</b> )	CDCl <sub>3</sub>	a	1.85	71.0	-
[Pt(CH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup> ( <b>4</b> )	D <sub>2</sub> O	-587	1.98	75.8	-

a Not measured

The NMR data for all complexes observed presented in this work are tabulated in Table 1.

## CONCLUSION

It has been shown that while the Pt – OC<sub>3</sub> bond in [Pt(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> (**2**) is very robust, hydrolysis does occur over a long period in aqueous perchloric acid. The reactions of **2** with halide ions to see the stability Pt – OC<sub>3</sub> bond has been reported previously [12].

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