Noble Metalates

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Alkaline Earth Guests in Polyoxopalladate Chemistry: From Nanocube to Nanostar via an Open-Shell Structure[**]

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***Abstract:** The three novel, discrete palladium(II)-oxo clusters $[CaPd_{12}O_8(PhAsO_3)_8]^{6-}$ (**CaPd$_{12}$**), $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]^{4-}$ (**SrPd$_{12}$**), and $[BaPd_{15}O_{10}(PhAsO_3)_{10}]^{8-}$ (**BaPd$_{15}$**) encapsulating alkaline earth metal ions were prepared and fully characterized by a multitude of solution and solid-state physicochemical techniques. We have discovered a structure-directing template effect induced by the respective size of the alkaline earth guest ion, which determines the detailed condensation arrangement of the peripheral Pd^{II}-oxo shell. The unprecedented **SrPd$_{12}$** with an open-shell type structure is of particular importance and reflects a successful strategy for deliberate design of new structural classes of polyoxo-noble-metalates. Furthermore, the unusual acetate–water ligand exchange phenomenon renders **SrPd$_{12}$** as a promising candidate for noble-metal-based catalysis.*

The frontier of polyoxometalates (POMs) based exclusively on d^8 metal centers (Pd^{II}, Pt^{III}, and Au^{III})[1] as addenda is currently progressing rapidly owing to their structural and compositional novelty, and promising applications as noble metal-based catalysts.[2] Polyoxopalladates(II) in particular constitute the most significant subclass of the known polyoxo-noble-metalate family and are continually developing.[3–5] Two dominant structure types have been identified hitherto, namely, a **MPd$_{12}$** cuboid-shaped assembly $[M^zPd_{12}O_8(LXO_3)_8]^{n-}$ ($M^z = Pd^{II}, Sc^{III}, Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Y^{III}, In^{III}$, and lanthanide(III); $X = As^V, P^V$, $L = O, Ph$; $X = Se^{IV}$, L = lone pair),[1b,3] and a **MPd$_{15}$** star-shaped assembly $[Pd_{15}O_{10}(LXO_3)_{10}]^{n-}$ ($X = P^V$, $L = O$; $X = Se^{IV}$, L = lone pair), as well as a few derivatives.[4] Attempts to prepare novel structural types of polyoxopalladates have been of limited success.[5] Apparently, the highly symmetrical palladium-oxo shells **Pd$_{12}$** with T_d and **Pd$_{15}$** with D_{5h} symmetry are particularly stable. It is thus a challenge to further expand the structural versatility of polyoxopalladates.

We decided to investigate the role of alkaline earth metal ions as templating guests in polyoxopalladate chemistry, and we successfully isolated three alkaline earth metal-centered, phenylarsonate-capped polyoxopalladates, $[CaPd_{12}O_8(PhAsO_3)_8]^{6-}$ (**CaPd$_{12}$**, Figure 1 a), $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]^{4-}$ (**SrPd$_{12}$**, Figure 1 b), and $[BaPd_{15}O_{10}(PhAsO_3)_{10}]^{8-}$ (**BaPd$_{15}$**, Figure 1 c) by using simple, one-pot reaction conditions.[6] As the radius of the guest ion increases,

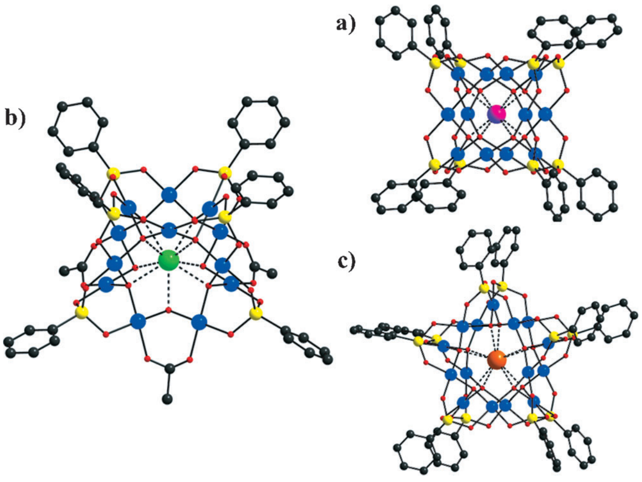

Figure 1. Ball-and-stick representation of a) **CaPd$_{12}$**, b) **SrPd$_{12}$**, and c) **BaPd$_{15}$**. Ca pink, Sr green, Ba orange, Pd blue, As yellow, O red, C black.

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the polyoxopalladate skeleton gradually transforms from nanocube (**$CaPd_{12}$**) via open-shell (**$SrPd_{12}$**) to nanostar (**$BaPd_{15}$**). In sharp contrast to the plenary cage-structures of **$CaPd_{12}$** and **$BaPd_{15}$**, the strontium derivative **$SrPd_{12}$** features an unprecedented open, intermediate cube-star structure type with low symmetry (C_s). Most interestingly, the structure of **$SrPd_{12}$** contains acetate capping groups along with phenylarsonate.

All three polyanions **$CaPd_{12}$**, **$SrPd_{12}$**, and **$BaPd_{15}$** were synthesized by simple reaction of $Pd(OAc)_2$ with nitrates of Ca^{II}, Sr^{II}, and Ba^{II}, respectively, and $PhAsO_3H_2$ in 0.5 M sodium acetate solution (pH 7), and isolated as hydrated sodium salts, $Na_4Ca[CaPd_{12}O_8(PhAsO_3)_8]\cdot 54\,H_2O$ (**Na-$CaPd_{12}$**), $Na_4[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]\cdot 2\,NaOAc\cdot 32\,H_2O$ (**Na-$SrPd_{12}$**), and $Na_5Ba_{1.5}[BaPd_{15}O_{10}(PhAsO_3)_{10}]\cdot 0.5\,NaOAc\cdot 46\,H_2O$ (**Na-$BaPd_{15}$**).

Single-crystal X-ray analysis revealed that the structure of **$CaPd_{12}$** is reminiscent of the parent $[Pd_{13}O_8(PhAsO_3)_8]^{6-}$ (**Pd_{13}**),[3a] with the central Pd^{II} ion replaced by a Ca^{II} guest, which is coordinated by eight oxygen atoms, leading to a $\{CaO_8\}$ cuboid fragment (Ca···O 2.382(4) Å), in which each μ_4-oxo ligand bridges the central Ca^{II} and three Pd^{II} ions. The resulting $\{CaO_8Pd_{12}O_{24}\}$ assembly has 24 "outer" oxygen atoms forming a truncated cubic shell, which is capped by eight $PhAs^{4+}$ groups.

By using the larger Sr^{II} ion as guest instead of Ca^{II}, neither the cube-like structure **MPd_{12}** nor the star-like **MPd_{15}** is formed, but rather a novel, lower-symmetry structure type **$SrPd_{12}$** (Figure 1 b). Such open-shell structure for **$SrPd_{12}$** is unprecedented and can be viewed as an intermediate between **MPd_{12}** and **MPd_{15}**. More precisely, three Pd^{II} centers and four $PhAsO_3^{2-}$ heterogroups from the plenary **Pd_{15}** shell are lost, and the corresponding empty positions are occupied by acetate ligands, to yield a novel "tri-lacunary" open-shell-type framework (Supporting Information, Figure S1). The central Sr^{II} ion is nine-coordinate with Sr···O distances in the range of 2.565(10)–2.656(9) Å. Considering the linkage of Pd^{II} to the oxygen atoms of the $\{O_9\}$ open cage, the latter can be divided into two subsets: six μ_4-bridging oxygen atoms, each connecting one Sr^{II} and three Pd^{II} ions, and three μ_3-bridging oxygen atoms ligated by a Sr^{II} and two Pd^{II} centers. Bond valance sum (BVS) calculations[7] suggested monoprotonation of the three distinct μ_3-O atoms (Supporting Information, Table S2). All of the Pd^{II} centers exhibit the expected square-planar coordination geometry and are linked by two oxygen atoms of the inner $\{O_9\}$ moiety. Six of the twelve Pd^{II} ions complete their coordination spheres with oxygen atoms from two adjacent $PhAsO_3^{2-}$ groups. The coordination spheres of the remaining six Pd^{II} ions are completed by one oxygen of a $PhAsO_3^{2-}$ heterogroup and an oxygen from one of the terminal acetate ligands.

When using the even larger Ba^{II} ion as guest, the star-type **Pd_{15}** cage is formed, encapsulating a ten-coordinated Ba^{II} ion (**$BaPd_{15}$**), rather than the anticipated open-shell structure. All oxygen atoms of the $\{O_{10}\}$ unit are coordinated to three Pd^{II} ions and the Ba^{II} guest, which is located in the body center of the cavity (Supporting Information, Figure S2). This is in contrast to the reported polyoxopalladates based on the **Pd_{15}** cage, where the Na^+ or Pd^{II} guests in **$NaPd_{15}$** and **$PdPd_{15}$**,[4a] and in **Pd_2Pd_{15}**[4c] are displaced towards one of the sides of the pentagonal channel, thus acting more like wheel caps. To date, **$BaPd_{15}$** encapsulates the largest guest in polyoxopalladate chemistry, as the Ba^{II} ion has an ionic radius of 1.66 Å, resulting in average Ba···O distances of 2.758 Å.[4]

For all three polyanions **$CaPd_{12}$**, **$SrPd_{12}$**, and **$BaPd_{15}$**, the "Matryoshka doll" analogy can be described (Supporting Information, Table S3).[1b,4a] Comparing **$SrPd_{12}$** with the plenary nanocube and nanostar cages, certain degrees of alteration can be noticed. We believe that the ionic radius of Sr^{II} is too large for the formation of the **Pd_{12}** shell and too small for the formation of the **Pd_{15}** shell, and hence the key driving force for the formation of the open-shell type structure. This strongly suggests a template effect being at work during the formation of the polyoxopalladates. We also attempted to synthesize derivatives of **$SrPd_{12}$** utilizing other capping groups (for example, $PhPO_3^{2-}$, AsO_4^{3-}, PO_4^{3-}, SeO_3^{2-}), but without success. It appears that the phenylarsonate heterogroup is particularly well-suited to cap alkaline earth centered polyoxopalladate cages (Supporting Information, Figure S3).

A systematic study of the reaction parameters revealed that the pH plays a crucial role in the formation of the novel compounds.[1,3–5,8] For example, the optimal pH range for the synthesis of **Na-$SrPd_{12}$** is 5.0–5.3. As the pH is increased, more and more of the known byproduct **Pd_{13}** is formed together with the target compound.[9] For the synthesis of **Na-$BaPd_{15}$**, the optimal pH range is 8.4–8.8, with the highest yield at pH 8.6. At pH < 8.4, the byproduct **Pd_{13}** is formed, and at pH > 8.8, a large amount of unidentified precipitate is formed.

The solution stability of the three polyanions **$CaPd_{12}$**, **$SrPd_{12}$**, and **$BaPd_{15}$** was examined by ^{13}C and ^{1}H NMR spectroscopy after redissolution of the product salts in H_2O/D_2O. The ^{13}C and ^{1}H NMR spectra display the expected resonances for each polyanion (Supporting Information, Figures S4 and S5). For the open-shell structure **$SrPd_{12}$** with C_s symmetry, six $PhAsO_3^{2-}$ heterogroups can be further classified into three subcategories, and each peak reflecting magnetically inequivalent carbon atoms can be perfectly identified in the spectrum (Figure 2). Furthermore, four other corresponding signals are also clearly detected and fully consistent with the two types of acetate ligands (Figures 1 b and 2; Supporting Information, Figure S4b): two of the three OAc^- groups are symmetry-related by the mirror plane and the unique one is located exactly on the plane of symmetry (^{13}C NMR: 185 ppm for the former and 183 ppm for the latter). It is noteworthy that the small peak appearing at 181 ppm in the ^{13}C NMR spectra of **$SrPd_{12}$** and **$BaPd_{15}$** is ascribed to free OAc^- groups originating from cocrystallized NaOAc. In the case of **$SrPd_{12}$**, another possibility is that some OAc^- ligands on the polyanion are labile and replaced by two water molecules from the solvent, which may also partially contribute to this signal.

To verify this hypothesis and provide additional structural details on the obtained polyoxopalladates, electrospray-ionization mass spectrometry (ESI-MS) was employed, which frequently allows characterizing the main species observed in aqueous solution and in the gas phase. The ESI-MS spectrum of **Na-$SrPd_{12}$** shows that all major envelopes are

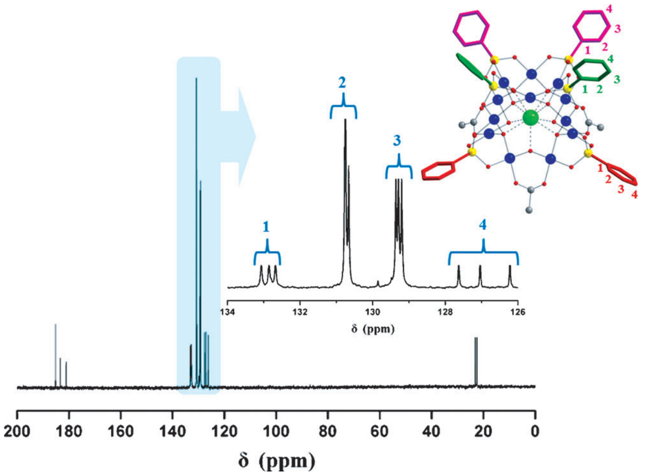

Figure 2. ^{13}C NMR spectrum of **Na-SrPd$_{12}$** recorded in H_2O/D_2O at room temperature. Inset: magnification of the range from 126–134 ppm. The four sets of three signals each can be assigned to the three magnetically inequivalent phenyl rings, as labeled.

related to the intact polyanion **SrPd$_{12}$** (Figure 3a). The main peak centered at $m/z = 963.23$ and its neighboring envelope situated at $m/z = 1000.90$ corresponds to -3 charged protonated or sodium form of **SrPd$_{12}$**, with abbreviated formulas such as $\{$H-**SrPd$_{12}$**$\}^{3-}$ and $\{Na(H_2O)_5$-**SrPd$_{12}$**$\}^{3-}$, respectively. In the case of **Na-BaPd$_{15}$**, a series of distribution peaks can be clearly assigned to species related to **BaPd$_{15}$** (Figure 3c). The main peak located at $m/z = 973.80$ corresponds to $\{H_4$-**BaPd$_{15}$**$\}^{4-}$. Two small envelopes positioned at $m/z = 873.60$ and $m/z = 934.81$ can be assigned to the vacant species $[BaPd_{15}O_{10}(C_6H_5AsO_3)_8]^{4-}$ and $[Na_2BaPd_{15}O_{10}(C_6H_5AsO_3)_9]^{4-}$. Considering the solution-stable character of **BaPd$_{15}$**, as confirmed by ^{13}C NMR, it is conceivable that these two fragments dissociate from the intact polyanion during the electrospray ionization process. Additional MS assignments for both polyanions **SrPd$_{12}$** and **BaPd$_{15}$** are summarized in the Supporting Information, Table S4.

It is worth noting that the ionic moiety observed at $m/z = 972.89$ and formulated as $[SrPd_{12}O_6(OH)_3(C_6H_5AsO_3)_6(CH_3COO)_2(H_2O)_5]^{3-}$ may derive from dissociation of the parent **SrPd$_{12}$**. This species indicates that one of the three OAc^- ligands may be removed from the original **SrPd$_{12}$** either in the solvent system spontaneously or during the ionization process. Intrigued by this observation, collision-induced dissociation (CID) mass spectrometry (MS/MS) was conducted with $\{$H-**SrPd$_{12}$**$\}^{3-}$ as precursor. The spectrum in Figure 3b demonstrates that the main product dissociated from $\{$H-**SrPd$_{12}$**$\}^{3-}$ can be unequivocally assigned to $[HSrPd_{12}O_6(OH)_3(C_6H_5AsO_3)_5AsO_3(CH_3COO)_3]^{3-}$ ($m/z = 937.88$), which implies that one phenyl group, rather than an acetate ligand, can be more easily removed from the POM matrix during the ionization process.

Theoretical methods have also been traditionally used to study structural and electronic properties of POMs.[10] Here, we performed DFT calculations to explore the structural properties of **SrPd$_{12}$** and **BaPd$_{15}$**, focusing specially on the lability of the OAc^- ligands. In general, the computed structures for **SrPd$_{12}$** and **BaPd$_{15}$** are well reproduced at the DFT level, although the DFT-based bond lengths for polyanions in aqueous solution are always somewhat longer than those based on XRD (Supporting Information, Table S5). For **SrPd$_{12}$**, the average Sr⋅⋅⋅O and Sr⋅⋅⋅OH distances were computed to be 2.700 Å and 2.773 Å, respectively, with a maximum deviation with respect to the experimental values of 0.110 Å. When the divalent strontium ion is encapsulated in the cubic **Pd$_{12}$** framework, the Sr⋅⋅⋅O distance is computed 0.132 Å shorter than in the open form. As a result, Sr^{II} would be the largest ion observed in the compact cavity formed by the cubic **Pd$_{12}$** framework. Interestingly, we were able to prepare the hypothesized $[SrPd_{12}O_8(PhAsO_3)_8]^{6-}$, but only as a very minor cocrystallized byproduct.[9] The Ba⋅⋅⋅O bond lengths were computed to be 2.741 Å in the hypothetical eight-coordinated **Pd$_{12}$** complex. This value seems excessively long, and this is why Ba^{II} is only observed as **BaPd$_{15}$**, for which the crystallographic structure is also well reproduced by theory. Some bond lengths for the reported structures are summarized in the Supporting Information, Table S6.

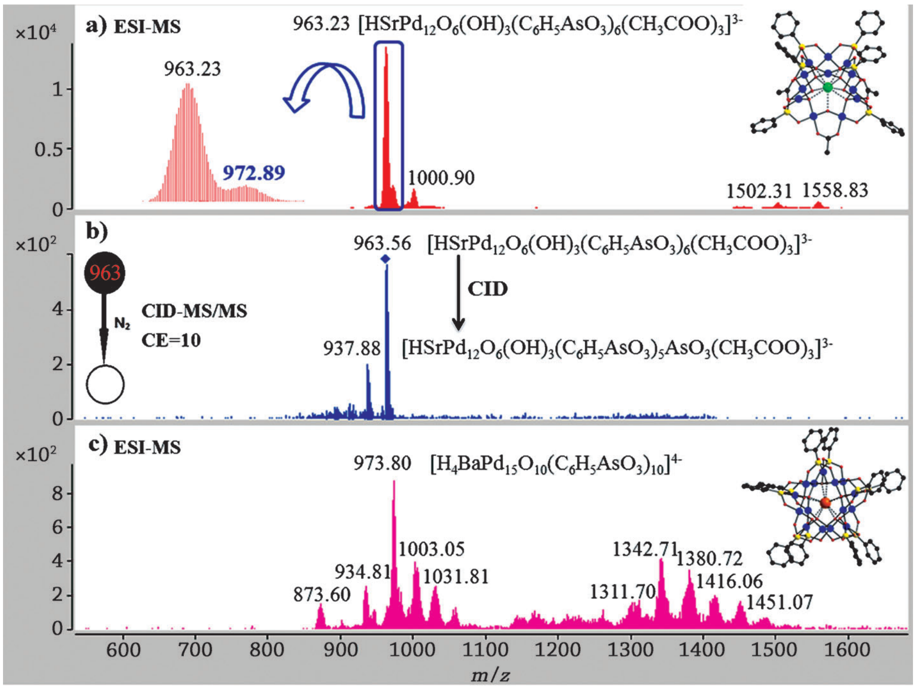

Figure 3. Negative-ion mass spectra of a) **Na-SrPd$_{12}$** and c) **Na-BaPd$_{15}$** in aqueous solution and b) the MS/MS spectrum of the precursor $\{$H-**SrPd$_{12}$**$\}^{3-}$ at CE = 10 V.

To determine the energetics associated with OAc^- replacement in **SrPd$_{12}$**, we computed the polyanion without one of the three acetate groups, the dissociation energy of the acetate ligand being rather high (+51.7 kcal mol^{-1}). It is likely that in the absence of the OAc$^-$ ligand, the vacant sites in the tricoordinated Pd^{II} ions are occupied by water ligands, as shown in the representation of $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_2(H_2O)_2]^{3-}$ in Figure 4. Notice that the two water ligands are stabilized by the interaction with the Pd^{II} ions, with bond lengths (2.142 and 2.181 Å) that are in reasonable agreement with other reported Pd^{II}-OH$_2$ bond lengths (2.10–2.15 Å),[11] and by a hydrogen bond between the two water ligands. The computed OH···H distance of 1.706 Å indicates the importance of the hydrogen bond interaction in $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_2(H_2O)_2]^{3-}$. Interestingly, +8.1 kcal mol^{-1} is the energy associated with the ligand exchange reaction $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]^{4-} + 2\,H_2O \rightarrow [SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_2(H_2O)_2]^{3-} + OAc^-$, which corresponds to a binding energy of about −22 kcal mol^{-1} per water ligand. It is very likely that the substitution reaction occurs through an intermediate in which OAc$^-$ acts as a monodentate ligand and the other free Pd site is occupied by a water ligand. This intermediate is found to be −7.5 kcal mol^{-1} lower in energy than the reactants and is stabilized by two hydrogen bonds, as shown in Figure 4. The energies given in Figure 4 suggest that the three structures are accessible at 80 °C and that acetate and water ligands can exchange in a concerted pathway; however, it should be taken into account that accurate energies would likely require to consider the protic solvent explicitly and not only as a continuum model.

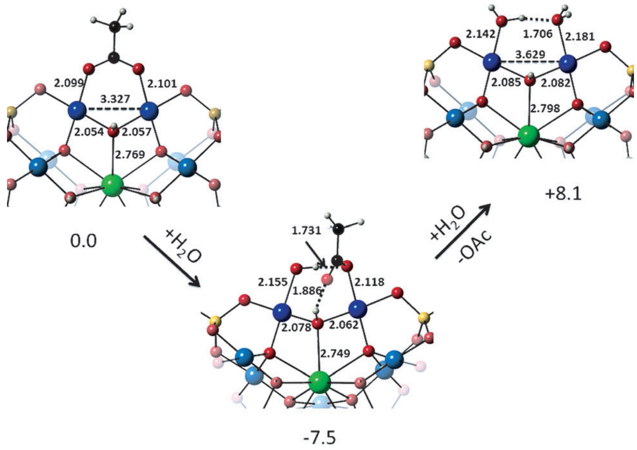

Figure 4. Fragment representations for **SrPd$_{12}$** (top left), $[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_2(H_2O)_2]^{3-}$ (top right), and a possible intermediate (bottom) in the ligand-exchange process. Bond distances are given [Å], relative energies [kcal mol^{-1}]. Pd^{II} ions coordinated to the leaving OAc$^-$ ligand are shown in dark blue.

Based on a combination of experimental support from ^{13}C NMR spectroscopy, ESI-MS, and MS/MS studies together with DFT calculations, we believe that the species formulated as $[SrPd_{12}O_6(OH)_3(C_6H_5AsO_3)_6(CH_3COO)_2(H_2O)_5]^{3-}$ very likely originates from aqueous solution (rather than being generated in the gas phase), as the unique OAc$^-$ ligand of **SrPd$_{12}$** can be replaced by water molecules. Moreover, the anticipated steady-state solution behavior and, especially, the unexpected ligand-exchange feature of **SrPd$_{12}$** in an aqueous solvent system as seen by ESI-MS/MS may give an indication for its potential usefulness in catalytic applications.

In conclusion, three novel, discrete palladium(II)-oxo clusters encapsulating alkaline earth metal ions were prepared and fully characterized by a multitude of physicochemical techniques. We have discovered a potentially important structure-directing template effect induced by the respective size of the guest ion, which determines the detailed condensation arrangement of the peripheral Pd^{II}-oxo shell. The unprecedented **SrPd$_{12}$** with an open-shell type structure is of particular importance and reflects a successful strategy for deliberate design of new structural classes of polyoxo-noble-metalates. Furthermore, the unusual acetate–water ligand exchange phenomenon renders **SrPd$_{12}$** as a particularly promising candidate for noble metal-based catalysis. Such work is currently in progress.

Experimental Section

Synthesis of $Na_4Ca[CaPd_{12}O_8(PhAsO_3)_8]\cdot 54\,H_2O$ (**Na-CaPd$_{12}$**): Pd(OAc)$_2$ (0.023 g, 0.102 mmol), PhAsO$_3$H$_2$ (0.020 g, 0.099 mmol), and Ca(NO$_3$)$_2$·4 H$_2$O (0.006 g, 0.024 mmol) were dissolved in 2 mL of 0.5 M NaOAc solution (pH 7.0). While stirring, the solution was heated to 80 °C for 1 hour. Then it was cooled to room temperature, filtered and allowed to crystallize in an open vial. Dark red, block-shaped crystals were obtained after one week, which were filtered off and air dried. Yield: 0.015 g (43 % based on Pd). Elemental analysis calcd (%) for Na 2.22, C 13.89, Ca 1.93, Pd 30.77, As 14.44; found Na 2.24, C 13.86, Ca 1.70, Pd 31.10, As 13.40. IR (2 % KBr pellet): $\tilde{\nu}$ = 1628 (m), 1479 (w), 1439 (m), 1094 (m), 796 (s), 744 (w), 694 (m), 615 (m), 532 cm^{-1} (s).

Synthesis of $Na_4[SrPd_{12}O_6(OH)_3(PhAsO_3)_6(OAc)_3]\cdot 2\,NaOAc\cdot 32\,H_2O$ (**Na-SrPd$_{12}$**): The compound was prepared by exactly the same procedure as **Na-CaPd$_{12}$**, but with Sr(NO$_3$)$_2$ (0.005 g, 0.024 mmol) instead of Ca(NO$_3$)$_2$·4 H$_2$O. Dark red, needle-like crystals were obtained after two weeks, which were filtered off and air dried. Yield: 0.013 g (41 % based on Pd). Elemental analysis calcd (%) for Na 3.71, C 14.85, Sr 2.35, Pd 34.31, As 12.08; found Na 3.86, C 14.50, Sr 2.57, Pd 34.00, As 12.50. IR (2 % KBr pellet): $\tilde{\nu}$ = 1634 (m), 1545 (s), 1417 (s), 1094 (m), 815 (s), 746 (m), 695 (m), 587 (w), 530 cm^{-1} (s).

Synthesis of $Na_5Ba_{1.5}[BaPd_{15}O_{10}(PhAsO_3)_{10}]\cdot 0.5\,NaOAc\cdot 46\,H_2O$ (**Na-BaPd$_{12}$**): Pd(OAc)$_2$ (0.023 g, 0.102 mmol), PhAsO$_3$H$_2$ (0.020 g, 0.099 mmol), and Ba(NO$_3$)$_2$ (0.006 g, 0.023 mmol) were dissolved in 2 mL of 0.5 M NaOAc solution (pH 7.0). While stirring, the solution was heated to 80 °C. After complete dissolution of the reagents, the pH of the reaction mixture was adjusted to 8.6 by addition of 1 M NaOH. The resulting solution was heated at 80 °C for 1 hour. Then it was cooled to room temperature, filtered and allowed to crystallize in an open vial. Dark red, rod-like crystals were obtained after two weeks, which were filtered off and air dried. Yield: 0.010 g (29 % based on Pd). Elemental analysis calcd (%) for Na 2.49, C 14.40, Ba 6.75, Pd 31.40, As 14.73; found Na 2.98, C 14.00, Ba 6.87, Pd 31.80, As 14.20. IR (2 % KBr pellet): $\tilde{\nu}$ = 1632 (m), 1559 (w), 1439 (m), 1094 (m), 814 (s), 746 (m), 695 (m), 576 (w), 519 cm^{-1} (s).

The thermograms (20–800 °C) and IR spectra of all three compounds are given in the Supporting Information.

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Keywords: cluster compounds · palladium · polyoxometalates · template effect · X-ray diffraction

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[6] Crystal data and details of the XRD experiment are discussed in the Supporting Information. CCDC 1012289 (**Na-CaPd$_{12}$**), 1012290 (**Na-SrPd$_{12}$**), and 1012288 (**Na-BaPd$_{12}$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[9] A few dark-red, parallelogram-shaped crystals appeared as a very minor, cocrystallized byproduct next to the major product **Pd$_{13}$**, and were characterized by single-crystal XRD. The Sr-centered 12-palladate $[\mathrm{SrPd}_{12}\mathrm{O}_8(\mathrm{PhAsO}_3)_8]^{6-}$ with the cuboid cage-like structure was identified (Supporting Information, Figure S12). Crystal data: triclinic, space group $P\bar{1}$, $a = 13.473(2)$, $b = 14.422(3)$, $c = 14.881(2)$ Å, $\alpha = 97.867(8)$, $\beta = 107.815(8)$, $\gamma = 103.479(9)°$, $V = 2608.5(8)$ Å^3, $Z = 1$, $R1 = 0.0664$, $wR2 = 0.2222$ $(I > 2\sigma(I))$.

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