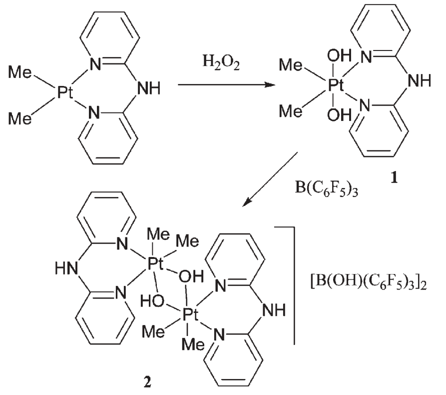
Organometallic molecular materials: self-assembly through hydrogen bonding of an organoplatinum network structure with zeolite-like topology

Fenbao Zhang, Michael C. Jennings and Richard J. Puddephatt*

Received (in Cambridge, UK) 28th November 2006, Accepted 9th January 2007
First published as an Advance Article on the web 29th January 2007
DOI: 10.1039/b617341a

The complex [Pt(OH)$_2$Me$_2$(dpa)], dpa = di-2-pyridylamine, undergoes a remarkable form of self-assembly through hydrogen bonding in the solid state; there are cyclic tetramer units formed by head-to-head association between pairs of hydroxyl groups, and cyclic hexamer units formed by head-to-tail association between NH and OH groups; these building blocks then self-assemble to form a complex network structure containing large interconnected cavities, reminiscent of zeolites.

There is much current interest in the formation of complex structures by self-assembly from simple molecular building blocks, and the formation of porous organometallic materials is of particular interest because of their potential as size-selective catalysts.[1] However, supramolecular organometallic chemistry is less developed than in organic or coordination chemistry, in part because many metal–carbon bonds are incompatible with the functional groups such as OH or NH groups commonly used in self-assembly through hydrogen bonding.[1,2] There are already several interesting examples of polymers or cyclic oligomers that can be formed by self-assembly from organoplatinum complexes with hydrogen bonding functional groups incorporated, some of which display interesting host–guest chemistry.[3,4] However, three-dimensional networks have proved to be elusive.[3,4] This article reports the dimethylplatinum(IV) complexes [Pt(OH)$_2$Me$_2$(dpa)], **1**, and [Pt$_2$(μ-OH)$_2$Me$_4$(dpa)$_2$][B(OH)(C$_6$F$_5$)$_3$]$_2$, **2**, dpa = di-2-pyridylamine, which contain both hydrogen bonding PtOH groups and NH groups, and the self-assembly of complex **1** to form a complex network structure, which appears to be the first "organometallic zeolite". The complex **1** was easily formed by oxidation of [PtMe$_2$(dpa)] by hydrogen peroxide, and **2** was formed by abstraction of a hydroxo ligand from **1** by reaction with B(C$_6$F$_5$)$_3$ (eqn (1)).



(1)

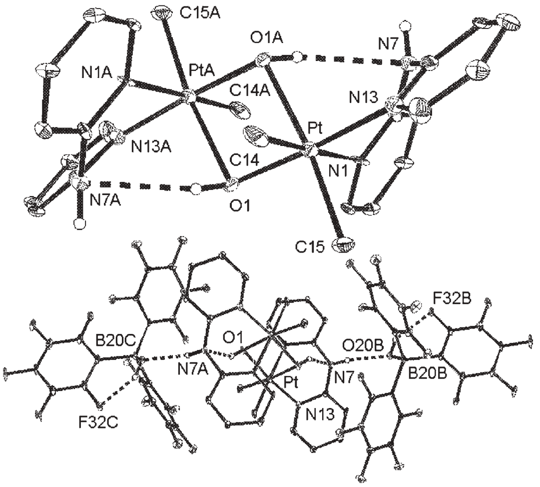


Fig. 1 The molecular structure of the complex **2**. Above: the OH···N hydrogen bonds with O1···N7a = 3.12(2) Å; below: the interion NH···OB hydrogen bonds with N7···O20B = 2.80(2) Å. Symmetry equivalents: A, 1.5 − *x*, 0.5 − *y*, 2 − *z*; B, 2 − *x*, *y*, 1.5 − *z*; C, −0.5 + *x*, 0.5 − *y*, 0.5 + *z*.

Note that in **1** both methyl groups are *trans* to dpa nitrogen atoms and the hydroxyl groups are mutually *trans*, but in **2** the hydroxyl groups are mutually *cis* and one methyl group on each platinum is *trans* to nitrogen and the other *trans* to oxygen.†

The structure of complex **2**, which contains two bridging hydroxyl groups and two NH groups, is shown in Fig. 1, and illustrates the hydrogen bonding potential of the NH and OH groups. The hydroxyl groups hydrogen bond intramolecularly to the amine nitrogen atoms, and then the NH groups hydrogen bond to the oxygen atoms of the anions. The strong hydrogen bonding between dpa ligands and anions has been noted before.[5]

The molecular structure of complex **1** is shown in Fig. 2. The complex contains an octahedral platinum(IV) centre with two methyl groups, two hydroxo groups and a dpa ligand. There is a short intramolecular contact O(16)···N(7) = 3.17(1) Å, which is indicative of a weak PtO–H···N hydrogen bond, similar to those observed for complex **2**.

It is apparent from Fig. 1 that there is one PtOH [PtO(17)H] and one NH group [N(7)H] available as H-bond donors and two oxygen atoms [O(16), O(17)] as H-bond acceptors for intermolecular hydrogen bonding. The self assembly that results from this hydrogen bonding is interesting. The hydrogen bonding between

---

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

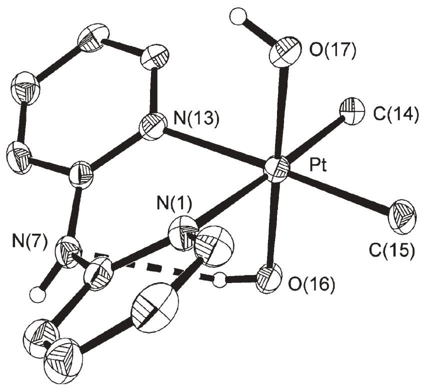


Fig. 2 The molecular structure of the complex [Pt(OH)$_2$Me$_2$(dpa)], **1**.

PtO(17)H groups occurs in a complementary head-to-head fashion to give cyclic tetramer units illustrated in Fig. 3(a), while the hydrogen bonding between N(7)H donors and PtO(16) acceptors occurs in a head-to-tail fashion to give the cyclic hexamers shown in Fig. 3(b).

Complex **1** crystallizes in the unusual space group $Fd\bar{3}c$, with Z = 192 and Z' = 1, and so the further self-assembly of the building blocks shown in Fig. 2 and 3 is particularly complex.[5] In order to visualize the higher order structure, only the platinum atoms are shown in the Fig. 4 and 5, and the connections through OH···O or NH···O hydrogen bonds are coded as solid (tetramer units) or dashed (hexamer units) lines between the platinum atoms that represent individual molecules. The way in which each tetramer is connected to four hexamers, or each hexamer is connected to six tetramers is shown in Fig. 4(a) or (b), respectively. These larger building blocks, shown schematically in Fig. 4, each contain 24 units of complex **1**.

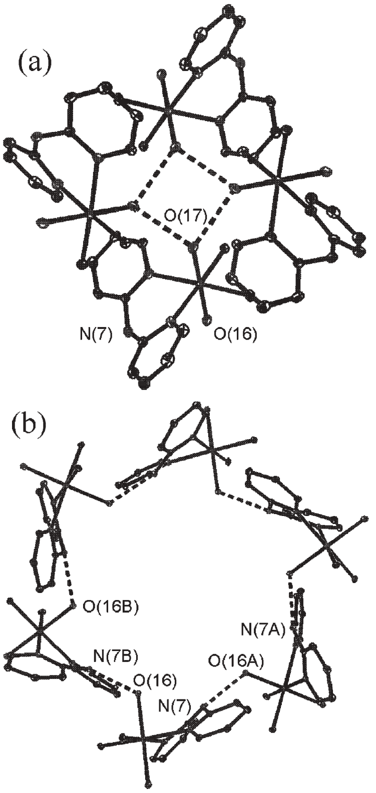


Fig. 3 (a) The cyclic tetramer formed by O–H···O hydrogen bonding [O(17)···O(17A) = 2.645(7) Å; symmetry equivalents in tetramer: A(adj), 1.75 − y, x, 1.25 − z; B(adj), y, 1.75 − x, 0.25 − z; C(opp), 1.75 − x, 1.75 − y, z], and (b) the cyclic hexamer formed by N–H···O hydrogen bonding [N(7)···O(16A) = 2.770(8) Å].

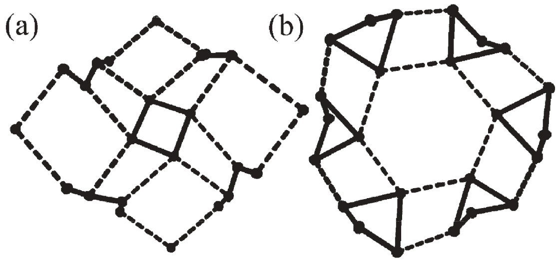


Fig. 4 The building up of the structure from (a) a central tetramer unit, and (b) a central hexamer unit. Each platinum atom shown represents a molecule of the complex, and a solid or dashed line represents an intermolecular OH···O or NH···O hydrogen bond, respectively.

One way to visualize the next higher order of the structure, in which cavities become apparent, is to consider that four of the units shown in Fig. 4(b) come together to form the four sides of a tetrahedron within a cube, as illustrated in two views shown in Fig. 5(a) and (b). Each tetrahedron contains a large central cavity in which the disordered solvent molecules are located. In Fig. 5(a) it is possible to locate, around the cube, three mutually orthogonal “square belts” that define the circumference of the cavity. Each belt contains eight tetramer units connected to each other by NH···O hydrogen bonds, and one of these belts is shown in Fig. 5(c) and Fig. 6. The dimensions of the “square” are 21.1 Å from side to side, and 27.1 Å from corner to corner as measured from Pt to Pt, and the side-to-side dimension is 16 Å between closest H-atoms. Analysis using the program “SQUEEZE” indicates that 46.7% of the cell volume is void, with two

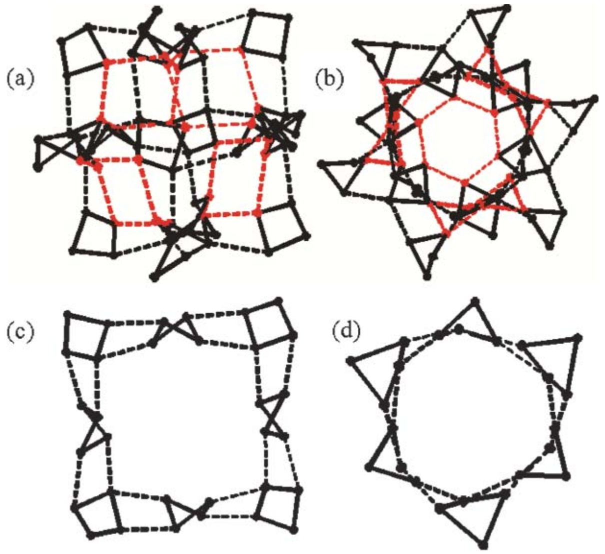


Fig. 5 A cavity in the structure: (a) side view and (b) a top view of a “tetrahedron”, with the four hexamer units at the centre of the four faces shown in red. (c) A cross section showing the eight tetramers that define the circumference of the cavity. (d) A set of six tetramer units that form a vertex of the tetrahedron, forming one of the four connections to the adjacent cavities.

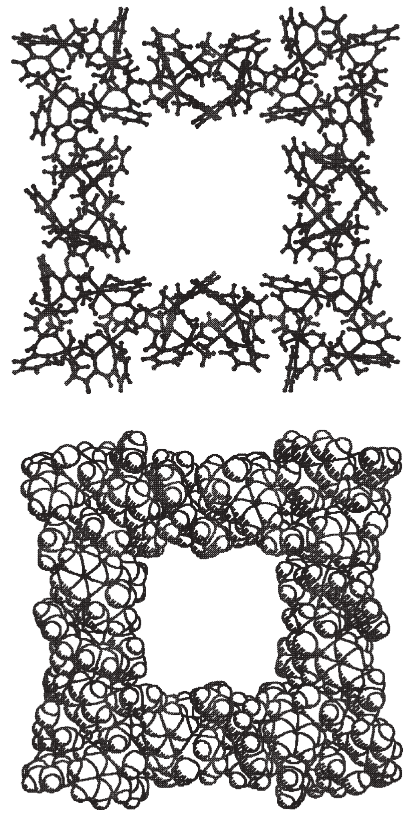


Fig. 6 Above, ball-and-stick and, below, space-filling representations of a cavity. The view is of the cross-section represented in Fig. 5(c).

(disordered) acetone molecules per void space.[7] At each vertex of the tetrahedron (Fig. 5(b)), where three units of the building block shown in Fig. 4(b) come together, there is a rough circle formed by six connected tetramer units, and these form a common vertex with the adjacent tetrahedron. One of these connector units is shown in Fig. 5(d). The diameter of the circle, as measured between platinum atoms or closest H-atoms, is 17.9 or 10 Å, respectively.

In summary, the simple complex **1** has a very complex supramolecular structure formed by connecting equivalent units of complex **1** through two types of intermolecular hydrogen bonding. The structure can be considered to build up in a stepwise manner. Individual molecules (Fig. 2) undergo supramolecular self assembly to give tetramer or hexamer units (Fig. 3), by considering the two forms of hydrogen bonding separately. These units connect to each other to give the next level of building blocks that contain both tetramer and hexamer units; each of these larger building blocks shown in Fig. 4 contains 24 units of **1**. These building blocks then combine to form large tetrahedral units, each of which has a cavity defined by the 72 shared molecules of **1** shown, through the central platinum atoms only, in Fig. 5(a) and (b). Each tetrahedron connects to four others through the four shared vertices, and there are pores that run through the structures. There is an obvious structural analogy to the well-studied inorganic porous materials, and compound **1** appears to be the closest organometallic analogue of the important zeolite materials. In the present case, loss of the guest solvent molecules causes collapse of the crystalline structure but complex **1** is significant as a model for porous organometallic molecular materials that may find applications in sensors or catalysis. The "organometallic zeolite" **1** complements a growing number of coordination complexes with zeolitic or related porous topologies.[6,8]

R. J. P. thanks the NSERC (Canada) for financial support and the Government of Canada for a Canada Research Chair.

Notes and references

† *Synthesis* of [Pt(OH)$_2$Me$_2$(dpa)], **1**. A solution of [PtMe$_2$(dpa)] (0.4 g) in acetone (25 mL) was treated with excess H_2O_2 (0.5 mL, 30% aq. solution). The product precipitated as a white solid and was crystallized from acetone solution. Yield 85%. Selected NMR data in acetone-d_6: δ_H 1.51 [s, J(PtH) = 70 Hz, PtMe]. *Synthesis* of [Pt$_2$(μ-OH)$_2$Me$_4$(dpa)$_2$][B(OH)(C$_6$F$_5$)$_3$]$_2$, **2**. A solution of [PtMe$_2$(dpa)] in acetone at −78 °C was treated with H_2O_2 (30% aq. solution) and B(C$_6$F$_5$)$_3$. The mixture was warmed to room temperature, the solvent was evaporated and the product was recrystallized from CH$_2$Cl$_2$. Yield 89%. Selected NMR data in CD$_2$Cl$_2$: δ_H 1.11 [s, 6H, ^2J(PtH) = 68 Hz, Pt–Me]; 1.22 [s, 6H, ^2J(PtH) = 66 Hz, Pt–Me]; δ_F −136.3 [d, 6F, ^3J(FF) = 21 Hz, *o*-F]; −161.8 [t, 3F, ^3J(FF) = 20 Hz, *p*-F]; −166.3 [t, 6F, ^3J(FF) = 18 Hz, *m*-F].

Crystal data and structure refinement. Complex **1**: $C_{12}H_{17}N_3O_2Pt$, M = 430.38, T = 150(2) K, λ = 0.71073 Å, cubic, space group $Fd\bar{3}c$, a = 47.3348(5), V = 106057(2) Å^3, Z = 192, D_c = 1.294 Mg m^{-3}, μ = 6.349 mm^{-1}, F(000) = 39168, abs. corr.: integration, Data/restr./param. 3908/0/164, Goof on F^2 = 1.078, $R1$ [$I > 2\sigma(I)$] = 0.045, $wR2$ [$I > 2\sigma(I)$] = 0.124. There are two disordered acetone molecules for each cavity unit (see text). The relationship of the structure to that of the simpler $Fd\bar{3}c$ structure NbO can be seen in Fig. 5(a), with a tetramer unit of **1** in place of the Nb and O atoms of NbO.[6] The CCDC contains only 25 independent structures in this space group $Fd\bar{3}c$. Complex **2**·3H$_2$O·1.2CH$_2$Cl$_2$: $C_{61.2}H_{42.4}B_2Cl_{2.4}F_{30}N_6O_7Pt_2$, M = 2040.69, T = 150(2) K, λ = 0.71073 Å, monoclinic, space group *C*2/*c*, a = 14.9330(5), b = 21.9706(7), c = 23.9595 Å, β = 101.809(2)°, V = 7694.4(5) Å^3, Z = 4, D_c = 1.76 Mg m^{-3}, μ = 3.897 mm^{-1}, F(000) = 4072, abs. corr.: integration, Data/restr./param. 6624/198/475, Goof on F^2 = 1.071, $R1$ [$I > 2\sigma(I)$] = 0.101, $wR2$ [$I > 2\sigma(I)$] = 0.271. CCDC 629049 and 629050. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617341a

1 I. Haiduc and F. T. Edelmann, *Supramolecular Organometallic Chemistry*, Wiley-VCH, Weinheim, 1999; D. Braga, L. Maini, M. Polito, L. Scaccianoce, G. Cojazzi and F. Grepioni, *Coord. Chem. Rev.*, 2001, **216–217**, 225; *Comprehensive Supramolecular Chemistry*, *Vol. 6, Solid State Supramolecular Chemistry: Crystal Engineering*, ed. J. L. Atwood, Pergamon, New York, 1996; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

2 D. Braga, A. L. Costa, F. Grepioni, L. Scaccianone and E. Tagliavini, *Organometallics*, 1997, **16**, 2070.

3 N. C. Gianneschi, E. R. T. Tiekink and L. M. Rendina, *J. Am. Chem. Soc.*, 2000, **122**, 8474; M. G. Crisp, S. M. Pyke and L. M. Rendina, *J. Organomet. Chem.*, 2000, **607**, 222; C. S. A. Fraser, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 1310; C. S. A. Fraser, D. J. Eisler, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2002, 1224; M. Rashidi, M. C. Jennings and R. J. Puddephatt, *CrystEngComm*, 2003, **5**, 65.

4 C. Muller, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1998, **120**, 9827; B. C. Tzeng, W. C. Lo, C. M. Che and S. M. Peng, *Chem. Commun.*, 1996, 181.

5 F. Zhang, E. M. Prokopchuk, M. E. Broczkowski, M. C. Jennings and R. J. Puddephatt, *Organometallics*, 2006, **25**, 2006; R. Romeo, N. Nastasi, L. M. Scolaru, M. R. Plutino, A. Albinati and A. Macchioni, *Inorg. Chem.*, 1998, **37**, 5460.

6 T. Niu, X. Wang and A. J. Jacobson, *Angew. Chem., Int. Ed.*, 1999, **38**, 1934; T. L. Andresen, F. C. Krebs, N. Thorup and K. Bechgard, *Chem. Mater.*, 2000, **12**, 2428; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1313; K. Ortner, L. Hilditch, Y. Zheng, J. R. Dilworth and U. Abram, *Inorg. Chem.*, 2000, **39**, 2801.

7 A. L. Spek, PLATON, SQUEEZE, Utrecht University, The Netherlands, 2003.

8 B. F. Abrahams, A. Hawley, M. G. Haywood, T. A. Hudson, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 2004, **126**, 2894; Q. R. Fang, G.-S. Zhu, M. Xue, J.-Y. Sun and S.-L. Qiu, *Dalton Trans.*, 2006, 2399.