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A route to small clusters: a twisted half-hexagon-shaped  $M_4(OH)_4$  cluster and its capacity for hosting closed-shell metals

Transition-metal hydroxy clusters with a heretofore unobserved core geometry have been synthesized by combining platinum centers with two different oxidation states and their corresponding different coordination indices and geometries.

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# A route to small clusters: a twisted half-hexagram-shaped $M_4(OH)_4$ cluster and its capacity for hosting closed-shell metals†

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By combining different oxidation states, coordination indices and bridging systems, it has been possible to obtain the structurally novel  $M_4(OH)_4$  cluster core ( $M$  = transition metal) found in the organometallic compound  $(NBu_4)_2[Pt^{IV}Pt^{II}_3(C_6Cl_5)_8(\mu_2-OH)_2(\mu_3-OH)_2]$  (1). The cluster is formed by two  $(\mu_3-OH)$  and two  $(\mu_2-OH)$  units that bond platinum atoms in different oxidation states. The cluster core geometry can best be described as a half-hexagram. Compound 1 is an excellent precursor for preparing heterometallic clusters since it can host  $d^{10}$  or  $s^2$  Lewis-acid metal centers through  $Pt \rightarrow M$  dative bonds, as demonstrated by its reaction with  $Ag(I)$  to produce the heterometallic  $[Ag_2Pt^{IV}Pt^{II}_3(C_6Cl_5)_8(\mu_2-OH)_2(\mu_3-OH)_2]$  (2), which has four unbridged  $Pt-Ag$  bonds.

We report here the preparation of a unique cluster possessing a tetranuclear  $Pt_4(OH)_4$  core with Pt centers in two different oxidation states and with a core structure that has no precedent in transition-metal hydroxide chemistry. This cluster, further, has hydroxy ligands that bridge two or three Pt atoms – in the latter case the metal centers are in two different oxidation states, in another heretofore unobserved core characteristic; and it can also serve as a stable metalloligand for the formation of new compounds with unsupported  $Pt \rightarrow M$  bonds.

Hydroxy-bridged multinuclear transition metal compounds constitute such a well explored area of chemistry that it may seem injudicious to expect that they have yet to yield products with substantive new features, especially for low-nuclearity systems. The ample body of science in which members of this family of compounds have been explored traverses such diverse contexts as biology and medicine, where hydroxo complexes

can be found in redox metalloenzymes<sup>1</sup> and in the mechanism of antitumor agents<sup>2</sup> or chemical catalytic processes,<sup>3</sup> such as water oxidation<sup>4</sup> or materials science, where such complexes have appeared as precursors for nanomaterials<sup>2a,5</sup> or as nodes for the formation of MOFs,<sup>6</sup> and magnetic materials.<sup>7</sup>

Coordination compounds with  $M_4(OH)_4$  cores are well known (Chart 1), and particularly so those in which each of the four  $OH^-$  ligands bridges three metal atoms,  $[(\mu_3-OH)_4]$ , giving a cubane structure, A in Chart 1.<sup>8</sup> Clusters in which each of the four  $OH^-$  ligands bridges just two metal atoms,  $(\mu_2-OH)_4$ , are also known although in lesser numbers;<sup>9</sup> these form eight-membered rings  $(M-OH-M-OH)_2$  (B in Chart 1) with differing conformations. Also known are compounds with  $M-M$  bonds, such as the molybdenum compound with two double OH bridges and  $Mo \equiv Mo$  bonds (C in Chart 1).<sup>10</sup> Clusters with two  $(\mu_2-OH)$  and two  $(\mu_3-OH)$  bridges are known, mainly for  $M = Cu$ . These are formed by three fused distorted squares, with the central ring sharing two opposite sides in a staircase or Z-shaped structure (D in Chart 1).<sup>11</sup>

Platinum hydroxocompounds have also been reported, some of them with interest in C-H activation, C-O bond formation, or the preparation of anticancer complexes.<sup>2,12,13</sup> Hydroxocomplexes, though, are not as frequent for Pt as for other transition metals;<sup>2b</sup> this is especially true for  $Pt^{II}$  because of its soft-acid character and

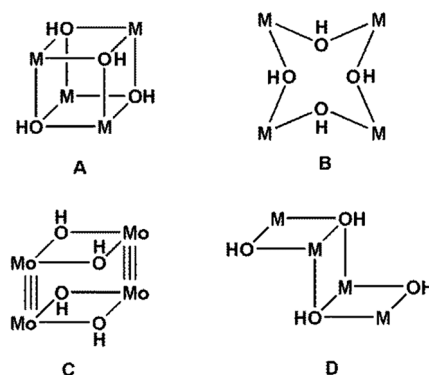


Chart 1 Structure types of " $M_4(OH)_4$ " clusters.

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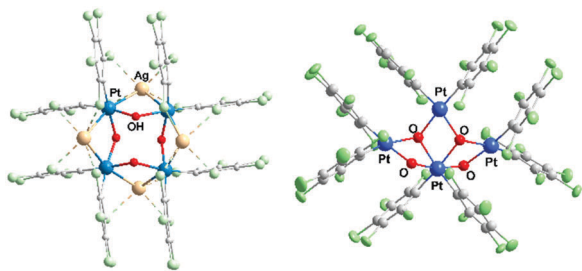


Fig. 1 (a)  $\{[\text{Pt}^{\text{II}}(\text{C}_6\text{Cl}_5)_2(\mu_2\text{-OH})(\mu_2\text{-Ag})]_4\}$  (**3**); (b)  $[\text{Pt}^{\text{IV}}\text{Pt}_3^{\text{III}}(\text{C}_6\text{Cl}_5)_8(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2]^{2-}$  (**1**).

the hard-base character of the  $\text{OH}^-$  ligand. Polynuclear  $\text{Pt}(\text{OH})$  compounds are scarce, but reported examples include one of type A in Chart 1, “ $\text{Pt}_4^{\text{IV}}(\text{OH})_4$ ”<sup>8a</sup> with  $(\mu_3\text{-OH})$ , and two of type B, with  $(\mu_2\text{-OH})$  joining two  $\text{Pt}^{\text{II}}$  atoms.<sup>9b,c</sup> An additional two platinum hydroxo compounds have been described previously, with the eight-membered ring (type B) and with  $\text{Hg}^{2+}$   $[\text{Pt}_4^{\text{II}}(\text{OH})_4(\text{Hg}^{\text{II}}\text{Cl})_2]$ <sup>14</sup> or  $\text{Ag}^+$   $[\text{Pt}_4^{\text{II}}(\text{OH})_4\text{Ag}_4]$  (**3**)<sup>15</sup> incorporated (Fig. 1a); the  $d^{10}$  metals ( $\text{Hg}^{2+}$  or  $\text{Ag}^+$ ) appear to exert a template effect. The Ag compound, *cyclo*- $[\{\text{Pt}(\text{C}_6\text{Cl}_5)_2(\mu_2\text{-OH})(\mu_2\text{-Ag})\}_4]$  (**3**),<sup>15</sup> is formed by the reaction of  $(\text{NBu}_4)_2[\text{Pt}^{\text{II}}(\text{C}_6\text{Cl}_5)_2(\mu_2\text{-OH})_2]$  (**4**)<sup>16</sup> with  $\text{Ag}^+$  in a 1 : 2 molar ratio (Scheme 1, A).

$\text{Pt}^{\text{II}}$  complexes, especially when anionic or with ligands that promote the  $d_{z^2}$  orbital to higher energy levels, can form heteronuclear compounds with Pt–M bonds ( $\text{M} = d^{10}$  or  $s^2$  Lewis-acid metal centers).<sup>17</sup> Since 1985, when the first two pentafluorophenyl compounds with unsupported Pt–Ag bonds were structurally characterized,<sup>18</sup> a large number of organometallic compounds with different organic groups and with other acceptor metals such as  $\text{Tl}(\text{I})$ ,  $\text{Cu}(\text{I})$ ,  $\text{Au}(\text{I})$ ,  $\text{Pb}(\text{II})$ ,  $\text{Hg}(\text{II})$ , and  $\text{Cd}(\text{II})$ ,<sup>17,19</sup> have been reported. The commonest acceptor metal is still Ag, and the most frequent organic group is  $\text{C}_6\text{F}_5$ .  $\text{X} \cdots \text{M}$  ( $\text{X} = \text{F}, \text{Cl}$ ) interactions help in the stabilization of these Pt–M donor–acceptor bonds.<sup>15,18</sup> Besides the wide variety of structural types that they present, these compounds are also interesting for the stabilization of unusual oxidation states,<sup>20</sup> for their optical properties,<sup>15,17,19b–d,21</sup> for the formation of extended structures,<sup>19c,d,22</sup> or for their participation in chemical processes such as halide abstraction<sup>23</sup> or methyl migration.<sup>24</sup> They are also intermediates in important catalytic processes such as inner-sphere oxidation reactions.<sup>25</sup>

Since  $\text{Pt}^{\text{IV}}$  is more suitable than  $\text{Pt}^{\text{II}}$  for the formation of hydroxo compounds, while  $\text{Pt}^{\text{II}}$  participates readily in Pt→M dative bond formation, and given that the commonest coordination

indices of  $\text{Pt}^{\text{IV}}$  (six) and  $\text{Pt}^{\text{II}}$  (four) are different, we expected that the incorporation of Pt in both oxidation states into the same species would produce novel compounds with interest in the contexts of both hydroxo complexes and Pt→M bonds.

On testing this proposal, we found that the partial oxidation of the above-mentioned dihydroxo compound  $(\text{NBu}_4)_2[\text{Pt}^{\text{II}}(\text{C}_6\text{Cl}_5)_2(\mu_2\text{-OH})_2]$  (**4**) by  $\text{I}_2$  in the presence of  $\text{Ag}^+$  ( $\text{AgNO}_3$ ) in a 2 : 1 : 2 molar ratio produces the anionic cluster  $[\text{Pt}^{\text{IV}}\text{Pt}_3^{\text{III}}(\text{C}_6\text{Cl}_5)_8(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2]^{2-}$ , reported here, which is isolated as the  $\text{NBu}_4^+$  salt (**1**) (Fig. 1b) as the bis-acetone solvate. The synthesis of **1** stands in contrast to the reaction of the same dihydroxo compound **4** with  $\text{Ag}^+$  in a 1 : 2 molar ratio, (Scheme 1) which as previously reported<sup>15</sup> produces the cyclic “ $\text{Pt}_4^{\text{II}}(\text{OH})_4\text{Ag}_4$ ” core in **3**.

Fig. 1b shows the structure of the novel anion in **1** as determined by single crystal X-ray diffraction, which can be compared with the differently-shaped neutral compound **3**; Fig. 2 presents a close-up view of the core of **1**. In the formation of **1**,  $\text{Ag}^+$  serves to remove the  $\text{I}^-$  produced in the oxidation of  $\text{Pt}^{\text{II}}$  (as insoluble  $\text{AgI}$ ), and also perhaps to facilitate the oxidation. The ratio  $\text{I}_2$  :  $\text{Ag}$  (1 : 2) is just sufficient to eliminate the  $\text{I}^-$  produced in the reaction, and so compound **1**, unlike **3**, does not contain silver.

The anionic cluster is formed by one  $\text{Pt}^{\text{IV}}$  (Pt1) and three  $\text{Pt}^{\text{II}}$  centers (Pt2, Pt3, Pt4), bridged by OH groups.  $\text{Pt}^{\text{IV}}$  is coordinated by the four OH groups, which is unusual, especially for organometallic compounds;<sup>26</sup> and each of the  $\text{Pt}^{\text{II}}$  atoms is coordinated by two OH. Also, each Pt center maintains the two terminal, mutually *cis*  $\text{C}_6\text{Cl}_5$  ligands that it has in the starting material. The coordination index is thus six for  $\text{Pt}^{\text{IV}}$  and four for the  $\text{Pt}^{\text{II}}$  centers, as is usual for these oxidation states. In the only  $\text{C}_6\text{Cl}_5$  derivative of  $\text{Pt}^{\text{IV}}$  to have been structurally characterized to date, the nominally four-coordinate, homoleptic  $[\text{Pt}(\text{C}_6\text{Cl}_5)_4]$ ,<sup>27</sup> the  $\text{Pt}^{\text{IV}}$  has two further close contacts, to *ortho*-Cl atoms of the  $\text{C}_6\text{Cl}_5$  ligands [ $\text{Pt} \cdots \text{Cl}$  2.559(2), 2.681(2) Å], and thus resides in what is effectively a very distorted octahedral environment.

The four Pt and the four ligated O atoms in **1** form three distorted rhombi, fused in pairs (Fig. 2), with the platinum atoms at the acute vertices [O–Pt–O range 73.25(16)–79.16(15)°; Pt–O–Pt 98.25(17)–107.1(2)°]. Acute vertices of all three rhombi coincide at the  $\text{Pt}^{\text{IV}}$  atom (Pt1), which acts as a lynchpin for the core structure. The central rhombus (Pt1/O2/Pt3/O3) shares one edge with each of its terminal neighbors. This central cycle, with its two O atoms coordinated in a mutually *cis* fashion to octahedral Pt1, forms dihedral angles of 74.82(11) and

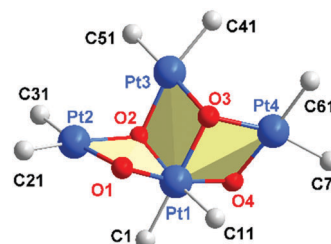
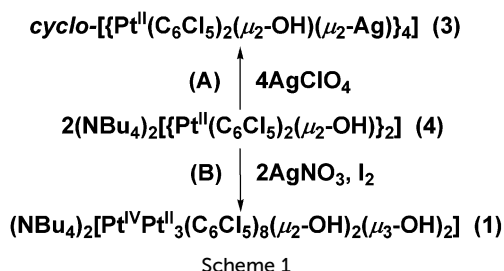


Fig. 2 Core of the anion in **1**, with atom labels. For  $\text{Pt}^{\text{IV}}$ , distances (Å): Pt–C 2.035(6) and 2.036(7); Pt–O 1.998(5)–2.167(4). Angles (°): *cis*-74.96(18)–103.2(2); *trans*-166.81(19)–173.2(2). For  $\text{Pt}^{\text{II}}$ , distances (Å): Pt–C 1.947(7)–2.010(7); Pt–O 2.079(5)–2.169(5). Angles (°): *cis*-73.25(16)–101.9(2); *trans*-165.75(19)–175.2(2).





73.72(14)° with the terminal rhombi containing O1 and O4, respectively. The two distal rings form a dihedral angle of 88.57(12)°. If the three rhombi were coplanar, the cluster core could be described as half of a six-point star (hexagram) with the Pt<sup>II</sup> atoms at three points of the star and Pt<sup>IV</sup> at the center. The (μ<sub>2</sub>-OH) groups at O1 and O4 bridge Pt<sup>II</sup> and Pt<sup>IV</sup> centers, a rare occurrence in hydroxo-platinum chemistry; the other two OH ligands (O2, O3) bridge three platinum atoms (μ<sub>3</sub>-OH) – two Pt<sup>II</sup> and one Pt<sup>IV</sup> in each case. O2 and O3 in **1** are the first examples of (μ<sub>3</sub>-OH) groups bridging Pt in different oxidation states. Thus, **1** should be a useful precursor for other Pt<sup>II</sup> or Pt<sup>IV</sup> hydroxo complexes, including mononuclear compounds with terminal OH groups with potential interest in catalytic processes<sup>12</sup> or antitumor studies.<sup>13</sup>

The core geometry in **1** has no precedent in the structures of tetranuclear tetrahydroxo transition metal clusters. At the periphery of the half-hexagram in this anionic, mixed-valence Pt<sup>IV</sup>Pt<sup>II</sup><sub>3</sub> compound, the central Pt<sup>II</sup> atom (Pt3) lies at 3.5589(3) and 3.6101(4) Å from the other Pt<sup>II</sup> atoms (Pt2 and Pt4, respectively) with a Pt2...Pt3...Pt4 angle of 112.98(1)°. The combination of anionic character and an open stellate periphery make the anion in **1** a potential multi-Pt donor ligand for d<sup>10</sup> or s<sup>2</sup> Lewis-acid centers such as Ag<sup>+</sup>, Tl<sup>+</sup>, Au<sup>+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and others. The presence of terminal C<sub>6</sub>Cl<sub>5</sub> ligands also favours such behavior, since these fragments are known to stabilize metal-metal dative bonds.<sup>15</sup>

Fig. 3(a) shows the “cage-chair” formed by two of the Pt(II) atoms (Pt2 and Pt3) and 4 of the *ortho*-chlorine atoms of the C<sub>6</sub>Cl<sub>5</sub> groups attached to those platinum atoms. This quite distorted “cage-chair” – whose distances are slightly different from those of the analogous “cage-chair” for Pt3 and Pt4, (Fig. S1, ESI†) shows the relative location of the atoms that may define the potential space for the d<sup>10</sup> or s<sup>2</sup> Lewis-acid centers.

Upon testing this proposition, we found that the reaction of **1** with AgSO<sub>3</sub>CF<sub>3</sub> produces a unique neutral Pt<sub>4</sub>Ag<sub>2</sub> cluster, [Ag<sub>2</sub>Pt<sup>IV</sup>Pt<sup>II</sup><sub>3</sub>(C<sub>6</sub>Cl<sub>5</sub>)<sub>8</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>] (**2**) (Fig. 4). Compound **2** has at its core the anion of **1**, to which two Ag<sup>+</sup> centers are adjoined, cradled in what was the open space between pairs of peripheral Pt<sup>II</sup> of the half hexagram and between corresponding pairs of their respective C<sub>6</sub>Cl<sub>5</sub> ligands. In the crystal of **2**, the two external rhombi are now crystallographically equivalent, related by a twofold axis (0.5 – x, 0.5 – y, z) (absent the bulky NBu<sub>4</sub><sup>+</sup> cations, the overall structure of neutral **2** is different from that of **1**). Two of the Pt<sup>II</sup> atoms (distal Pt2 and its symmetry relative Pt2') act individually as single Pt→Ag donors [Pt2–Ag1 2.7163(13) Å] while the central Pt<sup>II</sup> atom, Pt3, attaches the two symmetry-related Ag atoms in *trans*-positions [Pt3–Ag1 2.8855(12) Å, Ag1–Pt3–Ag1' 175.12(5)°].

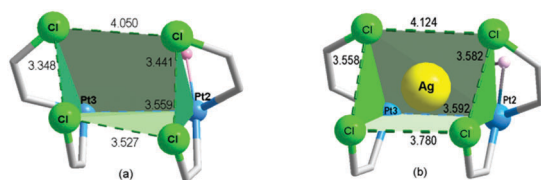


Fig. 3 (a) Space formed by Pt2, Pt3, Cl22, Cl32, Cl42 and Cl56 in complex **1**; (b) space formed by Pt2, Pt3, Cl2, Cl14, Cl20 and Cl6' in complex **2** showing the location of Ag.

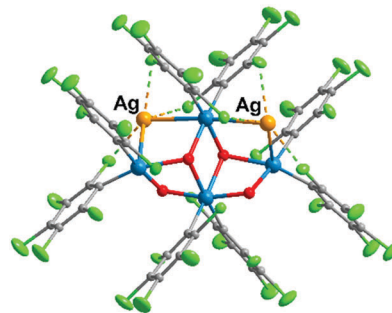


Fig. 4 [Ag<sub>2</sub>Pt<sup>IV</sup>Pt<sup>II</sup><sub>3</sub>(C<sub>6</sub>Cl<sub>5</sub>)<sub>8</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>] (**2**) showing the Pt–Ag bonds and the Cl...Ag interactions. Ag is in yellow. Pt–Ag distances (Å): 2.7163(13) and 2.8855(12); Ag...*ortho*-Cl distances (Å): 2.630(4), 2.694(4), 2.781(5), and 2.939(5).

Each silver atom accepts two *cis*-Pt–Ag bonds [Pt2–Ag1–Pt3 79.65(3)°]. The Pt–Ag distances are quite short for both the *trans*-Ag–Pt–Ag<sup>15</sup> and *cis*-Pt–Ag–Pt<sup>28</sup> fragments. Each Ag atom is also involved in short contacts with *ortho*-Cl atoms from C<sub>6</sub>Cl<sub>5</sub> groups. The shortest of these, [2.630(4) Å], is the shortest Ag...Cl–C(*ortho*) interaction observed to date involving C<sub>6</sub>Cl<sub>5</sub> groups and one of the shortest among all Ag...Cl–C interactions;<sup>29</sup> indeed, it lies within the range of Ag–Cl distances found for μ<sub>2</sub>-Cl bridges between silver atoms (2.6–2.7 Å). Fig. 3(b) shows the “cage-chair” formed by Pt2, Pt3 and the four *ortho*-chlorine atoms in compound **2** with the guest Ag<sup>+</sup> within. As can be seen, there has been a change in the shape and dimensions of the initial “cage-chair” [Fig. 3(a)], which shows that it is flexible enough to adapt to the presence of the guest. It is interesting that in order for the Ag<sup>+</sup> to reach the inside of the “cage-chair,” it must pass through one of the faces of the cage. The superposition of **2** with the anion of **1**, (Fig. S2, ESI†) shows that the “Pt<sub>4</sub>(OH)<sub>4</sub>” core does not change and the main difference between **1** and **2** lies in the orientations of the C<sub>6</sub>Cl<sub>5</sub> groups that participate in the Cl...Ag interactions in **2**.

The crystal of the neutral, nanosized molecule **2** acts as a clathrate, with benzene molecules accommodated in well defined voids. It is also porous, (Fig. S3, ESI†) with channels along the crystallographic *a*-axis.‡ The formation of channels was also observed in compound **3** and is likely the result of a preferred packing arrangement for the eight C<sub>6</sub>Cl<sub>5</sub> groups of the neutral heteronuclear compounds **2** and **3**.

Compound **2** is not the result of a template action by the silver atom, as was the case for the cyclic product **3** (Fig. 1a). Rather, **2** is the result of simple addition of the silver atoms to a stable, previously isolated compound (**1**), with the formation of four dative Pt→Ag bonds. Compound **1** should be a useful precursor for the formation of new types of clusters with other d<sup>10</sup> or s<sup>2</sup> metals; and since the incoming metal atoms are assumed into the core of the molecule, they should not significantly affect the size or shape of the resulting neutral compounds, although these compounds may present different physical or chemical properties according to the nature of the guest metal. It is conceivable that such compounds would be crystallographically isomorphous to **2**, in which case **1** would also be a useful precursor for molecular solids with both voids and pores.



In conclusion, the combination of compounds with different coordination index (6 and 4 in this case) and hydroxo groups can produce hydroxo clusters of unprecedented chemical and structural characteristics such as compound **1**; and this may be a way to obtain new clusters for metals and bridging ligands other than platinum or hydroxide. Compound **1** also raises interesting questions about the reactivity of the  $\mu_3$ -OH bridge to platinum atoms in different oxidation states; about the putative influence of  $\text{Ag}^+$  in the oxidation of the  $\text{Pt}^{\text{II}}$  starting material; and about the behavior of compound **1** as a metalloligand for the preparation of heteropolynuclear compounds with multiple  $\text{Pt} \rightarrow \text{M}$  dative bonds. The latter question, answered affirmatively by the preparation of **2**, in turn raises intriguing possibilities for the formation of new compounds which may display interesting physical properties, or for preparing void-containing systems enclosing organic molecules such as benzene, or for forming porous solids. Also, compound **1** should be a good precursor for new hydroxo compounds of platinum. We are presently investigating some of these possibilities.

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## Conflicts of interest

There are no conflicts of interest to declare.

## Notes and references

‡ Poorly defined electron density was observed in the channels and was modeled as partially occupied, disordered water. (In a separate refinement, not reported here, this electron density was masked using the SQUEEZE algorithm.<sup>30</sup>)

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