

Heteropoly-13-Palladates(II) $[\text{Pd}^{\text{II}}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ and $[\text{Pd}^{\text{II}}_{13}\text{Se}^{\text{IV}}\text{O}_{32}]^{6-}$

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Two discrete anionic palladium(II)–oxo clusters have been prepared: $[\text{Pd}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ (**1**) and $[\text{Pd}_{13}\text{Se}^{\text{IV}}\text{O}_{32}]^{6-}$ (**2**) were synthesized in one-pot self-assembly reactions of $\text{Pd}(\text{OAc})_2$ with PhAsO_3H_2 and SeO_2 and characterized by single-crystal X-ray analysis, IR, thermogravimetric analysis, elemental analysis, magnetic and electron paramagnetic resonance measurements, and electrochemistry.

Polyoxometalates (POMs) are discrete molecular metal–oxygen clusters with a large structural and compositional diversity and a unique combination of properties, such as thermal and oxidative stability, tunability of acidity and redox activity, and solubility in various media.¹ As a result, POMs have potential applications in different and diverse areas such as catalysis, magnetism, bio- and nanotechnology, and medical and materials sciences.²

For many years, POMs were known only for group 5 and 6 metals (V, Nb, Ta, Mo, and W). Recently, we reported the synthesis, structure, and some catalytic properties of the first polyoxometalate built by Pd^{II} ions $[\text{Pd}^{\text{II}}_{13}\text{As}_8\text{V}\text{O}_{34}(\text{OH})_6]^{8-}$ ($\text{Pd}_{13}\text{As}_8$) formed by a self-assembly reaction of PdCl_2 and As_2O_5 .^{3a} The unprecedented molecular nanocube $\text{Pd}_{13}\text{As}_8$ is the first example of a POM based on square-planar addenda atoms, in sharp contrast to all other known discrete polyanions.^{3b}

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Palladium-containing materials are known as catalysts of numerous chemical processes.⁴ The incorporation of Pd in polytungstates leads to compounds possessing excellent catalytic properties for various organic reactions including the oxidation of alkanes and alkenes by peroxides, for example, for the direct synthesis of acetic acid from ethylene.⁵

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(6) Synthesis of $\text{Na}_6[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ (**1a**): $\text{Pd}(\text{OAc})_2$ (0.140 g, 0.620 mmol) and PhAsO_3H_2 (0.125 g, 0.620 mmol) were dissolved in 5 mL of a 0.5 M NaOAc solution at a pH of 6.9 (prepared from a 0.5 M solution of HOAc by the addition of an appropriate amount of solid NaOH), while stirring and heating to 80 °C for 90 min. Then, the brown solution was cooled to room temperature and filtered to remove a small amount of Pd precipitate. Slow evaporation at room temperature led to 0.035 g (yield 20% based on Pd) of reddish octahedral crystals of **1a** after 2–3 weeks. The crystals were collected by filtration and air-dried. IR (2% KBr pellet, ν/cm^{-1}): 1622 (m), 1477 (w), 1437 (m), 1308 (w), 1177 (w), 1161 (w), 1091 (m), 1065 (w), 1021 (w), 1000 (w), 805 (s), 743 (s), 694 (s), 656 (s), 614 (s), 532 (s). Elem. anal. (%) calcd for $\text{Na}_6[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ (**1a**): Na, 3.7; Pd, 37.6; As, 16.3; C, 15.7; H, 2.4. Found: Na, 3.7; Pd, 37.5; As, 16.2; C, 17.1; H, 2.3. The thermogram of **1a** (25–900 °C) is discussed in the Supporting Information.

Synthesis of $\text{Na}_6[\text{Pd}_{13}\text{Se}_8\text{O}_{32}]10\text{H}_2\text{O}$ (**2a**): $\text{Pd}(\text{OAc})_2$ (0.140 g, 0.620 mmol) and SeO_2 (0.070 g, 0.630 mmol) were dissolved in 0.5 M solution of NaOAc (5 mL, pH 6.9), while stirring and heating to 80 °C. A light brown precipitate started to form after ~10 min. After 30 min of heating the pH was adjusted to 6.4 by adding several drops of diluted NaOH solution. Then the reaction mixture was heated with stirring for an hour. The precipitate was removed by filtration (*vide infra*)* and the solution was allowed to cool to room temperature. The filtrate was kept at room temperature for several days to produce dark red crystals (hexagonal plates) of **2a**, which were isolated by filtration, and air-dried. Yield: 15 mg (10% based on Pd). IR (2% KBr pellet, ν/cm^{-1}): 1618 (sh), 797 (s), 712 (s), 615 (s), 549 (s). Elemental analysis (%) calcd for $\text{Na}_6[\text{Pd}_{13}\text{Se}_8\text{O}_{26}(\text{OH})_6]10\text{H}_2\text{O}$ (**2a**): Na 4.8, Pd 48.7, Se 22.2, H 0.71; found: Na 4.6, Pd 48.9, Se 22.3, H 0.66. The thermogram of **2a** (25–1200 °C) is discussed in the Supporting Information.

* The above precipitate can be recrystallized from water resulting in a mixture of crystals of **2a** and a second product. Single-crystal XRD analysis on the guanidinium salt of the latter revealed a cyclic polyoxo-15-palladate with the formula $[\text{Pd}_{15}\text{Se}_{10}\text{O}_{50}]^{10-}$ (Crystal data: orthorhombic, space group $Cmc2_1$, $a = 22.563(3)$, $b = 16.130(2)$, $c = 18.4565(19)$ Å, $V = 6716.9(13)$ Å³, $Z = 4$, $T = 173(2)$ K, $R1 = 0.0539$, $wR2 = 0.1249$ ($I > 2(I)$)).

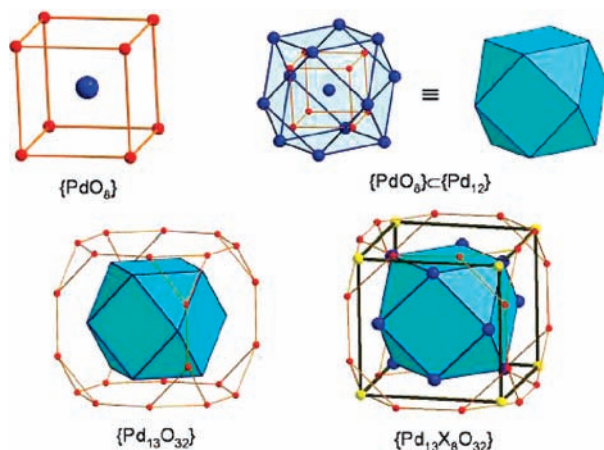


Figure 1. Structural representation of **1** in terms of Platonic and Archimedean solids. Color code: Pd, blue; As, yellow; O, red.

The preparation of discrete polyoxopalladates may result in unexpected structures and in materials providing new perspectives in homogeneous and heterogeneous catalysis. Indeed, it was shown that $\text{Pd}_{13}\text{As}_8$ is a stable and active catalyst for alcohol oxidation by dioxygen.^{3a}

Now, we have succeeded in the preparation of Pd_{13}L_8 derivatives with the $\text{As}^{\text{V}}\text{O}_4$ fragments replaced by organofunctionalized $\text{PhAs}^{\text{V}}\text{O}_3$ heterogroups in $\text{Na}_6[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ (**1a** \equiv $\text{Na}_6 \cdot \mathbf{1} \cdot 24\text{H}_2\text{O}$) or by a lone-pair containing $\text{Se}^{\text{IV}}\text{O}_3$ fragments in $\text{Na}_6[\text{Pd}_{13}\text{Se}_8\text{O}_{32}] \cdot 10\text{H}_2\text{O}$ (**2a** \equiv $\text{Na}_6 \cdot \mathbf{2} \cdot 10\text{H}_2\text{O}$).

The two novel palladium(II)-oxo clusters were obtained by the self-assembly of $\text{Pd}(\text{OAc})_2$ and the appropriate heteroatom-containing precursor (phenylarsonic acid for **1** and selenium dioxide for **2**) sodium acetate medium (pH = 6.4).⁶ A high concentration of Pd^{2+} ions (at least 0.1 M) and a pH value between 5 and 7 are essential for the formation of **1** and **2**. These compounds are stable in the solid state when exposed to air and light. They can also be repeatedly recrystallized from water at different concentrations.

In the first polyoxopalladate $[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}]^{6-}$ (**1**), one of the 13 Pd^{2+} ions is located in the center of the structure, and it is coordinated by eight oxygen atoms situated at the vertices of a cube (Figure 1, left on top). All eight Pd–O distances are crystallographically equivalent with a bond length of 2.338(7) Å. The other 12 Pd^{2+} ions surround the PdO_8 motif to form a cuboctahedron (Figure 1, right on top). Each oxygen atom of the “inner” PdO_8 fragment is coordinated by the central Pd atom and by three “external” palladiums situated on a trigonal face of the cuboctahedron. Each of the 12 external Pd^{2+} ions has a square-planar coordination geometry and coordinates two “inner” μ_4 -O (Pd–O = 1.974(7)–1.981(7) Å) and two “outer” μ_3 -oxo ligands (Pd–O = 2.023(7)–2.039(7) Å). The 24 “outer” oxygen atoms form a truncated-cube-shaped shell (Figure 1, left below), which is capped by eight positively charged AsPh^{4+} groups. The eight As atoms possess tetrahedral

(7) Crystal data for **1a**: $\text{C}_{48}\text{H}_{88}\text{As}_8\text{Na}_6\text{O}_{56}\text{Pd}_{13}$, $M_r = 3682.0$, tetragonal, space group $I4/m$, $a = 15.9515(8)$, $c = 25.1154(12)$ Å, $V = 6390.6(5)$ Å³, $Z = 2$, $T = 173(2)$ K, $D_{\text{calcd}} = 1.920$ g cm⁻³, 64 588 reflections collected, 3312 unique ($R(\text{int}) = 0.1081$), $R1 = 0.0510$, $wR2 = 0.1656$ ($I > 2\sigma(I)$). The Na cations in the structure of **1a** were highly disordered and could not be located by XRD, which is a common problem in POM crystallography. However, we clearly identified the presence of six Na^+ cations in **1a** by elemental analysis.

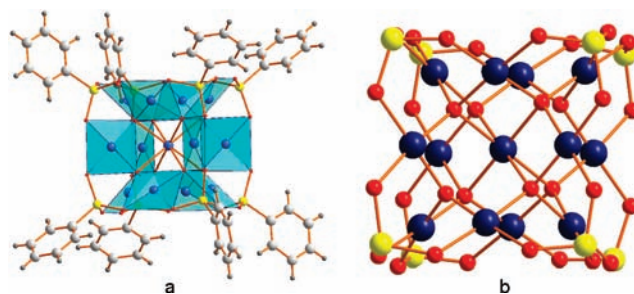


Figure 2. (a) Combined polyhedral/ball-and-stick representation of **1**. (b) Ball-and-stick structure of **2**. Color code: Pd, blue; As and Se, yellow; O, red.

coordination geometry (the As–O distances range from 1.685(7) to 1.686(8) Å, and the unique As–C distance is 1.897(10) Å) and form an external, cube-shaped shell (Figure 1, right below, and Figure 2a).⁷

The second polyoxopalladate $[\text{Pd}_{13}\text{Se}_8\text{O}_{32}]^{6-}$ (**2**) closely resembles the $[\text{Pd}_{13}\text{As}_8\text{O}_{32}]^{6-}$ core in **1**, but in **2**, the central Pd^{2+} ion is six-coordinate (trigonally compressed octahedron) with Pd–O bond lengths of 2.153(9) Å. This coordination sphere is biccapped by two other oxygen atoms of the “inner” distorted cube-shaped shell at a distance of 2.602(15) Å. These two oxygen atoms are coordinated each by three square-planar palladium ions, situated on a trigonal face of the cuboctahedron. The Pd–O distances of the 12 four-coordinated metal centers are in the normal range (1.911(2)–2.048(10) Å). The external, distorted cube-shaped shell is formed by eight Se^{IV} ions, which exhibit a trigonal-pyramidal geometry (Se–O = 1.689(10)–1.718(10) Å) with a stereochemically active, outward-facing lone pair (Figure 2b).⁸

Surprisingly, the central Pd^{2+} ion in the heteropolypalladates **1** and **2** has an unusually high coordination number: six in compound **1** and eight in compound **2** (with a trigonally compressed octahedral coordination sphere) and eight in compound **1** (with a cubic coordination sphere). All Pd–O distances are equivalent in both cases (vide supra). Bond valence sum (BVS) calculations are consistent with a +2 oxidation state of the central Pd atom; the calculated values are 1.8 for **1** and 2.2 for **2**, respectively.⁹ While some complexes with six-coordinated Pd^{2+} are described in the literature,¹⁰ there are no examples of an eight-coordinated Pd^{2+} ion to date.

In order to ascertain that such high coordination numbers of the central Pd^{2+} ions are real (and not due to crystallographic disorder due to random orientation of the polyanions in the solid state), we have also carried out an X-ray analysis of a mixed sodium–potassium salt of **1**,

(8) Crystal data for **2a**: $\text{H}_{20}\text{Na}_6\text{O}_{42}\text{Pd}_{13}\text{Se}_8$, $M_r = 2845.2$, trigonal, space group $R\bar{3}$, $a = 11.2946(3)$, $c = 39.5656(15)$ Å, $V = 4371.1(2)$ Å³, $Z = 3$, $T = 173(2)$ K, $D_{\text{calcd}} = 3.571$ g cm⁻³, 32 157 reflections collected, 2226 unique ($R(\text{int}) = 0.0692$), $R1 = 0.0503$, $wR2 = 0.1096$ ($I > 2\sigma(I)$).

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$\text{Na}_3\text{K}_3[\text{Pd}_{13}(\text{PhAs})_8\text{O}_{32}] \cdot 17\text{H}_2\text{O}$ (**1b** \equiv $\text{Na}_3\text{K}_3\text{-1} \cdot 17\text{H}_2\text{O}$).¹¹ This salt crystallizes in triclinic symmetry, and thus the $\{\text{Pd}_{13}\text{As}_8\text{O}_{32}\}$ core in **1b** does not possess as high a symmetry as that in **1a**. Nevertheless, the central Pd^{2+} ion is still eight-coordinated with Pd–O distances ranging from 2.244(5) to 2.437(7) Å.

We have also performed magnetic measurements on **1a** to prove that indeed the central Pd^{2+} ion is in a cubic coordination sphere. For this situation, we expect a paramagnetic $S = 1$ state, as opposed to a square-planar central Pd^{2+} ion, which would be diamagnetic.

Preliminary magnetic susceptibility measurements on a powder sample of **1a** as a function of temperature over 2–295 K yielded a ground-state spin value of $S = 1$, as expected for a cubic Pd^{2+} complex. Definitive confirmation of the $S = 1$ ground state was also obtained via high-frequency electron paramagnetic resonance (EPR) measurements. Figure S6 (see Supporting Information) shows a typical EPR spectrum of **1a** at 10 K at the very high frequency of 406.4 GHz. The spectra could be well-fitted, with a spin Hamiltonian requiring large zero-field-splitting parameters, D and E , and an anisotropic Landé g tensor. The best fit values are listed in Figure S6, confirming that **1** can indeed be described as a paramagnetic polyanion with two unpaired electrons. We note, however, that there are significant changes in the EPR signal line shape as the temperature is raised above 20 K (data not shown). The new features indicate that the spin value changes as the temperature is raised. The measurements continue to establish this interesting observation definitively.

The main cyclic voltammetry (CV) data for **1** and **2** are described in the Supporting Information. As expected, the CV characteristics of the two polyanions are distinct (Figure S7, Supporting Information). The reduction potentials for **1** and **2** appear to be more negative than for PdSO_4 . Such potential differences were observed previously for another heteropolypalladate.^{3a} However, one striking difference appears in the anodic patterns. In addition to the PdO formation, **1** shows a small, broad, ill-defined wave before the electrolyte discharge. In contrast, the corresponding second oxidation wave of **2** is well-defined ($E_{\text{peak}} = +0.890$ V versus saturated calomel electrode (SCE)). These second oxidation waves might feature further oxidation of PdO to the

Pd^{4+} state.¹² Actually, electrochemical generation and reduction of PdO are known to constitute very complex processes, which have received appropriate attention in the literature.¹² The present examples permit a particularly clear illustration of the PdO reduction dependence on the potential used for their generation (Figure S8, Supporting Information). Figure S9 (Supporting Information) highlights electrocatalytic water oxidation by a thin film of **2** on a glassy carbon electrode. In terms of onset potential, the observed activity is better than that obtained in modifying the electrode with PdSO_4 . The onset potential for this process compares favorably with the best literature values.¹³ Such electrodes fabricated with **1** or **2** are remarkably stable and exhibit good activity for water electrocatalytic oxidation both at pH 5.9 and at 7.0, respectively. Detailed studies of this process are currently underway.

Exhaustive electrolyses of **1** and **2** were carried out at pH 5.9 (at -0.650 V versus SCE for **1** and -0.570 V versus SCE for **2**). The numbers of electrons consumed per Pd were 2.0 ± 0.1 and 2.1 ± 0.2 for **1** and **2**, respectively. Electrolyses performed in a pH 7.0 medium also involved the same numbers of electrons. These results confirm that all 13 Pd centers in **1** and **2** have a +2 oxidation state.

In conclusion, we have shown that the AsO_4 groups in $\text{Pd}_{13}\text{As}_8$ can be replaced by $\text{PhAs}^{\text{VO}}_3$ groups as well as by lone-pair-containing $\text{Se}^{\text{IV}}\text{O}_3$ groups. Two novel heteropolypalladates have been isolated and characterized by single-crystal X-ray diffraction, elemental analysis, BVS calculations, IR, thermogravimetric analysis, and electrochemistry. Magnetic measurements performed on **1a** are fully consistent with an eight-coordinated central Pd^{2+} ion stabilized by a palladium–oxo shell.

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Supporting Information Available: Crystal packing, thermograms, electrochemical and magnetic study details, and crystallographic data in CIF format for **1a**, **1b**, and **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(11) Synthesis of $\text{K}_3\text{Na}_3[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}] \cdot 17\text{H}_2\text{O}$ (**1b**): The synthetic procedure for **1a** was followed exactly except that a 2 M NaOAc/2 M KOAc solution (pH = 6.9) was used instead of a 0.5 M NaOAc solution (pH = 6.9). We isolated red, needlelike crystals of **1b** with a yield of 0.033 g (19% based on Pd). IR (2% KBr pellet, ν/cm^{-1}): identical to **1a**. Elem. anal. (%) calcd for $\text{K}_3\text{Na}_3[\text{Pd}_{13}(\text{AsPh})_8\text{O}_{32}] \cdot 17\text{H}_2\text{O}$ (**1a**): Na, 1.9; K, 3.2. Found: Na, 1.8; K, 3.6. Crystal data for **1b**: $\text{C}_{48}\text{H}_{74}\text{As}_8\text{K}_3\text{Na}_3\text{O}_{49}\text{Pd}_{13}$, $M_r = 3604.2$, triclinic, space group $P\bar{1}$, $a = 13.4351(5)$, $b = 14.3952(5)$, $c = 14.8476(4)$ Å, $\alpha = 97.357(2)^\circ$, $\beta = 107.626(2)^\circ$, $\gamma = 103.969(2)^\circ$, $V = 2592.22(15)$ Å³, $Z = 1$, $T = 173(2)$ K, $D_{\text{calcd}} = 2.309$ g cm⁻³, 97 758 reflns collected, 12 204 unique ($R(\text{int}) = 0.0598$), $R1 = 0.0462$, $wR2 = 0.1479$ ($I > 2\sigma(I)$).

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