COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Isolation of a new mixed valence Pt molecular oxide using phosphine as protecting group

K. Noro,[a] Y. Ozawa,*[b] M. Taguchi[a] and A. Yagasaki*[a]

[a] Department of Chemistry, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan. E-mail: yagasaki@kwansei.ac.jp; Fax: +81 795 65 9077; Tel: +81 795 65 8396

[b] Department of Material Science, Himeji Institute of Technology, Harima Science Garden City, Kamigori 678-1297, Japan

Received (in Cambridge, UK) 17th May 2002, Accepted 2nd July 2002
First published as an Advance Article on the web 15th July 2002

A novel tetranuclear mixed valence cationic Pt molecular oxide $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$ is obtained by reacting $H_2Pt(OH)_6$ and $(Me_3P)_2Pt^{2+}$, whose NMR spectra suggest the existence of another species in solution that may serve as a starting point for further synthesis of Pt molecular oxides.

The chemistry of anionic molecular oxides, or polyoxoanions, flourished in the last quarter of the 20th century.[1] Our knowledge of *cationic* molecular oxides, on the other hand, is still very limited. This is not because such compounds are rare or do not exist at all. On the contrary, cationic molecular oxides are known to exist for virtually all metals of the periodic table.[2] The main hindrance in the study of cationic molecular oxides has been the isolation problem. Unlike their anionic counterparts, cationic molecular oxides have metal-rich composition and are expected to have metal atoms exposed on their surface. Those surface metal sites are supposedly very reactive and vulnerable to further uncontrollable condensation. One usually ends up getting insoluble (and amorphous in most cases) solids when attempting to prepare a solution that contains a high enough concentration of a cationic molecular oxide. To isolate cationic molecular oxides, we need to stabilize them by somehow protecting those surface metal sites.

One obvious thing to try is the hydrolysis of organometallic compounds. The organic group would block unwanted condensation. In fact, several organometallic molecular oxides have been prepared in this manner, where each metal atom is protected by one or more organic groups. However, in most cases the species obtained are small and too stable to develop further reaction.[3] The organic groups efficiently cover the surface of those species and make further reactions difficult.

If bare inorganic ions are too reactive and organometallic ions lead to a dead end, how about mixing the two together? This seemingly simple-minded approach does work as reported below.

Compound **1**, $[\{(Me_3P)_2Pt\}_3Pt(OH)_6](NO_3)_4$, was synthesized as pale-yellow block-shaped crystals by reacting $H_2Pt(OH)_6$ and $(Me_3P)_2Pt^{2+}$ in aqueous solution as follows. Platinic acid ($H_2Pt(OH)_6$, 0.60 g, 2.0 mmol) was dissolved in 22.8 mL of aqueous 0.21 M KOH solution. To 2.5 mL of this platinate solution was added a solution of $[(Me_3P)_2Pt](NO_3)_2$ (0.31 g, 0.66 mmol, in 7.5 mL of H_2O).[4] The mixed solution was stirred for 1 h before it was condensed to 1/10 of the original volume under vacuum. A small amount of precipitate that formed was removed by centrifugation and the supernatant clear solution was further concentrated in a desiccator over H_2SO_4 to yield the crystals, which weighed 0.16 g and analyzed as **1**$\cdot 4H_2O$ after drying under vacuum (0.099 mmol, 45%).[5] X-Ray structure analysis of a crystal that was not vacuum dried revealed the presence of NO_3^- anions, H_2O molecules of crystallization, and discrete $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$ cations that have a structure shown in Fig. 1.[6] The molecular cation is made up from four Pt units and ideally has 32 (D_3) symmetry. The central Pt^{IV} atom is octahedrally coordinated by six oxygen atoms, which are in turn connected to three peripheral Pt^{II} units in pairs. The square planar coordination of each of these Pt^{II} atoms is completed by two Me_3P groups. The coordination geometry including the bond distances is consistent with the assignment that the central Pt atom is in IV oxidation state and the three peripheral Pt atoms are II (see the caption of Fig. 1). The valence sums[7] for the O atoms are in the range 1.0–1.1 and significantly smaller than 2. This suggests that all six O atoms are protonated and actually are OH groups, although protons were not located by X-ray diffraction. The Pt–O distances in **1** agree well with those reported for Pt–OH in the literature.[4,8] The result of the elemental analysis was also consistent with the existence of six OH groups. All these OH groups are relatively close either to H_2O molecules or NO_3^- anions in the lattice (intermolecular O–O distances: 2.62–2.81 Å) and seem to be hydrogen-bonded to these molecules and anions. In other words, the protection provided by the surface methyl groups are imperfect and small molecules and ions can attack those bridging oxygen atoms.

In fact, compound **1** hydrolyzes slightly to make a weakly acidic solution when it is dissolved in water. A small triplet ($<10\%$ in intensity) assignable to $[\{(Me_3P)_2Pt\}_2(OH)_2]^{2+}$ is observed as well as the predominant signal of $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$ in the ^{31}P NMR spectra of the solution.[9] An equilibrium like

$$2[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+} + 2H_2O \rightleftarrows [(Me_3P)_2Pt(OH)]_2^{2+} + 2[\{(Me_3P)_2Pt\}_2Pt(OH)_6]^{2+} + 2H^+$$

seems to exist in solution. However, no separate peaks for the dissociation product $[\{(Me_3P)_2Pt\}_2Pt(OH)_6]^{2+}$ was observed in the ^{31}P spectra. Probably they are hidden under somewhat broad ($\Delta\nu_{1/2}$ = 20 Hz) peaks of $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$. This

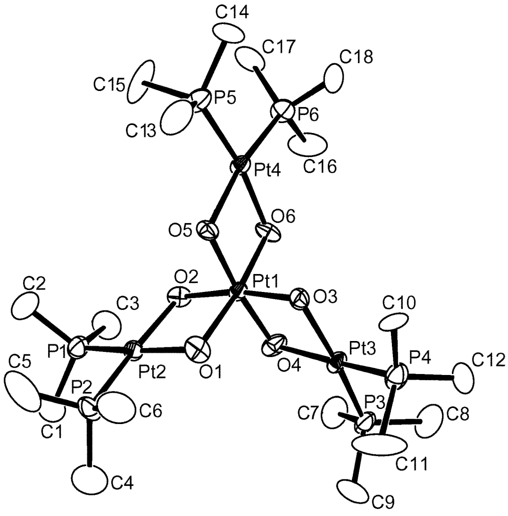
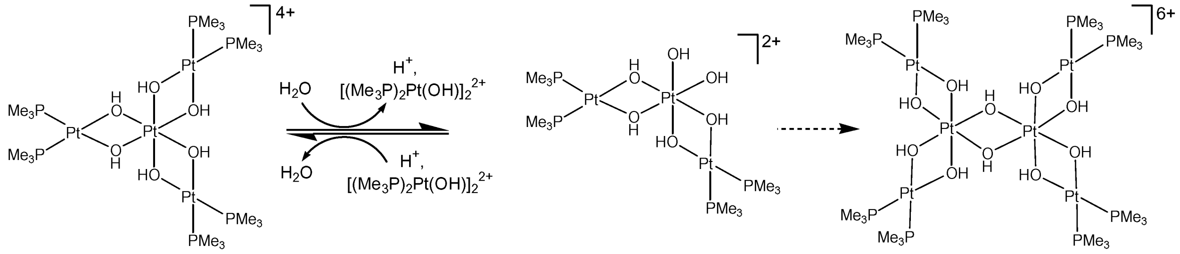


Fig. 1 Perspective drawing of $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$. Displacement ellipsoids are scaled to enclose 50% probability levels. Selected distances (Å): Pt1–O1 2.033(18), Pt1–O2 2.029(16), Pt1–O3 2.037(16), Pt1–O4 2.02(2), Pt1–O5 2.012(17), Pt1–O6 2.006(17), Pt2–P1 2.208(8), Pt2–P2 2.227(8), Pt2–O1 2.085(18), Pt2–O2 2.101(16), Pt3–P3 2.227(8), Pt3–P4 2.232(8), Pt3–O3 2.139(17), Pt3–O4 2.155(18), Pt4–P5 2.213(8), Pt4–P6 2.204(7), Pt4–O5 2.119(17), Pt4–O6 2.122(18).

DOI: 10.1039/b204804c



Scheme 1

presumption was supported by preliminary ^{195}Pt NMR experiments. Two singlets were observed in the typical Pt(IV) range (4045 and 3803 ppm) and three triplets appeared in the Pt(II) range (-4043, -4024, and -3895 ppm).[10,11] The triplet at –3895 ppm is assignable to $[\{(Me_3P)_2Pt\}_2(OH)_2]^{2+}$. This leaves two singlets in the Pt(IV) range and two triplets in the Pt(II) range, which is consistent with the equilibrium above.

The fact that the $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$ cation undergoes dissociation may seem troublesome at first. It means that the methyl groups of the phosphine ligands provide less than perfect protection as mentioned above. However, it actually indicates the existence of further interesting chemistry of this system. Not much chemistry is expected for a compound whose surface is efficiently covered with organic groups, as mentioned in the introduction. Vulnerability of the $[\{(Me_3P)_2Pt\}_3Pt(OH)_6]^{4+}$ cation to small molecules and ions makes this molecular oxide potentially useful as a starting material. Furthermore, the dissociation product, $[\{(Me_3P)_2Pt\}_2Pt(OH)_6]^{2+}$, would have two OH groups available for further condensation on the surface (Scheme 1). Dimerization of $[\{(Me_3P)_2Pt\}_2Pt(OH)_6]^{2+}$, for instance, would yield a larger molecular oxide like $[\{(Me_3P)_2Pt\}_2Pt(OH)_5]_2^{6+}$. Research effort in that direction is in progress.

The current result demonstrates that the seemingly simple-minded approach of mixing inorganic and organometallic ions to isolate cationic molecular oxide actually works. This approach might turn out to be a general method to isolate new molecular oxides.

Notes and references

1 For recent reviews, see: *Chem. Rev.*, 1998, **98**, 8.

2 C. F. Baes Jr. and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976.

3 M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1964, 1567; B. F. G. Johnson, J. Lewis, I. G. Williams and J. Wilson, *J. Chem. Soc., Chem. Commun.*, 1966, 391; D. A. Bright, *J. Chem. Soc., Chem. Commun.*, 1970, 1169; M. Herberhold and G. Süss, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 700; F. Bottomley, D. E. Paez and P. S. White, *J. Am. Chem. Soc.*, 1981, **103**, 5581; A. Nutton, P. M. Bailey and P. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1981, 1997; L. M. Babcock, V. W. Day and W. G. Klemperer, *J. Chem. Soc., Chem Commun.*, 1987, 858; F. Bottomley, *Polyhedron*, 1992, **11**, 1707 and the references cited therein; F. Bottomely, J. Chen, K. F. Preston and R. C. Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7989; R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich and P. A. Schubiger, *J. Chem. Soc., Dalton Trans.*, 1994, 2815; F. Ribot, C. Sanchez, R. Willem, J. C. Martins and M. Biesemans, *Inorg. Chem.*, 1998, **37**, 911; F. Banse, F. Ribot, P. Tolédano, J. Maquet and C. Sanchez, *Inorg. Chem.*, 1995, **34**, 6371; H. Reuter, *Angew. Chem., Int. Ed. Engl.*, 1991, **11**, 1482.

4 G. Trovó, G. Gandoli, U. Casellato, B. Corain, M. Nicolini and B. Longato, *Inorg. Chem.*, 1990, **29**, 4616.

5 Analysis found: C, 12.79; H, 3.93; N, 3.34; P, 11.4; Pt, 47.8%. Calc.: C, 13.03; H, 4.13; N, 3.38; P, 11.2; Pt, 47.0%. IR: ν/cm^{-1} (KBr) 1400 (s, br), 1300 (s), 1280 (m), 1088 (m), 1062 (m), 960 (s), 862 (m), 826 (m), 804 (w), 744(m), 732 (m), 678 (m), 542 (m) 400 (w). ^{1}H NMR (D_2O, TSP): δ 1.70 (d, J_P = 12 Hz). ^{31}P NMR (H_2O, H_3PO_4): δ -22.0 (J_{PPt} = 3560 Hz).

6 *Crystal data* for **1**·$6H_2O$: $C_{18}H_{72}N_4O_{24}P_6Pt_4$, M = 1694.94, monoclinic, $P2_1/n$, a = 13.311(8), b = 16.218(3), c = 22.777(9) Å; β = 94.21(2)°, U = 4904(4), Z = 4, T = 220 K, μ(Mo-Kα) = 11.6 mm^{-1}, 11953 reflections measured, 4393 unique (R_{int} = 0.054) which were used in all calculations. R = 0.066 (unique data), $R_w(F^2)$ = 0.142 (all data). Methyl hydrogen atoms were included in the structural model at idealized positions. It was not possible to locate the other hydrogen atoms on the cation or water molecules. CCDC 186292. See http://www.rsc.org/suppdata/cc/b2/b204804c/ for crystallographic data in .cif or other electronic format.

7 I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B*, 1985, **B41**, 244; N. E. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B*, 1991, **B47**, 192.

8 Von M. Trömel and E. Lupprioh, *Z. anorg. Allg. Chem.*, 1975, **414**, 160; G. W. Bushnell, *Can. J. Chem.*, 1978, **56**, 1773; H. G. Scott, *Acta Crystallogr. Sect. B*, 1979, **B35**, 3014; B. Longato, G. Pilloni, G. Valle and B. Corain, *Inorg. Chem.*, 1988, **27**, 956.

9 K. Hara, M. Taguchi and A. Yagasaki, *Polyhedron*, 2001, **20**, 1903.

10 C. Brevard and P. Granger, *Handbook of High Resolution Multinuclear NMR*, Wiley, New York, 1981, p. 201.

11 No long range Pt–P coupling, $^3J_{PtP}$, was observed, presumably due to large linewidths of the Pt signals ($\nu_{1/2}$ > 600 Hz). The $^3J_{PtP}$ is reported to be 10–30 Hz for related compounds. See: E. Costa, M. Murray, P. G. Pringle and M. B. Smith, *Inorg. Chim. Acta*, 1993, **213**, 25 and the references cited therein.