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A Noble-Metalate Bowl: The Polyoxo-6-vanado(V)-7-palladate(II) $[Pd_7V_6O_{24}(OH)_2]^{6-}$**

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Polyoxometalates (POMs) are discrete nanosized metal oxoanions with an enormous structural diversity and a multitude of interesting properties that lead to potential and real applications in catalysis, analytical chemistry, magnetism, nanotechnology, and medicine.[1]

Recently we reported a novel subclass in POM chemistry: polyanions composed of square-planar d^8 noble-metal ions.[2] In all cases the synthetic strategy was based on the condensation of $[Pd(H_2O)_4]^{2+}$ or $[Au(OH)_4]^-$ complexes in aqueous media. In sharp contrast to "classical" POMs that comprise Group 5 and 6 metals (V, Nb, Ta, Mo, and W) in high oxidation states, it seems to be absolutely necessary in the case of d^8 late-transition-metal ions to use a heterogroup in order to terminate the condensation process and to isolate discrete polyanions. To date, nonmetal-based oxoanions (e.g., arsenate, phenylarsonate, phosphate, and selenite) have been shown to be good heterogroups, the use of which resulted in polyoxopalladates of two structural types, $[MPd_{12}L_8O_{32}]^{n-}$ ($M = Pd^{2+}$, Y^{3+}, Ln^{3+}; $L = AsO^{3+}$, $PhAs^{4+}$, Se^{4+})[2a–d] and $[Pd_{15}L_{10}O_{40}]^{m-}$ ($L = PO^{3+}$, Se^{4+}),[2e,f] as well as a polyoxoaurate, $[Au_4As_4O_{20}]^{8-}$.[2g] Earlier, Wickleder and Pley reported the solid-state structure of the d^7 metal-cluster anion $[Pt^{III}_{12}O_8(SO_4)_{12}]^{4-}$, which is composed of six dumbbell-shaped $[Pt_2]^{6+}$ ions linked by oxo ligands and sulfate heterogroups. This compound was prepared by heating $Pt(NO_3)_2$ with concentrated H_2SO_4 at 350 °C.[3]

We thought about expanding the class of noble metalates towards species with heterogroups that can form POMs by itself, such as the vanadate ion. Vanadium is well known to form POMs with a large structural variety, from compact clusters, such as $[V_6O_{18}]^{6-}$, to open basket-, shell-, ring-, and cage-like host systems suitable for the uptake of neutral, cationic, and anionic guests. The structural flexibility of polyoxovanadates is based on the ability of vanadium to adopt different coordination geometries from tetrahedral to square-pyramidal and octahedral, and to form POMs in both +5 and +4 oxidation states, thus leading to mixed-valent or even fully reduced polyanions that can behave as nanoscale magnets.[1a,b,d,g,j,4] Moreover, it is well known that vanadium can easily replace one or more addenda atoms in polyoxomolybdates and -tungstates.[1a,c,5] Hayashi and co-workers reported $[Pd^{II}V^{V}_6O_{18}]^{4-}$, a cyclic hexavanadate with an incorporated Pd^{II} center, which was synthesized in an organic medium.[4e] Therefore, we hypothesized that mixed-metal POMs might result from the controlled condensation of aquapalladate(II) in the presence of vanadate in aqueous medium.

Herein we report the noble metalate $[Pd^{II}_7V^{V}_6O_{24}(OH)_2]^{6-}$ (Pd_7V_6), which was prepared by heating $Pd(OAc)_2$ and either sodium meta- or orthovanadate in a potassium acetate solution (2 M, pH 7.5), and which was crystallized as the hydrated mixed potassium and sodium salt $K_5Na[Pd_7V_6O_{24}(OH)_2]\cdot 7H_2O$ (**1**). At least three main competing processes occur in the reaction mixture: 1) self-assembly of Pd_7V_6, 2) formation of potassium decavanadate (which is always present as a side product), and 3) aggregation of Pd^{II} aqua and hydroxo complexes with formation of insoluble $Pd(OH)_2$. To minimize the third process we used an excess of vanadate ions in the synthesis of Pd_7V_6, and indeed this resulted in a higher yield of **1**. The isolation of pure crystalline **1** can be achieved by fractional crystallization; here the evaporation rate of the solvent is rather important (see the Experimental Section for details). Compound **1** is soluble in water and is stable in the solid state and after redissolution when exposed to air and light.

The IR spectrum of **1** shows strong bands at 564 and 456 cm^{-1} that correspond to the $\{PdO_4\}$ groups. The sharp band at 918 cm^{-1} is due to the stretching vibrations of terminal V=O groups, while the peaks at 788, 746, and 636 cm^{-1} are attributed to symmetric and asymmetric V–O–V and Pd–O–V vibrations.[6]

Pd_7V_6 is bowl-shaped with idealized C_{2v} symmetry, and is composed of two identical $\{Pd_3V_3O_{11}\}$ units (Figure 1, upper left), linked through four μ_2-oxo bridges and one additional Pd^{II} center that forms the bottom of the "bowl".[7] The

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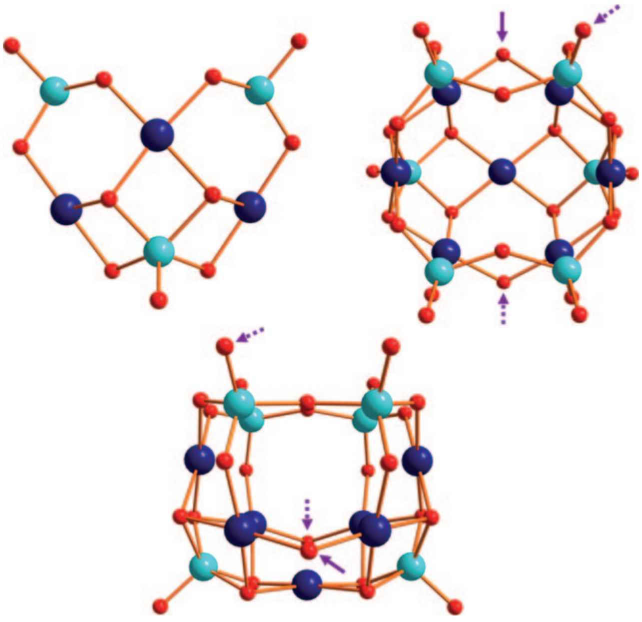

Figure 1. Ball-and-stick representation of the $\{Pd_3V_3O_{11}\}$ fragment (top left) and of Pd_7V_6, which is shown with a view into the cavity along the twofold axis (top right) and from the side (bottom). Pd dark blue, V turquoise, O red. The fully protonated oxygen atom is highlighted by a solid arrow and the partially protonated oxygen atoms are highlighted by dashed arrows.

$\{Pd_3V_3O_{11}\}$ fragment consists of three square-planar Pd^{II} and three V^V ions of two structural types (one with square-pyramidal coordination and the other two with tetrahedral coordination). Three Pd^{II} ions surround the V^V center of the first type in such a way that every Pd ion is coordinated by two *cis*-related oxygen atoms of the $\{O_4\}$ base of the $\{VO_5\}$ pyramid. The fourth position in the $\{(O{=}V)(OPd)_4\}$ "star" is occupied by an additional Pd^{II} center that links two $\{Pd_3V_3O_{11}\}$ fragments together (Figure 1, upper right). Thus, every oxygen atom of the square face of the $\{VO_5\}$ pyramid is μ_3-bridging by linking the V^V center with two Pd^{II} ions (V–O 1.84(2)–1.97(3) Å; Pd–O 1.96(2)–2.05(2) Å), while the fifth oxygen atom forms a terminal double bond with vanadium (V=O 1.58(2)–1.60(2) Å).

Both upper V^V ions of the $\{Pd_3V_3O_{11}\}$ unit (Figure 1) are tetrahedrally coordinated. Two of the four oxygen atoms bonded to these V^V ions are μ_2-bridging to the central Pd^{II} ions of $\{Pd_3V_3O_{11}\}$ (V–O 1.65(3)–1.76(3) Å, Pd–O 1.96(2)–2.08(2) Å). Another oxygen atom is terminally coordinating with V=O bond lengths in the range of 1.62(3)–1.67(3) Å. The fourth oxygen atom joins two adjacent V^V centers, thus providing a link between the two $\{Pd_3V_3O_{11}\}$ fragments (V–O 1.77(3)–1.82(3) Å). An additional connection between the two parts of the bowl is achieved by two oxygen atoms that complete the square-planar coordination sphere of the two equivalent Pd^{II} ions in each $\{Pd_3V_3O_{11}\}$ subunit (Pd–O 1.92(2)–2.08(2) Å; Figure 1, lower). According to bond valence sum calculations,[8] one of these two oxygen atoms is monoprotonated and is hence a μ_2-bridging hydroxo ligand, whereas the second oxygen atom is only partially monoprotonated. The other position of this second proton is on a terminal oxygen atom of one of the tetrahedrally coordinated V^V centers (see the Supporting Information for details).

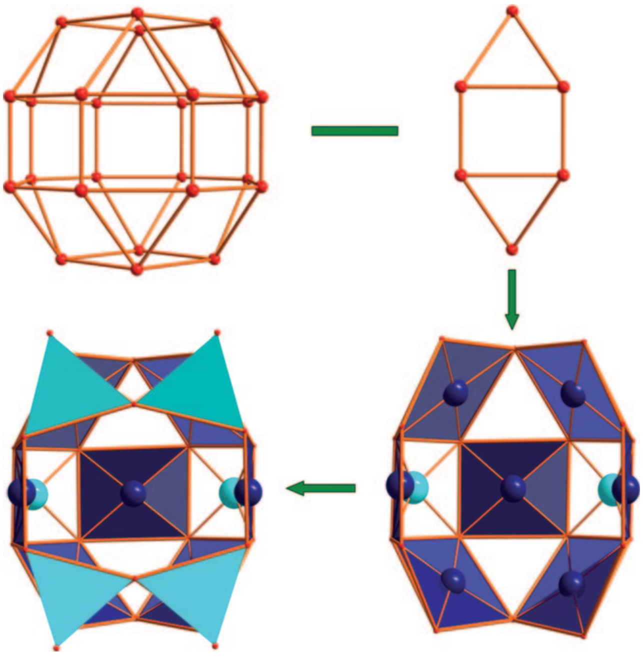

Figure 2. Ball-and-stick representation of the $\{O_{24}\}$ rhombicuboctahedron (upper left) and the $\{O_6\}$ unit which is removed from $\{O_{24}\}$ leading to a "lacunary" rhombicuboctahedron $\{O_{18}\}$ in Pd_7V_6. Combined polyhedral/ball-and-stick representation of the $\{Pd_7V_2O_{18}\}$ fragment (lower right) in Pd_7V_6 and of Pd_7V_6 itself (lower left). O red, V turquoise, Pd dark-blue; $\{PdO_4\}$ dark blue squares, $\{VO_4\}$ turquoise tetrahedra.

The structure of Pd_7V_6 shows some analogies to the well-known polyoxovanadates of the $\{V_{18}O_{42}\}$ type with respect to the arrangement of the oxygen atoms. The 24 μ_3-oxo ligands in the polyanions $[H_7V^{IV}_{16}V^{V}_2O_{42}(VO_4)]^{6-}$ and $[V^{IV}_{12}V^{V}_6O_{42}(SO_4)]^{8-}$ reported by Müller and co-workers[9a,b] and the polyanion $[V^{IV}_{14}V^{V}_4O_{42}(PO_4)]^{11-}$ reported by Yamase and co-workers[9c] form a distorted rhombicuboctahedron (an Archimedean solid with eight triangular and eighteen square faces, Figure 2, upper left), whereby every square face is capped by a V=O group. In Pd_7V_6, 18 oxygen atoms (excluding those that are terminal and the two oxygen atoms linking tetrahedrally coordinated vanadium atoms) constitute a "lacunary" rhombicuboctahedron. This object can be rationalized by formal removal of six oxygen atoms that form a square with two edge-shared triangular faces (Figure 2, upper right) from a complete ("holo")rhombicuboctahedron (Figure 2, upper left). Thus, our $\{O_{18}\}$ lacunary rhombicuboctahedron possesses nine square faces: seven of these faces are capped by Pd^{II} ions and the remaining two squares, which are edge-shared to the Pd^{II}-capped squares, are capped by pentacoordinated V^V centers. The Pd^{II} ions are situated directly in the idealized $\{O_4\}$ plane whereas the $V^V({=}O)$ centers are located 0.57 Å above their respective $\{O_4\}$ plane (Figure 2, lower right). The four triangular faces surrounding the "lacuna" of Pd_7V_6 are not edge-shared with square faces as in the holo-rhombicuboctahedron, but with triangular faces (pairwise corner-shared) from the four tetrahedral, capping V^VO_4 groups.

The cavity of the polyanion bowl Pd_7V_6 is free of any guests, including water molecules, probably because of the small inner diameter of around 1.1 Å. This result is in contrast to other known bowl-shaped polyoxovanadates, where the inner cavity is occupied by neutral or anionic guests, as for example in $[CH_3CN\subset(V_{12}O_{32})]^{4-}$ and $[C_6H_5CN\subset(V_{12}O_{32})]^{4-}$ reported by Klemperer and co-workers,[10a,b] $[(NO)^-\subset(V_{12}O_{32})]^{5-}$ reported by Ozeki, Yagasaki and co-workers,[10c] $[Cl^-\subset(V_{14}O_{36})]^{5-}$ reported by Hong and co-workers,[10d] and $[Cl^-\subset(HV_{12}O_{32})]^{4-}$ reported by Hayashi and co-workers.[10e] The self-assembly of Pd_7V_6 demonstrates on one hand that it is not always necessary to use a template in order to obtain an open structure. On the other hand, the lacunary $\{O_{18}\}$ rhombicuboctahedron fragment of Pd_7V_6 suggests that in the presence of suitable templates other structural types of mixed palladium–vanadium POMs, including a closed-structure analogue of $\{V_{18}O_{42}\}$ with the hypothetical formula $[Pd_9(VO)_9O_{24}]^{3-}$, can perhaps be formed.

To complement our results on Pd_7V_6 in the solid-state and to determine if this structure persisted in the solution state, we performed ^{51}V NMR measurements on solutions of **1** in H_2O/D_2O. The ^{51}V NMR spectrum of Pd_7V_6 shows the expected two peaks ($\delta = -284.8$ and -485.3 ppm) with approximate relative intensities of 1:2 (Figure 3). The signal at -284.8 ppm corresponds to the two vanadium atoms with square-pyramidal coordination and the signal at -485.3 ppm to the four vanadium atoms with tetrahedral coordination. This spectrum is hence in complete agreement with the solid-state structure. Chemical shifts for tetrahedrally coordinated vanadium ions in $[(VO_3)_n]^{n-}$ species ($n = 3$–6) in aqueous media (pH 7–8) have been reported to be in the range of -560 to -580 ppm, and the coordination of a vanadate oxygen atom by an additional metal center leads to a downfield shift of the ^{51}V NMR signal.[11] For example, $[PdV_6O_{18}]^{4-}$ reported by Hayashi and co-workers exhibits a ^{51}V NMR signal at -499 ppm in acetonitrile, which is attributed to the V^V centers linked to Pd^{II} by μ_2-oxo bridges, and the ^{51}V NMR signals of tetravanadate-supported organometallic noble-metal complexes in the same solvent appear from -446 to -504 ppm.[4e,12] This result further supports our assignment of the signal at -485.3 ppm for Pd_7V_6 to the four tetrahedrally coordinated V^V centers linked to two Pd^{II} ions by two μ_2-oxo bridges. Furthermore, all four oxygen atoms that form the basal plane in $\{VO_5\}$ are coordinated by two additional Pd^{II} ions in Pd_7V_6, which results in deshielding of the pentacoordinated V^V centers, thus explaining the observed peak at -284.8 ppm. We also performed temperature-dependent ^{51}V NMR measurements on Pd_7V_6 (Figure S1 in the Supporting Information), and observed slow decomposition at 60 °C that resulted in the formation of the tetravanadate ion $[V_4O_{12}]^{4-}$ (see the Supporting Information for details).

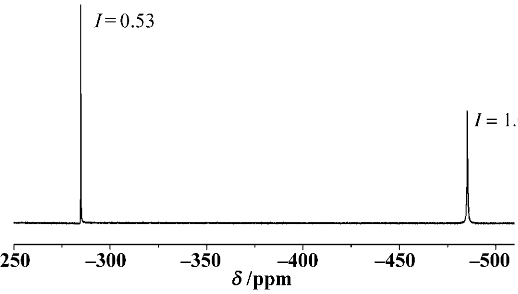

Figure 3. ^{51}V NMR spectrum of **1** in H_2O/D_2O at room temperature. The peak area integrals are also shown.

To gain further insight into the structure of Pd_7V_6 in solution, we carried out DFT calculations (Amsterdam density functional code ADF 2009[13]). All structures were fully optimized (by using the GGA BP functional[14a,b]), and relativistic corrections (ZORA formalism and spin–orbit coupling) as well as the solvent medium (by the COSMO method) were taken into account. By following the same computational protocol as reported earlier[15] and by considering the experimental XRD data for the crystallization of Pd_7V_6 as **1**, we calculated the ^{51}V NMR chemical shifts of a series of geometries (by employing the model SAOP functional[14c]). We simulated the bare polyanion, as well as derivatives that comprise one to seven counterions (K^+ and Na^+, see the Supporting Information for details).

Our calculations show that the characteristic bowl shape of Pd_7V_6 is relatively rigid and maintained in solution. Moreover, the solvated Pd_7V_6 anions exist in the form of ion pairs, being surrounded by a relatively dense, positively charged shell of cations, rather than bare polyanions with a dynamic solvent shell. We discovered that the number and position of the K^+ ions strongly influence the shielding of the two vanadium centers in Pd_7V_6 with square-pyramidal coordination geometry. Only if a complete cationic shell (at least 7 K^+ or 6 K^+ ions plus 1 Na^+ ion) was modeled in the vicinity of Pd_7V_6 could the experimental ^{51}V NMR shifts be confirmed computationally with only a minor difference (Table S3(B) in the Supporting Information). Furthermore, the calculations show that the shielding of the vanadium is also sensitive to the positions of the two protons in the solvated Pd_7V_6 species. Interestingly, the best agreement with the experimental ^{51}V NMR chemical shifts is achieved for a structure that possesses one monoprotonated μ_2-bridging oxygen atom that links palladium centers and a second proton located in the inner cavity of the polyanion in the vicinity of the other oxygen atom of the same type (Figures S4(C) and S5 in the Supporting Information). For this geometry, the calculated chemical shifts ($\delta_{CALC} = -274.8$ ppm and -487.3 ppm for the vanadiums with square-pyramidal and tetrahedral coordination, respectively) correspond very well to the experimental data of Pd_7V_6 ($\delta = -284.8$ and -485.3 ppm).

On the basis of our calculations, we conclude that Pd_7V_6 is present in aqueous solution as singly charged ion-pair assemblies of the types $\{NaK_6H[Pd_7V_6O_{25}(OH)]\}^+$ and $\{K_7H[Pd_7V_6O_{25}(OH)]\}^+$, which involve a shell of alkali cations that occupy the positions indicated in Figure S6 in the Supporting Information. In these species, one of the two protons forms a relatively stable μ_2-bridging hydroxo ligand between Pd centers, whereas the other proton is rather flexible (see above). Within the timescale of the NMR experiment, this proton most probably moves about in the vicinity of the second μ_2-(Pd)-bridging oxygen atom and either forms a transient second OH ligand, or enters slightly into the POM inner cavity. Interestingly, the arrangement of the seven cations in the model for the solvated Pd_7V_6 suggested by the computations is quite similar to the observed positions of the seven inner K^+ ions in the solid state (see structures in Figure S6 in the Supporting Information), thus suggesting a rather stable ion-pair structure.

Further evidence for the existence of an intact Pd_7V_6 polyanion in solution and its exact stoichiometric composition was obtained from electrospray mass spectrometry.[16–18] The ESI-FT mass spectrum is shown in Figure 4. Peak 5 can be unambiguously assigned to the singly charged molecular cation $\{K_7[Pd_7V_6O_{24}(OH)_2]\}^+$ on the basis of the m/z value (Table 1) and the highly resolved isotope splitting (Figure 4, inset). Exchange of one or two potassium ions by sodium leads to the peaks 4 $\{NaK_6[Pd_7V_6O_{24}(OH)_2]\}^+$ and 3 $\{Na_2K_5[Pd_7V_6O_{24}(OH)_2]\}^+$, respectively. This result supports the hypothesis of a Pd_7V_6 polyanion stabilized by potassium ions not only in the solid state but also in solution and even as an intact unit in the gas-phase.

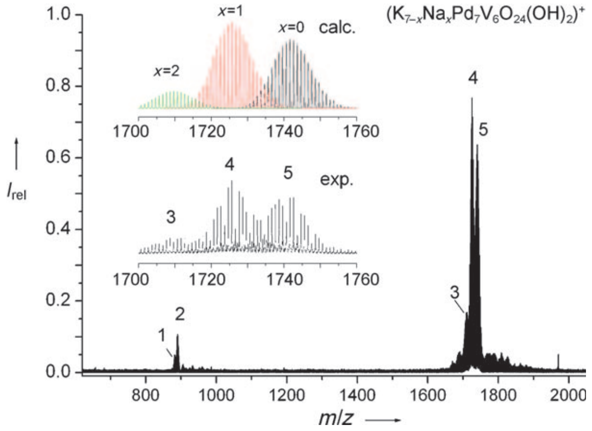

Figure 4. ESI mass spectrum (positive-ion mode) of **1** in aqueous solution. Inset: comparison of the calculated isotope splitting of the $\{K_{7-x}Na_x[Pd_7V_6O_{24}(OH)_2]\}^+$ ion with $x=0$, 1, 2 and the observed isotope splitting of peaks 3, 4, and 5. For peak assignments, see Table 1.

In summary, we have prepared the bowl-shaped mixed-metal polyanion Pd_7V_6 formed by both Pd^{II} and V^V addenda ions. The agreement of experimental and computational ^{51}V NMR chemical shifts as well as ESI MS data provide unequivocal evidence for the structural integrity of Pd_7V_6 in aqueous solution as well as in the gas phase. We believe that the discovery of Pd_7V_6 may allow access to an entire POM subclass that comprises mixed d^8 noble metal (e.g. Pd^{II}, Pt^{II}, Au^{III}) and V^V addenda ions. We expect this family of compounds to show a large structural diversity from open-shell bowls to closed-shell spheres. Currently we are investigating the interaction of Pd^{II}, Pt^{II}, and Au^{III} salts with different vanadium(V) precursors under various conditions and in the presence of potential neutral, anionic, and cationic guests. We also plan to perform catalytic studies on the title polyanion.

Table 1: Assignment of the observed peaks in the ESI mass spectrum of an aqueous solution of **1** and comparison to the calculated m/z values (see Figure 4).

Peak	m/z		Ion
	exp.	calcd.	
1	882.815	882.792	$\{K_7Na[Pd_7V_6O_{24}(OH)_2]\}^{2+}$
2	890.801	890.805	$\{K_8[Pd_7V_6O_{24}(OH)_2]\}^{2+}$
3	1709.684	1709.674	$\{K_5Na_2[Pd_7V_6O_{24}(OH)_2]\}^+$
4	1726.665	1726.647	$\{K_6Na[Pd_7V_6O_{24}(OH)_2]\}^+$
5	1742.631	1742.621	$\{K_7[Pd_7V_6O_{24}(OH)_2]\}^+$

Experimental Section

Synthesis of **1**: $Pd(OAc)_2$ (0.140 g, 0.620 mmol) and $NaVO_3$ (0.100 g, 0.820 mmol) were added to a solution of KOAc (2 M, 5 mL, pH 6.9) under stirring and heating to 80 °C. After 15 min of heating the pH value of the reaction mixture was adjusted to 7.5 by the addition of several drops of 6 M NaOH solution. Then the reaction mixture was heated and stirred at 80 °C for 1 h and subsequently filtered to remove an insoluble dark brown precipitate of $Pd(OH)_2$. The resulting brown solution was allowed to cool to room temperature and was placed in an open 25 mL beaker for evaporation. The evaporation of the solution initially led to the formation of orange needle-like crystals of potassium decavanadate ($K_6[V_{10}O_{28}]\cdot nH_2O$) which had to be removed by filtration from time to time (once or twice a day). After 2–7 days, dark-red crystals of **1** started to form in the solution. These crystals were collected by filtration and were washed with a mixture of acetone and water (9:1) to remove a KOAc impurity. The filtrate was left for further evaporation, which resulted in another large portion of crystals of **1** within a few days. The obtained crystals were collected by filtration, washed with a mixture of acetone and water (9:1), and then air-dried. Total yield: 0.033 g (21 % based on Pd). Evaporation in a 20 mL GC vial always led to a mixture of crystals of **1** and decavanadate ions, but the single crystals of **1** were suitable for XRD studies. If the temperature in the crystallization room is above 22 °C, the fractional crystallization is more complicated and the isolation of pure Pd_7V_6 can only be achieved by several (2–4) recrystallizations of the product from water. Compound **1** can also be prepared using Na_3VO_4 (0.100 g, 0.544 mmol) instead of $NaVO_3$. The optimal temperature of heating was 50 °C in this case. Yield: 0.011 g (7 % based on Pd).

IR (2 % KBr pellet, 1000–400 cm^{-1}): $\tilde{\nu}=918$ (s), 788 (s), 746 (s), 636 (s), 564 (s), 543 (s), 456 (s); elemental analysis calcd (%) for $H_{16}K_5NaO_{33}Pd_7V_6$ (**1**): K 10.8, Na 1.3, Pd 41.1, V 16.9, H 0.79 %; found: K 10.7, Na 1.2, Pd 41.2, V 16.7, H 0.81.

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