Polyoxometalates

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Self-Assembly of a Heteropolyoxopalladate Nanocube: $[\mathrm{Pd}^{\mathrm{II}}{}_{13}\mathrm{As}^{\mathrm{V}}{}_{8}\mathrm{O}_{34}(\mathrm{OH})_{6}]^{8-}$**

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Self-assembly of large, discrete, anionic metal oxide clusters by condensation of small metal oxide anions is a topic of continuing interest.[1] Polyoxometalates (POMs) are known for Group 5 and 6 metals (V, Nb, Ta, Mo, and W) in high oxidation states. POMs are primarily used as catalysts in oxidation reactions, owing to their structural robustness, oxidative stability, and the possibility to incorporate various transition metals for fine tuning of the redox properties.[2]

Palladium oxide containing materials have attracted much attention over the last decade, mainly as catalysts.[3] For example, a Pd–perovskite catalyst has been used for efficient automotive emissions control.[3a] This "intelligent catalyst" self-regenerates and exhibits a dramatically prolonged catalyst lifetime. A combination of POMs (anionic transition-metal oxide clusters) and palladium could be a promising system for both homogeneous and heterogeneous oxidation catalysis as well as acid-catalyzed reactions.[2a] A mixture of a well-known Keggin-type heteropolyacid and a palladium catalyst has been industrialized for the direct synthesis of acetic acid from ethylene.[3c] Incorporation of palladium ions into the polytungstate core was a crucial step in the synthesis of new catalysts having useful properties such as selective and efficient transformation of organic substrates.[2d,e,4] However, the existence of a "pure" polyoxopalladate cluster was not predicted.

The synthesis of nanostructured materials is also an area with a great potential,[5] partially owing to their high surface-to-volume ratio. Nanosized palladium-containing materials might also show improved catalytic properties. In particular, palladium oxide containing nanomaterials are a current research topic, but only a few (and rather complex) synthetic methods are known.[3e–g] These are generally based on oxidation of metallic palladium thin films or nanoparticles, because to date no molecular palladium oxide cluster has been reported.

Herein we report the first example of a molecular palladium oxide cluster. In our attempts to isolate $\mathrm{Pd}^{\mathrm{II}}$-containing tungstoarsenates(V), we discovered that in aqueous acetate buffer, PdCl_2 interacts with $\mathrm{As}_2\mathrm{O}_5$ in a one-pot reaction to form the discrete molecular polyoxopalladate $[\mathrm{Pd}^{\mathrm{II}}{}_{13}\mathrm{As}^{\mathrm{V}}{}_{8}\mathrm{O}_{34}(\mathrm{OH})_{6}]^{8-}$ (**$\mathbf{Pd_{13}}$**, Figure 1). This **$\mathbf{Pd_{13}}$** anion is a distorted cube with edge lengths of about 1 nm. The thirteen palladium(II) ions retain square-planar geometry, in marked contrast to all other discrete POMs, which generally have metals in octahedral environments.[1]

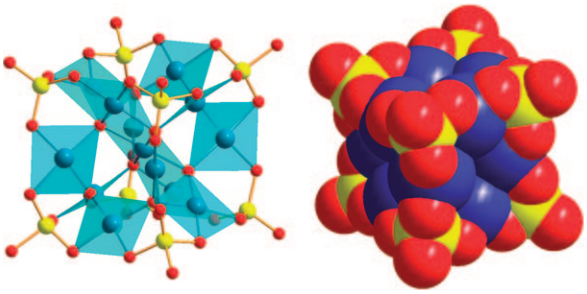

Figure 1. Left: Combined polyhedral/ball-and-stick representation of $[\mathrm{Pd}^{\mathrm{II}}{}_{13}\mathrm{As}^{\mathrm{V}}{}_{8}\mathrm{O}_{34}(\mathrm{OH})_{6}]^{8-}$ (**$\mathbf{Pd_{13}}$**). Right: Space-filling view of **$\mathbf{Pd_{13}}$**. Pd blue, O red, As yellow.

The self-assembly of **$\mathbf{Pd_{13}}$** is quite sensitive to the concentration of $\mathrm{Pd}^{\mathrm{II}}$ and the pH value of the aqueous solution. For example, significantly concentrated ($c = 0.1$–$0.15\,\mathrm{M}$) palladium(II) solutions are required, and the pH value should be between 5 and 7. Polyanion **$\mathbf{Pd_{13}}$** was crystallized as the hydrated sodium salt $\mathrm{Na}_8[\mathrm{Pd}_{13}\mathrm{As}_8\mathrm{O}_{34}(\mathrm{OH})_6]\cdot 42\,\mathrm{H}_2\mathrm{O}$ (**Na-$\mathbf{Pd_{13}}$**).[6] This compound is stable in solution and in the solid state when exposed to air and light. For example, **Na-$\mathbf{Pd_{13}}$** can be repeatedly recrystallized from water at different concentrations. Also, after redissolution **$\mathbf{Pd_{13}}$** is stable in a pH range of at least 3–9. Such properties are an excellent basis for detailed solution studies of the deeply colored **$\mathbf{Pd_{13}}$** by UV/Vis spectroscopy, which will be reported elsewhere.

The structure of **$\mathbf{Pd_{13}}$** can be described as a "Keplerate," as it is comprised of Platonic and Archimedean solids (regular polyhedra and polyhedra with two types of faces but only one

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type of vertex, respectively) such as the cube, truncated cube, cuboctahedron, and icosahedron. In **Pd_{13}** these assemblies are arranged one inside another, resembling a Russian "Matryoshka" doll (Figure 2 and Figure S1 in the Supporting Information).[7] Twelve palladium(II) atoms surround the thirteenth, central palladium(II) atom, resulting in an approximately icosahedral arrangement (distorted towards a cuboctahedron), as shown by single-crystal X-ray diffraction analysis (Figure 2, top left). The positive charges of the Pd^{2+} ions are compensated by eight "inner" oxo groups, forming a distorted cube-shaped shell (Figure 2, top right), and 24 "outer" oxo groups, forming a truncated-cube shell. This $\{Pd^{II}_{13}O_{32}\}^{38-}$ truncated-cube assembly (Figure 2, bottom left) is capped by eight positively charged $(As^{V}O)^{3+}$ groups (Figure 2, bottom right).

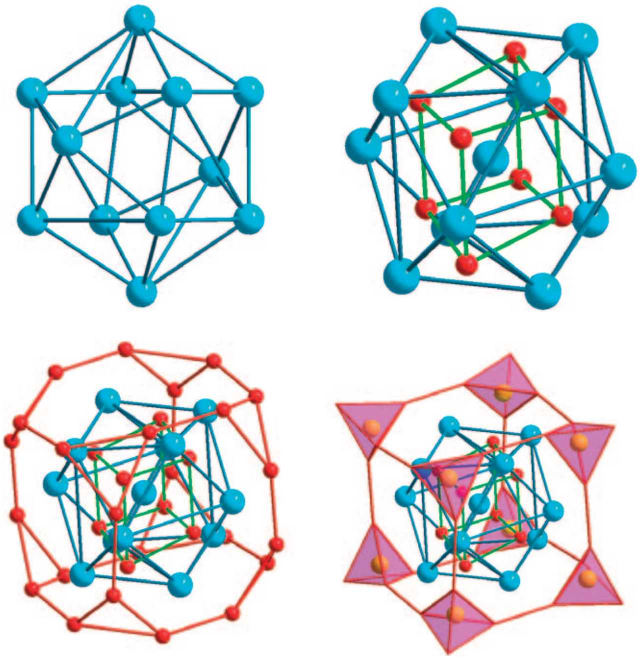
Figure 2. Representation of the "Matryoshka doll" shell structure of **Pd_{13}**.

The terminal As–O bonds range from 1.653(4) to 1.762(4) Å (As2–O2As 1.653(4), As1–O1As 1.678(4), As3–O3As 1.753(4), As4–O4As 1.762(4) Å). Our analytical data (XRD, elemental analysis, bond valence sums (BVS)) are consistent with six protons being associated with the eight terminal oxygen atoms of **Pd_{13}**. The eight capping arsenic(V) ions posses four-coordinate tetrahedral geometry. The thirteen palladium atoms in **Pd_{13}** have the four-coordinate square-planar environment usual for Pd^{II} (Figure 1). The palladium centers are connected to each other through bridging μ_3-oxo and μ_4-oxo ligands with "normal" Pd–O distances in the range 1.95–2.09 Å. The resulting "molecular nanocube" **Pd_{13}** has an edge length of about 1 nm and hence a volume of about 1 nm^3. In the solid state, individual molecules of **Pd_{13}** are associated with eight non-disordered sodium cations (which were all located by XRD) and 42 waters of hydration (determined by thermogravimetric analysis) through a framework of strong hydrogen bonds.

The structure of **Pd_{13}** exhibits some analogies to the well-known Keggin ion $[XO_4W_{12}O_{36}]^{n-}$ (Figure S2 in the Supporting Information). In **Pd_{13}** the twelve peripheral palladium atoms form a distorted icosahedron/cuboctahedron, and in the Keggin ion the twelve octahedral MO_6 addenda units are also located on the vertices of a distorted cuboctahedron. However, in **Pd_{13}** the twelve outer Pd^{II} ions, as well as the central one, exhibit square-planar coordination geometry (Figure 1). This is in contrast to all other known POMs in which the metal-atom geometry is octahedral (or more rarely tetrahedral, square-pyramidal, or seven-coordinate).[1] Hence we have discovered the first example of a discrete molecular heteropolyanion based exclusively on square-planar $Pd^{II}O_4$ addenda units.

Some extended oxide structures containing oxopalladate(II) building units such as $[Pd_6O_{12}]^{12-}$ were known before.[8] However, they are generally not soluble in common solvents, and most importantly, they do not contain any discrete polyoxopalladate molecules.

By preparing **Pd_{13}** we have demonstrated for the first time that Pd^{II} ions also form POMs, and we see no reason why this should not also be true for other d^8 transition metals such as Pt^{II}, Au^{III}, Rh^{I}, or Ir^{I}. We also believe that the $As^{V}O_4$ heterogroups can perhaps be replaced by 1) other XO_4 groups (e.g. $X = P^{V}$, Si^{IV}, Ge^{IV}), 2) lone-pair-containing XO_3 groups (e.g. $X = As^{III}$, Se^{IV}), or 3) RXO_3 groups with pendant organic functionalities (e.g. $X = As^{V}$, P^{V}, Si^{IV}, Ge^{IV}; R = alkyl, aryl).

The structure of **Pd_{13}** has an interesting relationship to Pd^{0}_{13}, which is the smallest stable bare metal cluster of the Jellium model having a closed electronic shell.[9,10] This metal cluster theoretically has icosahedral symmetry, consisting of 13 palladium(0) atoms: one at the center and 12 others on each of the 12 equivalent vertices of an icosahedron. On the other hand, in **Pd_{13}** the 12 outer palladium(II) atoms have square-planar geometry and they occupy the vertices of a distorted icosahedron. In the family of clusters with closed shells, M^{0}_{13} is the smallest and has the highest surface-to-volume ratio, which is extremely important for catalysis. The "naked" Pd^{0}_{13} unit does not exist alone, but it can perhaps be stabilized by a ligand shell.

Nanometer-sized particles are of increasing importance in surface science, particularly in electrocatalysis, where they are used to fabricate modified electrodes. Among the most efficient are the Pd-based electrocatalysts. Electrochemistry has allowed us to use **Pd_{13}** as a precursor for the design of such electrodes. The main observations are described in detail in the Supporting Information. In short, the cyclic voltammogram of **Pd_{13}** exhibits essentially the same characteristics as the deposition of Pd^{0} from Pd^{2+} solutions on the glassy carbon (GC) electrode surface, as supported by comparison with literature results. X-ray photoelectron spectroscopy (XPS) analysis indicates that this deposit contains mostly Pd^{0} with a very small amount of Pd^{2+} (see Figure S5 in the Supporting Information). The presence of arsenic was also detected in the deposit, as expected. This deposit exhibits faster electrochemical kinetic behaviors than the film deposited from

$PdSO_4$ under analogous conditions (see Figure S4C in the Supporting Information).

Such observations are important, because they allow us to envision the use of such films to improve the kinetics of electrocatalytic processes. The challenging and important problem of electrochemical detection of hydrazine was selected as a test example for the behavior of an electrode modified with a film deposited from a $\mathbf{Pd_{13}}$ solution. The electrocatalytic behavior of Pd nanoparticles deposited on carbon materials has been described, but no stable detection was found with GC as a substrate.[11] In a control experiment, we have also checked that Pd^0 deposited from $PdSO_4$ gives good but not durable results for hydrazine oxidation.

Figure 3 shows the hydrazine oxidation pattern obtained in a pH 7.0 medium with the catalyst deposited from $\mathbf{Pd_{13}}$ on a GC electrode. This wave is remarkably well-behaved, a feature that underscores the fast kinetics of the associated processes. The electrode baseline in the absence of hydrazine is also represented in Figure 3 (curve 1). The inset shows a perfectly linear peak current increase with increasing hydrazine concentration from 2.0×10^{-4} to 1.4×10^{-3} M. Note that such good linearity was also obtained for smaller concentrations of hydrazine (4.12×10^{-5} to 1.34×10^{-4} M, Figure S7 in the Supporting Information). The hydrazine oxidation appeared to be diffusion-controlled.

It should be noted that the peak potential was routinely measured between −0.020 and +0.070 V versus NHE in several independent replications of electrode preparation and hydrazine electrooxidation experiments. To date, the voltammetric peak with the best electrode for hydrazine oxidation has been observed with a Pd-particle-decorated carbon nanotube (+0.282 V vs. NHE in a pH 7 buffer).[11] This improvement of 0.200 to 0.300 V in peak potential observed with the Pd^0 film deposited on GC from $\mathbf{Pd_{13}}$ is worth emphasizing. A direct consequence is that hydrazine oxidation occurs far from the potential domain where the voltammetric stripping of palladium particles would take place, thus explaining the remarkable stability of our system. This observation constitutes the first example of a stable Pd-modified GC electrode for the oxidation of hydrazine. In particular, $\mathbf{Pd_{13}}$ is expected to exhibit such remarkable behavior in fuel cells, for which nanostructured metal oxide active layers are expected to solve most of the durability and catalytic issues.

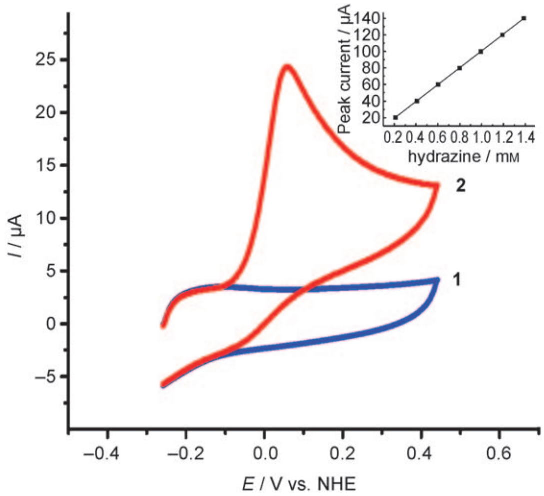

Figure 3. Cyclic voltammogram showing the baseline of a GC electrode modified in a 4×10^{-5} M $\mathbf{Pd_{13}}$ solution in 1 M CH_3COOLi/H^+ pH 6 buffer. The electrode was taken out of the deposition solution, thoroughly rinsed with Millipore water, and studied in a pure supporting electrolyte (pH 7, 0.4 M (NaH_2PO_4+NaOH), curve 1). Curve 2 shows the oxidation of 2.01×10^{-4} M hydrazine on this modified electrode in the same pH 7 medium. The potentials are quoted against the NHE reference electrode. The inset shows the variation of the peak current intensity for hydrazine oxidation as a function of its concentration in the pH 7 medium. $R^2=0.999$. The scan rate was 100 mV s^{-1} throughout.

The development of new types of catalysts with higher efficiency for reactions in water—an economical, safe, and environmentally benign solvent—is greatly desired.[12] The heteropolypalladate $\mathbf{Pd_{13}}$ has a large surface-to-volume ratio and is therefore an ideal homogeneous catalyst. On the other hand, $\mathbf{Pd_{13}}$ might be capable of being anchored on a support in a highly dispersed form, resulting in a heterogeneous catalyst.[13] Furthermore, $\mathbf{Pd_{13}}$ might also be useful as a novel, molecular precursor for the design of unsupported or supported nanocatalysts at the atomic or molecular level.

Water-stable palladium catalysts (with bathophenanthroline or neocuproine ligands) for the selective oxidation of alcohols in aqueous media using oxygen as the terminal oxidant were studied recently.[14] In these oxidations, coordination of the π-acidic aromatic nitrogen ligand to the palladium metal center was required to prevent the precipitation of the catalyst as insoluble Pd^0 prior to aerobic reoxidation to Pd^{II}. In the palladium neocuproine case, we later showed that nanoclusters are formed under when a cosolvent is used. These catalysts are among the most active palladium catalysts reported for alcohol oxidation,[15] and TOFs of over 500 h^{-1} could be reached in the oxidation of 2-octanol to 2-octanone.[14c]

This prompted us to study the activity of the $\mathbf{Pd_{13}}$ solution both under aqueous conditions and with cosolvent. In initial experiments benzyl alcohol was studied as a key example of a primary alcohol. The reaction was conducted at 100 °C and 30 bar pressure (2.1 bar oxygen partial pressure); in this case 54 % yield of benzaldehyde was observed after 12 hours together with 11 % benzoic acid (Table 1). This consecutive oxidation of benzaldehyde could not be inhibited by the addition of TEMPO as radical inhibitor (Table S2 in the Supporting Information, TEMPO = 2,2,6,6-tetramethylpiper-

Table 1: Oxidation of alcohols in water using $\mathbf{Pd_{13}}$ as the catalyst.[a]

	mol % Pd	*t* [h]	TON[d]	Selectivity [%][e]
benzyl alcohol	0.5	12	106	80
benzyl alcohol	1.0	5	40	100
benzyl alcohol[b]	0.5	5	98	100
2-hexanol[b,c]	0.5	5	10	100

[a] Reaction conditions: 5 mmol benzyl alcohol, 25 mL H_2O, 30 bar $O_2(8\%)/N_2$ mixture, 100 °C. [b] 50 bar 8 % O_2 mixture. [c] 10 mmol 2-hexanol, 25 mL H_2O/ethylene carbonate mixture (1:1). [d] TON: mmol product (benzaldehyde or 2-hexanone) per mmol Pd. [e] Selectivity for aldehyde or ketone based on alcohol converted.

idine-1-oxyl radical, free radical). However, when performing the reaction in a shorter time frame and using more oxygen (Table 1), no overoxidation to benzoic acid occurred. In this case, 100% selectivity to benzaldehyde could be realized, with a 49% yield for benzaldehyde after 5 hours and a TON of 49 (based on total Pd). Under similar conditions, albeit using a cosolvent, 2-hexanol could also be oxidized. We observed a TON of 10 (based on total Pd) of 2-hexanone after 5 hours.

These results indicate that $\mathbf{Pd_{13}}$ is a stable and active catalyst for alcohol oxidation. No π-acidic aromatic nitrogen ligands are required to stabilize intermediate Pd^0 in solution during oxidation by oxygen. Further studies will be directed at optimizing the conditions to increase the activity of $\mathbf{Pd_{13}}$.

In summary, we have prepared a truly new, discrete, molecular, late-transition-metal polyoxoanion using solution chemical techniques. The last few decades have seen much progress in polyoxoanion chemistry, but this progress has focused mainly on early-transition-metal polyoxoanions, and efforts to extend this chemistry to the late-transition-metal elements have been of limited success. Our work can be considered a breakthrough with the solution synthesis of a discrete polyoxopalladate, possibly opening up an area of research that promises to be rich both in new chemistry and in new applications.

Experimental Section

Preparation of $\mathbf{Pd_{13}}$: $PdCl_2$ (0.110 g, 0.62 mmol) and As_2O_5 (0.044 g, 0.191 mmol) were dissolved in NaAc buffer solution (5 mL, 0.5 M, pH 6.1). The solution was stirred and heated to 80 °C for 90 min. Gradually the solution became dark red-brown. Then it was cooled to room temperature and filtered. Slow evaporation of the solution at room temperature resulted in red-brown blocks within a day. crystallize the product, the solution was filled into crystallization vials and allowed to evaporate at room temperature. Within 4–24 h, dark red-brown blocks formed. Yield: 0.050 g (28%). IR (2% KBr pellet, 1300–400 cm^{-1}): $\tilde{\nu} = 860$(m), 800(s), 667(m), 654(sh), 621(m), 542(s), 526(sh), 474(sh), 459(sh), 420(w) cm^{-1}. Elemental analysis (%) calcd for $Na_8[Pd_{13}As_8O_{34}(OH)_6]\cdot 42\,H_2O$ ($\mathbf{Na\text{-}Pd_{13}}$): Na 5.15, Pd 38.8, As 16.8; found: Na 5.25, Pd 38.7, As 16.8. The thermogram of $\mathbf{Na\text{-}Pd_{13}}$ (20–1200 °C) is shown in the Supporting Information.

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[6] Crystal data for $Na_8[Pd_{13}As_8O_{34}(OH)_6]\cdot 42\,H_2O$ ($\mathbf{Na\text{-}Pd_{13}}$): A red block of $\mathbf{Na\text{-}Pd_{13}}$ with dimensions $0.11 \times 0.06 \times 0.05$ mm^3 was mounted on a glass fiber with epoxy glue for indexing and intensity data collection at 296 K on a Bruker D8 APEX II CCD using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Of the 90737 reflections collected ($2\theta_{max} = 54.98°$, 99.2% complete), 9204 were unique ($R_{int} = 0.119$) and 6236 reflections were considered observed ($I > 2\sigma(I)$). Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program (G. M. Sheldrick, Siemens Analytical X-ray Instrument Division: Madison, WI, **1995**). Direct methods were used to locate the palladium atoms (SHELXS-97). Then the remaining atoms were found from successive Fourier maps (SHELXL-97). The final cycle of refinement, including the atomic coordinates and anisotropic thermal parameters (Pd, As, Na, and O atoms)

converged at $R = 0.045$ ($I > 2\sigma(I)$) and $R_w = 0.106$ (all data). In the final difference map the deepest hole was $-1.22\,e\,Å^{-3}$ and the highest peak $1.96\,e\,Å^{-3}$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419698.

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