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A Supramolecular Heteropolyoxopalladate $\{Pd_{15}\}$ Cluster Host Encapsulating a $\{Pd_2\}$ Dinuclear Guest: $[Pd^{II}_2\subset\{H_7Pd^{II}_{15}O_{10}(PO_4)_{10}\}]^{9-}$

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Supporting Information

ABSTRACT: A high-nuclearity polyoxopalladate compound, $[Pd^{II}_2\subset\{H_7Pd^{II}_{15}O_{10}(PO_4)_{10}\}]^{9-}$ $\{Pd^{II}_{17}\}$, comprising a $\{Pd_{15}\}$ host occupied by a $\{Pd_2\}$ guest and the parent pristine "empty" $[H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}]^{13-}$ $\{Pd_{15}\}$ cluster have both been prepared and characterized by single-crystal X-ray crystallography, ^{31}P NMR, CSI-MS, and XPS. The encapsulated $\{Pd_2\}$ has a short $Pd^{II}-Pd^{II}$ distance within the $\{Pd_{15}\}$ host. Solution studies indicate that the empty host and filled guest complex are in equilibrium with each other, and UV titrations revealed a binding constant of ca. 10^3 for the guest Pd^{II} ions, with a binding stoichiometry of almost 2.

Polyoxometalates (POMs)[1] are polynuclear metal oxides based on early transition metals, most commonly V, Nb, Ta, Mo, and W, but recently "unconventional" Pt-, Au-, and Pd-based oxo clusters have redefined the area. For example, the cluster $[Pt_{12}O_8(SO_4)_{12}]^{4-}$,[2] and a number of POM complexes containing Pd in the framework cages have been reported,[3−5] as well as a handful of pure palladium-based systems: $[H_6Pd^{II}_{13}O_8(As^{V}O_4)_8]^{8-}$,[6] $[Pd^{II}_{13}O_8(Se^{IV}O_3)_8]^{6-}$ and $[Pd^{II}_{13}O_8(PhAs^{V}O_3)_8]^{6-}$,[7] and $[Pd_{0.4}Na_{0.6}\subset H_{6.6}Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}]^{12-}$ ($\{Pd_{15.4}\}$).[8] These show that the family of POMs can be extended to palladium, i.e., polyoxopalladates. Herein, we present a high nuclearity polyoxopalladate compound, $[Pd_2\subset\{H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}\}]^{9-}$ ($\{Pd_2\subset Pd_{15}\}\equiv\{Pd_{17}\}$; Figure 1), and we also present a new "empty" $[H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}]^{13-}$ ($\{Pd_{15}\}$) and show how this pristine $\{Pd_{15}\}$ cage can act as a supramolecular host for two palladium(II) ions, giving a $\{Pd_2\subset Pd_{15}\}$ supramolecular host−guest complex that is stable in solution, where the included $\{Pd_2\}$ guest has a short Pd−Pd distance of 2.76 Å and the $\{Pd_{15}\}$ cage binds the $\{Pd_2\}$ with a binding constant of ca. 1.2×10^3.

The $\{Pd_2\subset Pd_{15}\}$ cluster is formed by heating a solution of $Pd(OAc)_2$ in $NaH_2PO_4-Na_2HPO_4$ buffer, followed by crystallization under slow evaporation. However, the formation of the cluster complex is extremely sensitive to the reaction and crystallization conditions, and we found that the choice of the $NaH_2PO_4-Na_2HPO_4$ buffer solution and pH is crucial for successful synthesis. Subtle changes of these conditions can result in faster crystallization of the transient compound $\{Pd_{15.4}\}$ with disordered Pd(II) centers. The $\{Pd_{15}\}$ cluster is isolated by careful separation from the solution of $\{Pd_{15.4}\}$ by isolating the very first crystal crop. Consistent with the observation of a single peak in the ^{31}P NMR of the $\{Pd_{17}\}$ structure ranging from 16 to 18 ppm, the spectrum of $\{Pd_{15}\}$ in D_2O also shows a single peak rather than the four peaks found for the $\{Pd_{15.4}\}$, suggesting that we have obtained a pristine $\{Pd_{15}\}$ cage (Figure 1).

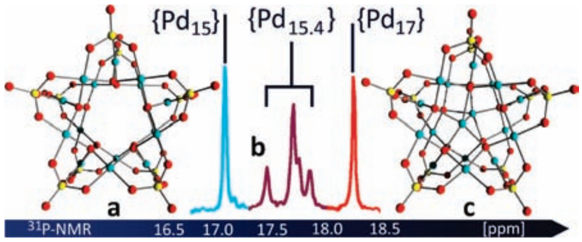

Figure 1. (a) Top view of the structure $[H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}]^{13-}$. (b) ^{31}P NMR chemical shifts of phosphate ligand in the structures $\{Pd_{15}\}$(blue), $\{Pd_2\subset Pd_{15}\}$ (red), and reported $\{Pd_{15.4}\}$ (purple). (c) Top view of the structure of $[Pd_2\subset\{H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}\}]^{9-}$. Pd = blue, P = yellow, O = red spheres.

The structure of cluster $[Pd_2\subset\{H_7Pd^{II}_{15}O_{10}(P^{V}O_4)_{10}\}]^{9-}$ consists of an outer $\{Pd_{15}\}$ metal oxide cage defined by the phosphate ligand shell which "complexes" two Pd(II) ions within the cage to yield the overall $\{Pd_2\subset Pd_{15}\}$ cluster. Further, all 17 Pd atoms are bridged by 10 internal μ_4-oxo groups. As such, the $\{Pd_{17}\}$ can be viewed as three pentagonal $\{Pd_5\}$ layers, which arrange in ABA mode, with an encapsulated $\{Pd_2\}$ moiety. The average distance between the two adjacent palladium atoms in each pentagonal layer is 3.45, 4.22, and 3.44 Å, respectively. Since each of the five palladium atoms located in the middle layer has four nearest neighboring palladium atoms from both the upper and lower layers (the range of Pd−Pd distances is 3.03−3.36 Å), the $\{Pd_{17}\}$ metal core can also be viewed as a pentagonal prism with 10 Pd(II) ions at the vertices, and the five side faces of the prism are capped by five additional palladiums (Figure 2). In the peripheral ligand shell, each of the 10 phosphate anions ligates

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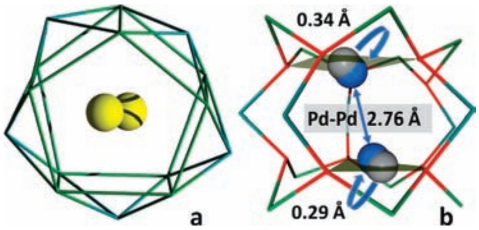

Figure 2. (a) Geometry of the Pd_{17} metal core, consisting of 10 Pd atoms in two pentagons with five capped Pd and two encapsulated Pd atoms (yellow spheres). (b) Distortion of two encapsulated four-coordinated Pd atoms from the less-square equatorial planes of the four coordination oxygen atoms, which is 0.30 and 0.27 Å, respectively. O = red; Pd = green or blue spheres; dummy centers of oxygen planes = gray spheres.

ions in the adjacent layers via three pendant oxygen atoms, thereby acting as a bridging "pincer" ligand, and within each $\{Pd_5\}$ fragment, the overall mean Pd−O distance is 1.98 Å (ranging from 1.94 to 2.05 Å), and O−Pd−O angles are close to 90°. This indicates that all the cage Pd(II) ions adopt a square planar coordination geometry. Compared to the 15 square planar Pd(II) ions found in the pentagonal units, the two central palladiums, featuring a short Pd−Pd distance of ca. 2.76 Å, show a distortion (Figure 2) and thus indicate a possible Pd−Pd interaction. This is very intriguing since several bimetallic metal cores of the square planar Rh^{I}, Ir^{I}, and Pt^{II} have been found to possess interesting photophysical properties,[9] and the dinuclear $Pt^{III}-Pt^{III}$ dumbbell is the building unit in the fabrication of the cluster $[Pt_{12}O_8(SO_4)_{12}]^{4-}$. In this context, it is important to ascertain the valence of the Pd ions within the $\{Pd_2\}$ "core" unit. Although single-crystal X-ray diffraction structural studies and bond valence sum calculations did not give definitive proof, XPS studies show that these internal Pd centers also are in the 2+ oxidation state, despite the short Pd−Pd distance of 2.76 Å when compared to the literature, e.g., d^8-d^8 Pd(II)−Pd(II) distances, which are reported to be in the range 2.98−3.13 Å.[10]

Inspired by the easy complexation of Pd^{2+} into the $\{Pd_{15}\}$ cavity followed by its crystallization, we postulated that the two Pd^{2+} cations in $\{Pd_2 \subset Pd_{15}\}$ are exchangeable while the empty box of $\{Pd_{15}\}$ can encapsulate Pd^{2+} cations within its cavity. Thus, the host−guest chemistry was investigated between these two compounds. Here, ^{31}P NMR investigation was undertaken by titrating Pd^{2+} into the solution of $\{Pd_{15}\}$. The observation of the downfield shifting of the P signals in the NMR is consistent with that expected for the binding event from $\{Pd_{15}\}$ to $\{Pd_{17}\}$. However, some observed overshifting indicates a large number of binding modes for the Pd^{2+} cations within and perhaps even outside the cavity when excess Pd^{2+} was added.

By carefully adding a specific amount of Pd^{2+} into the solution of $\{Pd_{15}\}$, the preliminary UV measurements (Figure 3) can be analyzed to give a crude indication of binding of the $\{Pd^{II}{}_2\}$ guest.[11] In all binding studies, deionized water was used as the solvent for $Pd(NO_3)_2$, $\{Pd_{15}\}$, and $\{Pd_{17}\}$. To minimize the dilution effects, very small volumes (μL) of 6.25 mM $Pd(NO_3)_2$ stock solution were added to 3 mL of 0.0111 mM $\{Pd_{15}\}$ solution. The absorbance values at the wavelength of 261 nm with increasing Pd^{2+} concentration were used in the evaluation of the binding number and constant, according to eq 1:

$$\lg[(A_{eq} - A_0)/(A_{max} - A_{eq})] = \lg K + n\lg\,[Pd^{2+}] \qquad (1)$$

where A_{eq} is the equilibrium absorbance of the Pd^{2+}-bound $\{Pd_{15}\}$(product); A_0, the absorbance of pure $\{Pd_{15}\}$, and A_{max}, the absorbance of $\{Pd_{17}\}$. K is the binding constant, and n is the number of bound Pd^{2+} ions. Using this approach we deduced the number of bound Pd^{2+} ions to be 1.80 ± 0.18 and the overall binding constant, K, to be $1.19 \times 10^3 \pm 2.07 \times 10^0$, for the host molecule $\{Pd_{15}\}$ with the guest Pd^{2+}. The number of bound Pd^{2+} ions is almost 2, but it is important to note that more than two species are involved in binding, as postulated in Figure 4. Further, the presence of this equilibrium also gives a very strong indication that the guest Pd ions are in the 2+ oxidation state, since we add Pd^{II} for the binding measurements and we see no evidence for any redox processes occurring upon Pd binding/release.

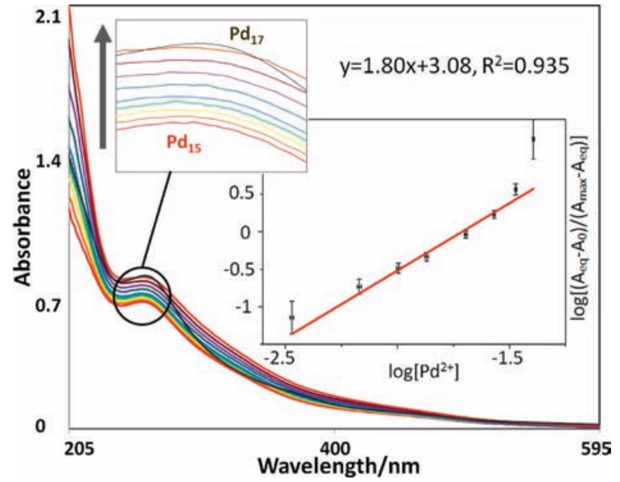

Figure 3. UV−vis spectral changes observed on addition of 6.25 mM $Pd(NO_3)_2$ in water to 0.0111 mM $\{Pd_{15}\}$ solution in water.

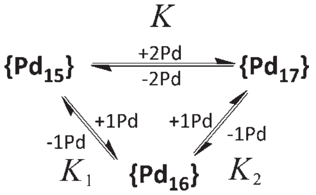

Figure 4. Possibility that the complexation of the Pd^{2+} ions could occur stepwise, via a $\{Pd_{16}\}$ cluster. The presence of more than one species is indicated by the UV−vis measurements and also by preliminary mass spectrometry measurements.

To investigate these two clusters in more detail, we opted to investigate the clusters in solution using CSI-MS (Figure 5).[12] These studies revealed that both the $\{Pd_{15}\}$ and $\{Pd_2 \subset Pd_{15}\}$ species are present in their solution, as observed crystallographically, but as a multitude of charged states resulting from the variable number of protons and sodium ions (giving overlapping envelopes). For instance, the peaks in $\{Pd_{17}\}$ observed at m/z = 749.2 and 1006.6 could be assigned to 4^- and 3^--charged nonaprotonated species unambiguously, with the typical formulas $[H_9Na_3O_{50}P_{10}Pd_{17}]^{4-}$ and $[H_9Na_4O_{50}P_{10}Pd_{17}]^{3-}$. In the mass spectrum of $\{Pd_{15}\}$ solution, the peaks at m/z = 700.5 and 907.7 can be assigned to 4^- -charged diprotonated and 3^--charged 17-protonated species, with the typical formulas $[H_2Na_{14}O_{50}P_{10}Pd_{15}(H_2O)_2]^{4-}$ and $[H_{17}O_{50}P_{10}Pd_{15}]^{3-}$. Meanwhile, the peaks at m/z = 1165.6 and 1242.8 could be assigned to the $\{Pd_{15}\}$ and $\{Pd_2 \subset Pd_{15}\}$ dimer, $[H_{25}Na_{10}O_{100}P_{20}Pd_{30}(H_2O)_9]^{5-}$ and

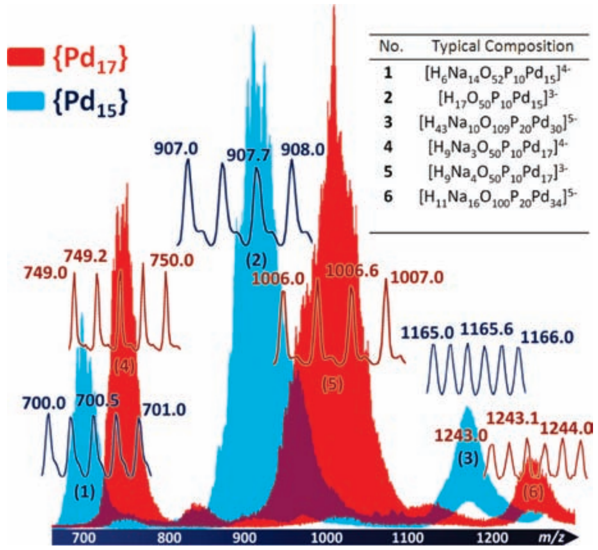

Figure 5. Negative ion mass spectra of $\{Pd_{15}\}$ (blue) and $\{Pd_{17}\}$ (red) in water, showing typical species (1) $[H_2Na_{14}O_{50}P_{10}Pd_{15}(H_2O)_2]^{4-}$, (2) $[H_{17}O_{50}P_{10}Pd_{15}]^{3-}$, (3) the $\{Pd_{15}\}$ dimer, $[H_{25}Na_{10}O_{100}P_{20}Pd_{30}(H_2O)_9]^{5-}$, (4) $[H_9Na_3O_{50}P_{10}Pd_{17}]^{4-}$, (5) $[H_9Na_4O_{50}P_{10}Pd_{17}]^{3-}$, and (6) the $\{Pd_{17}\}$ dimer, $[H_{11}Na_{16}O_{100}P_{20}Pd_{34}]^{5-}$ at m/z = 700.5, 907.7, 1165.6, 749.2, 1006.6, and 1243.1.

$[H_{11}Na_{16}O_{100}P_{20}Pd_{34}]^{5-}$, respectively. Furthermore, preliminary titrations with potassium salts gave data consistent with the hypothesis that it is possible to remove the $\{Pd_2\}$ core from $\{Pd_{15}\}$ host.

In conclusion, we report the largest known crystallographically determined polyoxopalladate compound, which is a supramolecular host−guest compound with the formula $[Pd_2\subset\{H_7Pd^{II}_{15}O_{10}(P^VO_4)_{10}\}]^{9-}$, and its host compound with an pristine $\{Pd_{15}\}$ cage structure, $[H_7Pd^{II}_{15}O_{10}(P^VO_4)_{10}]^{13-}$. Both of the novel structures are well characterized and unambiguously distinguishable by not only X-ray crystallographic analysis but also ^{31}P NMR and CSI-MS. Comparison with the parent compound reveals the possibility that this class of compounds defines a new type of host−guest chemistry, proven by our preliminary UV−vis binding studies. The intriguing Pd−Pd short distance in $\{Pd_{17}\}$ indicates that a unique interactive $\{Pd_2\}$ core is encapsulated in the center of the cluster. In future work, we will characterize the system theoretically, as well as carry out further binding studies to extract the microscopic binding constants and to further investigate this interesting system.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data of $\{Pd_{17}\}$ and $\{Pd_{15}\}$ (CIF); experimental preparation and analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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