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# The Stability and Reactivity of Dihydroxy Bis(trimethylphosphine)platinum(II)

T. Ken MIYAMOTO,* Yoshitsugu SUZUKI, and Hikaru ICHIDA
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A dihydroxy platinum(II) compound, *cis*-$[Pt(PMe_3)_2(OH)_2]\cdot nH_2O$ (Me=methyl, n = 2—3 ; **1**) has been isolated. The presence of several water molecules is required for the stabilization of the complex. The solution equilibria of **1** with some equivalents of nitric acid has been observed by $^{31}P$ NMR spectroscopy, as well as the reaction of **1** with aqueous hydrogen peroxide. Leaving **1** in air gives carbonatoplatinum(II), *cis*-$[Pt(PMe_3)_2(CO_3)]\cdot 2H_2O$. The crystal structure determination has revealed that the carbonate anion forms a 4-membered chelate with a platinum atom.

Coordination chemistry of platinum–oxygen bond (except for carboxyl complexes) has been left relatively unexplored by comparison with that of platinum–carbon bond.[1)] Especially dihydroxy platinum(II) with phosphine ligands has not been isolated yet in spite of the fact that the analogous dialkoxides have been prepared successfully.[1)] Choice of an aqueous medium may be an alternative way out of the difficulty. However there have been very few cases of water-soluble phosphine complexes to date.[2, 3)] The situations make a remarkable contrast to a variety of am(m)ineplatinum(II) complexes whose aqueous chemistry not only has been well developed, but also has formed a fascinating subject of chemotherapy for the last two decades.[4)]

Totani et al. reported the utilization of the anion-exchange resin for *in situ* preparation of dihydroxy diam(m)ineplatinum(II) in aqueous solution.[5)] In our hands, the method was very effective for the syntheses of a variety of diam(m)ineplatinum(II) complexes.[6)]

We report here the successful use of the anion-exchange method to a phosphine platinum complex. When an aqueous solution of the compound, *cis*-$[Pt(PMe_3)_2(NO_3)_2]$ (**2**) (pH≈2.1 at 0.030 M),[3)] was passed through a column packed with the anion-exchange resin (DIAION SA10AOH), the eluate showed high pH (pH≈11.2 at 0.015 M). The solution was evaporated in vacuo (< 5 °C) to give very hygroscopic white powder. Its $^{31}P$ or $^{195}Pt$ NMR spectrum (in $D_2O$) showed only a set of signals of which both the shift value and the coupling constant differ from those of known complexes,[3, 7)] such as **2** and a dimer complex, *cis*-$[Pt(PMe_3)_2(\mu\text{-}OH)]_2(NO_3)_2$ (**3**). The $^{13}C$ NMR again confirmed the *cis* geometry of the phosphine ligands. Thus it is assumed that dihydroxy bis(trimethylphosphine)platinum(II) species is formed in solution.

Elemental analysis and IR data (nujol mull) suggest that the white powder sample (**1**) contains a certain amount of water.[8)] Its $^{1}H$ NMR spectrum was also recorded either in $D_2O$ or $CD_2Cl_2$ solution. Each spectrum gave a multiplet due to trimethylphosphine ligands and a broad singlet. The spectral intensity of the broad signal suggests that **1** has several water molecules (n = 2—3) in addition to the hydroxy protons. The $^{31}P$, $^{195}Pt$, $^{13}C$,and $^{1}H$ NMR parameters are summarized in Table 1.

The thermal stability of **1** has been examined in a simple fashion. The white powder of **1** scarecely

Table 1. $^{31}P$, $^{195}Pt$, $^{13}C$,and $^{1}H$ NMR Parameters[a, b] (in ppm) of **1**

| Nucleus | in $D_2O$ | in $CD_2Cl_2$ |
|---|---|---|
| $^{31}P$ | –31.37 ( s, $^{1}J_{PtP}$=3320 ) | –31.30 ( s, $^{1}J_{PtP}$=3254 ) |
| $^{195}Pt$ | –4107 ( t ) | –4043 ( t ) |
| $^{13}C$ | 15.82 ( m, $\vert {}^{1}J_{CP}+{}^{3}J_{CP}\vert$ =43 )[c] | |
| $^{1}H$ | 1.39 ( m, $\vert {}^{2}J_{HP}+{}^{4}J_{HP}\vert$ =11.2 )[c]<br>4.62[d] | 1.57 ( m, $\vert {}^{2}J_{HP}+{}^{4}J_{HP}\vert$ =10.8 )[c]<br>2.40[d] |

a) The coupling pattern and the coupling constants in Hz in parentheses. b) Abbr. s=singlet flanked by satellites, t=triplet, m=multiplet. c) Parameters due to the trimethylphosphine ligands ($X_3AA'X'_3$ or $X_9AA'X'_9$ system respectively, see reference 9). d) A broad singlet due to the water molecules and the OH anion.

showed any coloration at a room temperature (15—20 °C) under a nitrogen atmosphere at least for 1 week, but it turned dark brown with the desiccation at a high temperature (40—50 °C). Enforced removal of water molecules might arouse the decomposition of **1**. These observations indicate that several water molecules are essential to the stabilization of dihydroxy bis(trimethylphosphine)platinum(II).

The solution-stability of the compound has also been checked. Although the dissolution of **1** into $CD_2Cl_2$ gave initially a yellow solution, its color turned black within 30 minutes. In the $D_2O$ solution, however, any change of the color was not observed at least for 1 week. The $^{31}P$ NMR spectrum also suggests that the dihydroxy species tends to decompose in $CD_2Cl_2$, but is stable in $D_2O$. Thus it is inferred that water is a preferable solvent to dichloromethane as far as the solution-stability of the dihydroxy species is concerned.

The acid-base equilibria in aqueous solution were surveyed qualitatively. Some equivalents of aqueous nitric acid were added to the solution of **1** (in $D_2O$, in a molar ratio; 2:1, 1:1 or 1:2 respectively). The $^{31}P$ NMR measurement (after 28 h) identified three main solution-species, referenced to those of authentic samples;[7)] nitrate **2**, dimer **3**, and dihydroxide **1**. The representative spectra and the proposed scheme are shown in Fig. 1.

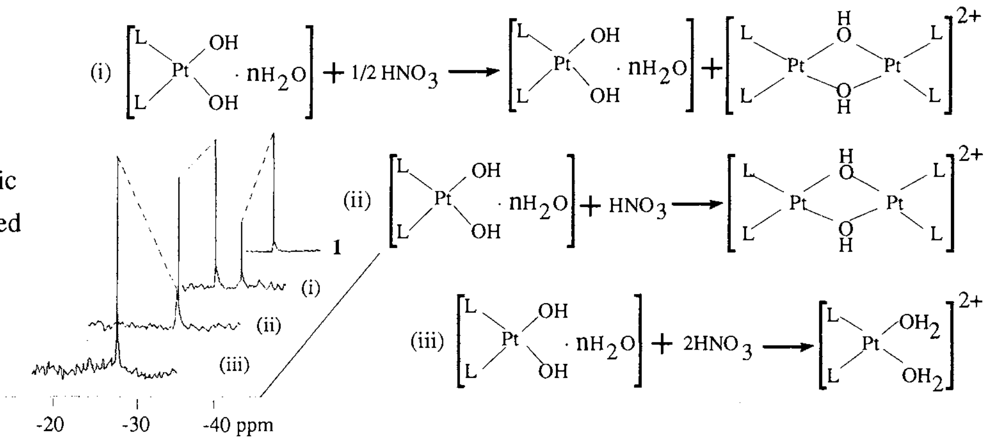


Fig. 1. The change of $^{31}P$ NMR spectra with some equivalents of nitric acid (satellites are omitted for clarity) and the proposed scheme. L = $PMe_3$.

Other researchers reported that addition of NaOH to **2** forms **3**.[3)] Extension of their experiments to further high pH region has been attained by this work. A stoichiometric amount of $NaOD/D_2O$ was added to the solution of **3** (in $D_2O$, in a molar ratio; 4:1, 2:1 or 1:1 respectively), then $^{31}P$ NMR spectrum was measured (after 24 h). The reaction scheme is proposed in Fig. 2.

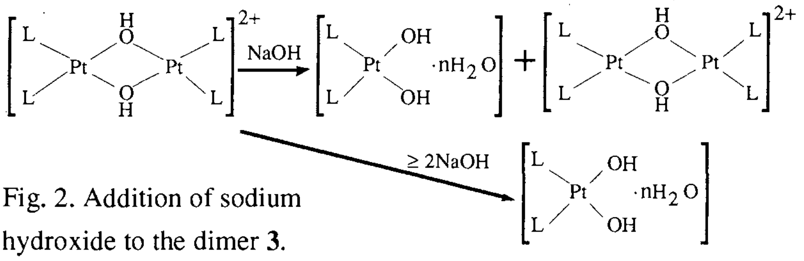


Fig. 2. Addition of sodium hydroxide to the dimer **3**.

Thus the overall equilibria are

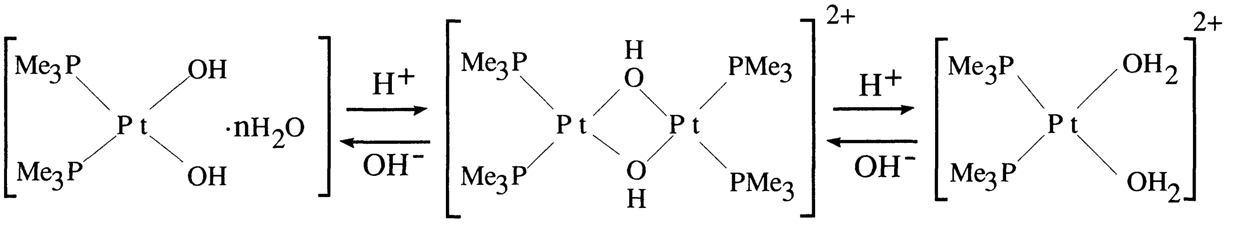


Fig. 3. Equilibria in an aqueous solution ($^{31}$P NMR).

shown in Fig. 3.

The acid-base equilibria seem to be different from those of the ammine complexes.10) In the ammine-platinum system, the formation of the hydroxo-bridged trimer is well known.11) The corresponding trimethylphosphine trimer has not so far been isolated by our trials, and not even been detected by $^{31}$P NMR spectroscopy. A heavy steric congestion of the phosphine ligands around the platinum atoms might hinder the formation of the trimer. Figure 4a or 4b shows the visual image of diammine trimer, *cis*-$[\mathrm{Pt(NH_3)_2(\mu\text{-}OH)}]_3^{3+}$, or bis(trimethylphosphine) trimer, *cis*-$[\mathrm{Pt(PMe_3)_2(\mu\text{-}OH)}]_3^{3+}$, respectively.

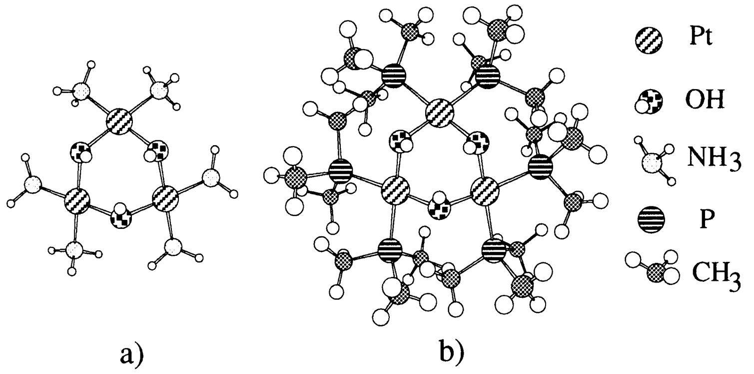
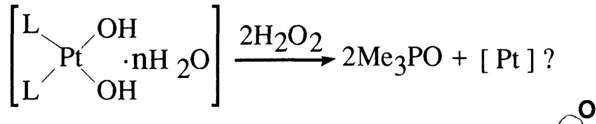


Fig. 4. Visual images of trimers.

The reaction of **1** with hydrogen peroxide was also traced qualitatively by the $^{31}$P NMR spectroscopy. Aqueous hydrogen peroxide was added to the $D_2O$ solution of **1** (in a molar ratio; 2:1, 1:1 or 1:2 respectively). As the original colorless solution turned light orange within 1 hour, the $^{31}$P NMR spectrum was measured after leaving the sample solution at least 2 hours. A new singlet due to trimethylphosphine oxide12, 13) appeared (52.90 ppm) with the increase in the amount of $H_2O_2$. The $^{195}$Pt NMR spectrum showed a singlet14) when two-equivalent amounts of $H_2O_2$ were added to $D_2O$ solution. Unfortunately, at present stage, we have no strong evidence for the identification of the platinum species and of the oxidation state.



$$\left[\begin{matrix}\mathrm{L} & & \mathrm{OH} \\ & \mathrm{Pt} & \cdot n\mathrm{H_2O} \\ \mathrm{L} & & \mathrm{OH}\end{matrix}\right] \xrightarrow{2\mathrm{H_2O_2}} 2\mathrm{Me_3PO} + [\,\mathrm{Pt}\,]\ ?$$

Scheme 1. Addition of $H_2O_2$ to **1** ($^{31}$P NMR).

Table 2. Selected Bond Lengths(Å) and Angles(°)

| Compound **4** | |
|---|---|
| Pt–O | 2.116(7)<br>2.046(7) |
| Pt–P | 2.216(4)<br>2.209(3) |
| P–Pt–P | 95.09(12) |
| O–Pt–O | 63.8(3) |

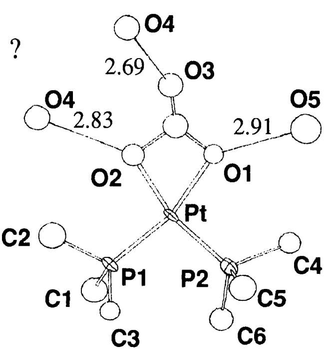


Fig. 5. Molecular structure of **4**, *cis*-$[\mathrm{Pt(PMe_3)_2(CO_3)}]\cdot 2\mathrm{H_2O}$. Symbols(O4 and O5) represent water molecules.

The reaction is represented in Scheme 1.

When **1** was left in air, it absorbed atmospheric $CO_2$ gas and carbonatoplatinum(II) (**4**) formed. The product was recrystallized from chloroform solution. The X–ray structural analysis revealed that $CO_3^{2-}$ ligand constitutes four-membered ring together with the platinum(II) atom.[15] Molecular structure of **4** is shown in Fig. 5. The selected bond distances and angles are shown in Table 2. The formation of **4** may be attributed to the inherent preference of a base **1** to a weak acid, $HCO_3^-$ or $CO_3^{2-}$.

The reaction of **1** with oxalic acid dihydrate ($H_2ox{\cdot}2H_2O$) or 1, 1-cyclobutanedicarboxylic acid ( $H_2cbdca$) gave the phosphine complex, $[Pt(PMe_3)_2(ox)]$ (**5**) or $[Pt(PMe_3)_2(cbdca)]{\cdot}H_2O$ (**6**) respectively in a quantitative yield. In this way, the dihydroxide **1** can provide a wide variety of the water-soluble phosphine platinum(II) complexes by simple neutralization with inorganic and/or organic acids.

The moiety of "*cis*-$Pt(PMe_3)_2$" is a good spin system for multinuclear NMR spectroscopy, and hence provides much information about the solution species as demonstrated in this paper. In particular, the highly water-soluble compounds **1** or **2** would serve as the useful spin-marker to the identification of the platinum-linkage site to the water-soluble polymers such as natural proteins. Extension to the biological system is under way in our laboratory.

References

1) H. E. Bryndza and W. Tam, *Chem. Rev.*, **88**, 1163 (1988).

2) D. Sinou, *Bull. Soc. Chim. Fr.*, **3**, 480 (1987); K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle, and M. B. Smith, *J. Chem. Soc., Chem. Commun.*, **1989**, 1096.

3) G. Trovo, G. Bandoli, U. Casellato, B. Corain, M. Nicolini, and B. Longato, *Inorg. Chem.*, **29**, 4616 (1990).

4) S. L. Bruhn, J. H. Toney, and S. J. Lippard, "Prog. Inorg. Chem.," Wiley-Interscience, John Wiley & Sons, Inc., New York (1990), Vol. 38, pp. 477—516.

5) T. Totani, K. Aono, M. Komura, and A. Adachi, *Chem. Lett.*, **1986**, 429.

6) T. K. Miyamoto, K. Okude, K. Maeda, H. Ichida, Y. Sasaki, and T. Tashiro, *Bull. Chem. Soc. Jpn.*, **62**, 3239 (1989); T. K. Miyamoto and H. Ichida, *Chem. Lett.*, **1991**, 435; T. K. Miyamoto and H. Ichida, *Bull. Chem. Soc. Jpn.*, **64**, 1835 (1991).

7) Our measurements on authentic samples gave the following results (cf. Ref. 3).
**2** : $^{31}P$ NMR ($D_2O$) $\delta$=-25.31 ppm ( s, $J_{PtP}$ =3745 Hz ) ; $^{195}Pt$ NMR ($D_2O$) $\delta$=-4346 ppm (t).
**3** : $^{31}P$ NMR ($D_2O$) $\delta$=-25.64 ppm ( s, $J_{PtP}$ =3401 Hz ) ; $^{195}Pt$ NMR ($D_2O$) $\delta$=-3921 ppm (t).

8) Anal. Found : C, 16.62 ; H, 5.51%. Calcd for $C_6H_{20}O_2P_2Pt{\cdot}2.5H_2O$ : C, 16.90 ; H, 5.91%.

9) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

10) T. G. Appleton, J. R. Hall, S. F. Ralph, and C. S. M. Thompson, *Inorg. Chem.*, **28**, 1989 (1989).

11) R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **16**, 1192 (1977).

12) G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds," Wiley-Interscience, a Division of John Wiley & Sons, Inc., New York (1972), Vol. 3, Chap. 6, pp. 341—500.

13) The $^{31}P$ chemical shift of the tertiary phosphine oxide has large solvent effects (cf. Ref. 12). For the avoidance of the ambiguous assignment, we prepared trimethylphosphine oxide by an independent authentic method (Ref. 12) and it was confirmed that its $^{31}P$ NMR spectrum in $D_2O$ solution showed a singlet at 52.50 ppm.

14) $^{195}Pt$ NMR ($D_2O$) $\delta$=-169 ppm (s).

15) Crystallographic Data **4** ; Fw=443.27, orthorhombic, space group Pbca, a=17.249(3), b=13.497(5), c=12.210(3) Å, V/Å$^3$=2843(1), Z=8, *Dcalc* (g cm$^{-3}$)=2.071, *Dobs* (g cm$^{-3}$ )=2.06, *R*=0.069, *Rw*=0.058 for 2321 reflections.

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