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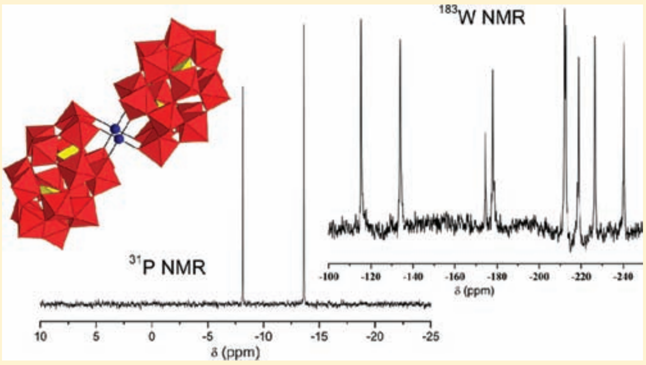
Noble Metals in Polyoxometalate Chemistry: Palladium-Containing Derivatives of the Monolacunary Keggin and Wells–Dawson Tungstophosphates

Natalya V. Izarova,*,† Abhishek Banerjee, and Ulrich Kortz*

School of Engineering and Science, Jacobs University, P.O. Box 750 561, 28725 Bremen, Germany

Supporting Information

ABSTRACT: We have prepared the three novel Pd^{II}-containing tungstophosphates $[Pd_2(\alpha\text{-}PW_{11}O_{39}H_{0.5})_2]^{9-}$ and two structural isomers of $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_n)_2]^{(16-2n)-}$ via simple synthetic procedures and characterized their potassium salts by single-crystal X-ray diffraction, elemental analysis, and IR and multinuclear (^{31}P and ^{183}W) NMR spectroscopy. This study sheds light on the long-standing question about the nature and structure of the actual products formed in the reaction of Pd^{II} ions with monolacunary Keggin-type $[\alpha\text{-}XW_{11}O_{39}]^{n-}$ and Wells–Dawson-type $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ heteropolytungstates.



INTRODUCTION

Polyoxometalates (POMs) containing noble metals, in particular palladium, have gained special interest over the last years mainly because the incorporation of noble metal ions into POM frameworks allows for keeping the noble metal ions soluble in aqueous or organic media and at the same time encapsulated in a fully inorganic, thermally stable and redox-stable metal–oxo matrix. With respect to potential applications in oxidation catalysis, such features offer a distinct advantage over noble-metal-based coordination complexes, displaying a set of organic ligands or organometallic moieties, susceptible to thermal and oxidative degradation.

In this light, the interaction of monolacunary Keggin-type $[XW_{11}O_{39}]^{n-}$ ($X = B^{III}, Si^{IV}, Ge^{IV}, P^{V}$) and Wells–Dawson-type $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ POMs with Pd^{II} ions has attracted the attention of several research groups around the world.[1−9] Thus, in 1987 Maksimov et al. reported a study of the $[PW_{11}O_{39}]^{7-}/Pd^{II}/H_2O$ system in the pH range of 2.0–6.0. On the basis of multinuclear (^{17}O, ^{31}P, and ^{183}W) NMR studies in solution and ^{31}P MAS NMR measurements, IR spectroscopy, and elemental analysis, the formation of several species with the general formula $[PW_{11}PdLO_{39}]^{n-}$ ($L = H_2O$, $n = 5$; $L = OH, Cl$, $n = 6$, depending on the starting Pd^{II} salt and pH value) was proposed. A square-pyramidal coordination geometry for the Pd^{II} ions was suggested, by the four oxygen atoms of the monolacunary PW_{11} species and an additional, terminal ligand L.[1] Almost a decade later, Kuznetsova et al. proposed the formation of monomeric $[PW_{11}O_{39}Pd]^{5-}$ and dimeric $[PW_{11}O_{39}PdOPdO_{39}W_{11}P]^{12-}$ polyanions at low Pd/POM ratios and oligomeric palladium hydroxo species stabilized by polytungstate ligands at Pd/POM ratios >1 in the pH range of 2.0–4.0, based on ^{31}P NMR spectroscopy. Despite uncertainties regarding the detailed composition and structure of the Pd^{II}-containing polyanions formed, the obtained aqueous solutions were applied for the catalytic oxidation of benzene with a O_2/H_2 gaseous mixture in a biphasic liquid system.[2]

At about the same time, Gazarov and co-workers proposed the formation of polyanions formulated as $[SiM_{11}O_{39}Pd]^{6-}$ (M = Mo, W), prepared by reacting $PdCl_2$ with the corresponding monolacunary polyanion at pH 4.5. The materials obtained as such were supported on a Al_2O_3/SiO_2 surface and used as precatalysts for the reduction of nitrogen oxides to N_2 by CH_4 in industrial exhaust gases with a high selectivity of the DeNOx process.[3]

In the following years, Liu and co-workers reported a series of polyanions with the formulas $[XW_{11}O_{39}Pd(H_2O)]^{n-}$ (X = B, $n = 7$; X = Si or Ge, $n = 6$; X = P, $n = 5$),[4] $[PMo_{11}O_{39}Pd(H_2O)]^{5-}$,[5] and $[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$,[6] all obtained by the reaction of $PdCl_2$ with the respective monolacunary polyanion precursor in aqueous media and then isolated as tetra-*n*-butylammonium (TBA) salts by precipitation of the products with TBABr. The Pd^{II} center incorporated into these polyanions was claimed to possess octahedral coordination geometry, coordinating five oxygen atoms of the vacant site of the monolacunary Keggin/Wells–Dawson POM and an additional, terminal water molecule.

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Two years ago, Burns and co-workers demonstrated the catalytic activity for the compound formulated as $(TBA)_{7.5}K_{0.5}[P_2W_{17}O_{61}Pd(H_2O)]$ for the oxidation of allylic alcohols by H_2O_2.[7] In 2002, the potassium salt of $[PW_{11}O_{39}Pd(H_2O)]^{5-}$ placed on a γ-Al_2O_3 support was used by Neumann and co-workers as the precatalyst for the hydrogenation of arenes to cycloalkanes.[8] In the preceding years, some Chinese groups prepared glassy carbon electrodes modified with $[SiW_{11}Pd(H_2OH)O_{39}]^{6-}$ and $[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$, which showed electrocatalytic activity for H_2O_2 and nitrite reduction, respectively.[9]

It becomes apparent that the true identity (detailed structure and composition) of all of the above-mentioned Pd^{II}-containing POMs remains unclear, because to date, no single-crystal X-ray structural analysis has been carried out for any of them. Therefore, we decided to resolve this issue by carefully investigating the actual products formed in reactions of Pd^{II} salts with monolacunary Keggin-type $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and Wells−Dawson-type $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ tungstophosphates.

RESULTS AND DISCUSSION

Synthesis. The reactions were carried out by reacting aqueous solutions of the potassium salts of the respective POM precursor ($K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 13H_2O$ or $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 17H_2O$) with either $PdCl_2$ or $Pd(NO_3)_2$ at 50−60 °C for 30 min. The pH of the reaction mixture was varied from 2.0 to 6.5 by the addition of HNO_3 or KOH. In all cases, the Pd^{II}-containing products isolated in the solid phase by crystallization were $K_9[Pd_2(\alpha\text{-}PW_{11}O_{39}H_{0.5})_2]\cdot 37H_2O$ (**K-1**), $K_{14}Li[\mathit{anti}\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_{0.5})_2]\cdot 50H_2O$ (**KLi-2**), or $K_{10}[\mathit{syn}\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_3)_2]\cdot 50H_2O$ (**K-3**), depending on the POM precursor used. We found that use of a slight excess of the Pd^{II} salt with respect to the POM precursor increases the yields of the above products because some amount of Pd^{II} ions precipitates in the form of insoluble hydroxides during the heating of the reaction mixtures. Also, the amount of $Pd_xO_y\cdot nH_2O$ precipitate increases with an increase of the temperature of heating.

The preparation of pure, crystalline **K-1** was not trivial because this compound has a very high solubility in water, and therefore the crystals of **K-1** appeared only after almost all of the solvent had evaporated. Therefore, the pure product could not be prepared by simple solvent evaporation of the reaction mixture. We decided to add spectator salts such as CH_3COOK or KNO_3 during the reaction in order to increase the ionic strength of the solution and thus speed up the crystallization process. This indeed led to a crystalline, apparently pure, material, which then turned out to be contaminated because of cocrystallization of **K-1** with KNO_3 (or CH_3COOK) within the same crystal [see the structure of **K-1N** (CSD 423270) in the Supporting Information, SI]. In order to prepare truly pure **K-1**, the reaction solution obtained after heating of an aqueous solution of $K_7[PW_{11}O_{39}]\cdot 13H_2O$ and $PdCl_2$ (without pH adjustment) was evaporated overnight on a watch glass. The obtained dry material was then redissolved in a minimum amount of water, and the solution was placed in a refrigerator (4 °C). The crystals of **K-1** appeared overnight in moderate yield (28%).

In contrast to **K-1**, the potassium salt of polyanion **2** (**K-2**) is not very soluble, and its precipitate already appeared while the reaction solution was cooling down to room temperature. However, the solubility of this product significantly increases in the presence of Li^+ ions, and therefore this precipitate was collected on the third day and recrystallized from a 0.2 M LiCl solution, providing a pure, crystalline material of **KLi-2**. The identity of the polyanions in **K-2** and **KLi-2** was confirmed by ^{31}P NMR spectroscopy. Evaporating the filtrate obtained after removal of **K-2** leads to brown crystals of **K-3** within 2−3 weeks.

Because most catalytic reactions are performed in organic media, we also prepared the corresponding TBA salts **TBA-1** and **TBA-2** [soluble in common organic solvents such as CH_3CN, $(CH_3)_2O$, CH_2Cl_2, $CHCl_3$] by the dropwise addition of aqueous solutions of either **K-1** or **KLi-2** to a saturated aqueous solution of $TBANO_3$, followed by washing of the obtained precipitate with plenty of water.

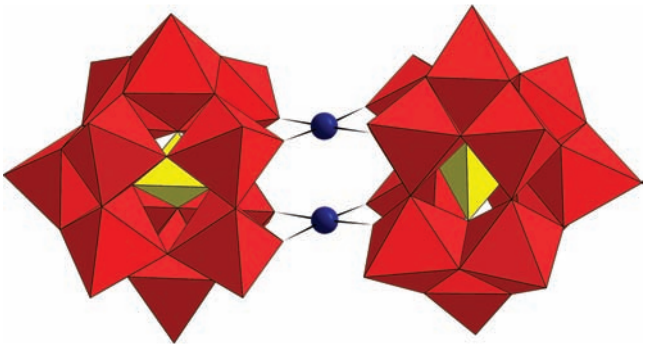

Figure 1. Combined polyhedral/ball-and-stick representation of **1**. Color legend: WO_6, red octahedra; PO_4, yellow tetrahedra; Pd, dark-blue balls.

Crystal Structures. The compound **K-1** crystallizes in a monoclinic lattice, in the space group $P2_1/c$. The polyanion $[Pd_2(\alpha\text{-}PW_{11}O_{39}H_{0.5})_2]^{9-}$ (**1**) consists of two monolacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ units linked via two Pd^{II} ions in an anti conformation (with respect to the relative orientation of the two $\{PW_{11}\}$ Keggin units; Figure 1). Every Pd^{II} center possesses square-planar coordination geometry and coordinates side-on to two oxygen atoms at the vacant site of each $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ ligand [Pd−O 1.88(4)−2.02(4) Å]. Thus, in contrast to all previous hypotheses (*vide supra*), every lacunary site of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ is coordinated not by one but by two heterometal centers, so that the inner oxygen atom associated with the PO_4 group remains completely noncoordinated (Figure 1). This bonding mode is not unprecedented for complexes of monolacunary Keggin- and Wells−Dawson-type POMs with late-transition-metal ions. In 1993, Finke and co-workers reported $[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$ in which two $\{\alpha_2\text{-}P_2W_{17}O_{61}\}$ POM units are linked by a Cl−Ru−O−Ru−Cl motif. In analogy to polyanion **1**, every Ru^{IV} center is coordinated by four oxygen atoms of two $\{\alpha_2\text{-}P_2W_{17}O_{61}\}$ units, while the octahedral coordination of the heterometal in this POM is completed by a terminal chloride anion and an oxo ligand bridging two Ru^{IV} centers.[10] Recently, also a Keggin-type Ru^{IV} derivative $[O\{Ru^{IV}(OH)(\alpha\text{-}PW_{11}O_{39})\}_2]^{10-}$[11] and the rhenium analogue of Finke's polyanion $[O\{Re^{V}(OH)(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$[12] were reported by Proust's and Kato's groups, respectively. In 1994, Angus-Dunne et al. prepared $[Pd_2W_{10}O_{36}]^{8-}$, where two square-planar Pd^{II} ions link two monovacant Lindquist-type units $[W_5O_{18}]^{6-}$ in a fashion very close to that observed in this work.[13] Also, monomeric polyanion structures in which two noble metal ions coordinate four oxygen atoms at the lacunary site of $[PW_{11}O_{39}]^{7-}$ have been reported by Pope's group, e.g., $[PW_{11}O_{39}\{Rh_2(O_2CR)_2\}]^{5-}$ comprising the $\{Rh^{II}{}_2(O_2CR)_2\}$ motif.[14] Very recently, Kato et al. reported

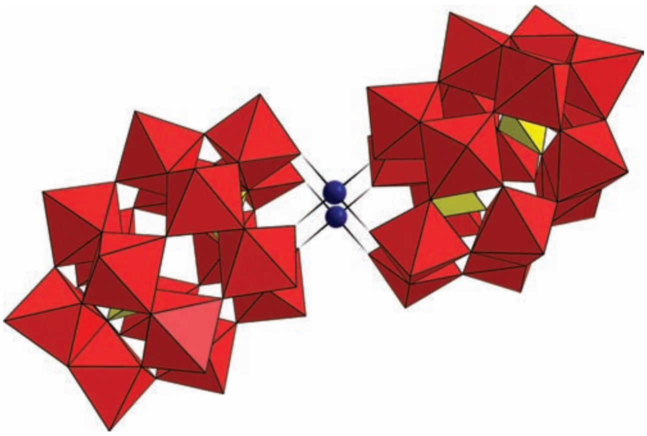

Figure 2. Combined polyhedral/ball-and-stick representation of **2**. Color legend: same as that in Figure 1.

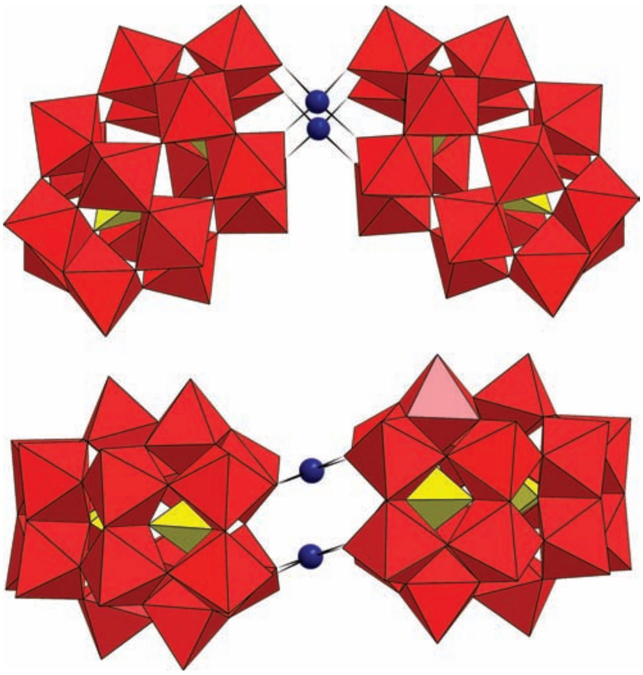

Figure 3. Combined polyhedral/ball-and-stick representation of **3**: side view (upper); view from the top (lower). Color legend: same as that in Figure 1.

$[\alpha\text{-PW}_{11}\text{O}_{39}\{cis\text{-Pt(NH}_3)_2\}_2]^{3-}$, for which the structure with a $\{\text{PW}_{11}\text{O}_{39}\}$ unit grafted by two $\{cis\text{-Pt}^{\text{II}}(\text{NH}_3)_2\}$ groups at the lacunary site has been proposed, based on multinuclear NMR spectroscopy, IR, and elemental analysis.[15]

Overall, polyanion **1** has idealized C_{2h} symmetry, with the C_2 axis passing through both Pd$^{\text{II}}$ ions (Figure 1). The Pd···Pd distance in **1** is 3.015(5) Å, which is comparable to the Pd···Pd distance of 3.014(5) Å in Angus-Dunne et al.'s $[\text{Pd}_2\text{W}_{10}\text{O}_{36}]^{8-}$ and a little bit shorter than the M···M distances in the above Ru- and Re-containing polyanions [3.538(3)−3.549(22) Å].

The polyanion $[anti\text{-Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_{0.5})_2]^{15-}$ (**2**) has a structure similar to that of **1** consisting of two monolacunary $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ moieties linked via two square-planar Pd$^{\text{II}}$ ions [Pd−O 1.93(2)−2.00(2) Å and Pd···Pd 3.000(4) Å; Figure 2]. In analogy to **1**, polyanion **2** also adopts an *anti* conformation, with respect to the relative orientation of the two $\{\text{P}_2\text{W}_{17}\}$ ligands, resulting in a structure with C_{2h} symmetry. Such a conformation is also characteristic of $[\text{O}\{\text{Ru}^{\text{IV}}\text{Cl}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{16-}$ and $[\text{O}\{\text{Re}^{\text{V}}(\text{OH})(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ and was also seen by Cadot and co-workers for $[(\text{P}_2\text{W}_{17}\text{O}_{61})_2\text{-}\{\text{Mo}_4\text{S}_4\text{O}_4(\text{OH}_2)_2\}]^{16-}$.[10,12,16]

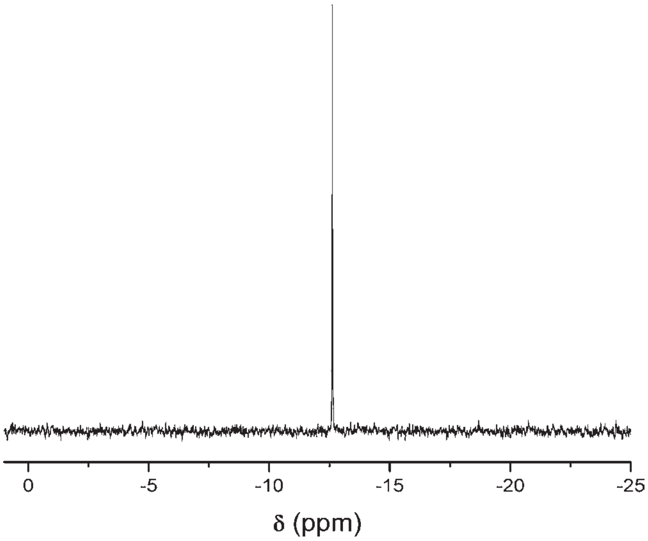

Figure 4. ^{31}P NMR spectrum of **K-1** redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (room temperature).

We were also able to crystallize the noncentrosymmetrical *syn* isomer of $[\text{Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_3)_2]^{10-}$ (**3**; Figure 3). In analogy to other sandwich-type polyanions with *syn* conformation, e.g., $[\text{M}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{n-}$ where M is lanthanide,[17] actinide,[18] Zr^{4+} or Hf^{4+} ion,[19] polyanion **3** does not possess the expected, idealized C_{2v} symmetry in the solid state, most likely because of electrostatic repulsion between two highly negatively charged $\{\text{P}_2\text{W}_{17}\}$ units. Unlike in $[\text{M}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{n-}$, where the electrostatic repulsion is alleviated by an antiprismatic distortion of the heterometal's coordination geometry, in **3** it is achieved by a slight displacement of the monolacunary $\{\text{P}_2\text{W}_{17}\}$ units along the Pd$^{\text{II}}$−Pd$^{\text{II}}$ axis (Figure 3, bottom). The angle between the $\{\text{PdO}_4\}$ planes and the local mirror plane disecting each $\{\text{P}_2\text{W}_{17}\}$ unit is 20.5° for one of them and 23.0° for the other. This results in **3** not having any symmetry elements, and hence the polyanion is chiral. However, in the crystals of **K-3**, both enantiomers of $[\text{Pd}^{\text{II}}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_3)_2]^{10-}$ were present in equal amounts, leading to a racemic mixture. The Pd−O [1.92(3)−2.01(3) Å] and Pd···Pd [3.051(5) Å] distances in **3** are similar to those in polyanions **1** and **2**.

The number of protons in the formulas of **1**−**3** was determined by elemental analysis and from charge-balance considerations. We were not able to locate the exact positions of these protons in the crystal structures of **K-1**, **KLi-2**, and **K-3**, but some slightly elongated terminal W═O bonds [1.75(4)−1.79(3) Å] suggest that the protons might be disordered between terminal oxo ligands of the POM units.

IR Spectroscopy. The IR spectrum of **K-1** is very similar to that of the monolacunary POM precursor $\text{K}_7[\alpha\text{-PW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ (Figure S1 in the SI). The splitting of the ν(P−O) mode into two bands at 1059 and 1102 cm^{-1} is retained, in full agreement with the absence of bonding interactions between the

Table 1. ^{31}P NMR Chemical Shifts of Pd^{II}-Containing Tungstophosphates and Some Palladium-Free Derivatives Observed in PW_{11}/Pd^{II} and P_2W_{17}/Pd^{II} Reaction Solutions[a]

polyanion	^{31}P NMR signals, ppm	ref	polyanion	^{31}P NMR signals, ppm	ref
$[Pd_2(\alpha\text{-}PW_{11}O_{39}H_{0.5})_2]^{10-}$ (**1**)[b]	−12.6 (−12.8)[c]	this work	$[PW_{11}O_{39}Pd(H_2O)]^{5-}$	no signal [c]	4
$[PW_{11}PdLO_{39}]^{6-}$ (L = Cl, OH)	−12.6 [d]	1	$[PW_{11}O_{39}Pd(H_2O)]^{5-}$ or $[(PW_{11}O_{39}Pd)_2O]^{12-}$	−15.17	8
$[PdP_2W_{20}O_{70}(H_2O)_2]^{8-}$ [b]	−12.85	22	$[anti\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_{0.5})_2]^{15-}$ (**2**)[b]	−8.1, −13.6 (−9.3, −12.8)[c]	this work
$[PW_{11}O_{39}Pd(H_2O)]^{5-}$	−12.9 [d]	1	$[syn\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_3)_2]^{10-}$ (**3**)[b]	−8.2, −13.7	this work
$[PW_{11}O_{39}Pd{-}O{-}PdO_{39}W_{11}P]^{12-}$	−12.8	2	$[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$	−11.9 [c]	6
$[Pd_xO_yH_zPW_{11}O_{39}Pd]^{n-}$	∼−13	2	$[P_2W_{17}O_{61}Pd(H_2O)]^{8-}$	−11.8 [c]	7
$[P_2W_{21}O_{71}(H_2O)_3]^{6-}$[b]	−13.2	23	$[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ [b]	−12.8	23
$[PW_{11}O_{39}Pd]^{5-}$	−13.2	2	$[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ [b]	−6.9, −13.7 (pH > 4.5)	23
$[Pd_3(PW_9O_{34})_2]^{12-}$	−12.23	22	$[\alpha\text{-}PW_{12}O_{40}]^{3-}$ [b]	−14.5	25
$[Pd_3(PW_9O_{34})_2]^{12-}$	−12.7 (pH 2.0), −12.5 (pH 3.7), −12.1 (pH 4.8)	24	$[\alpha\text{-}PW_{12}O_{40}]^{3-}$ [c,b]	−14.7 [c]	26
$[P_2W_{20}O_{70}(H_2O)_2]^{10-}$	−12.4	2	$[\alpha\text{-}PW_{11}O_{39}]^{7-}$[b]	−10.2 (pH 3.1)	25

[a] With respect to 85% H_3PO_4 as the external standard. [b] Assignment is supported by the crystal structure. [c] In CH_3CN (all other entries in an aqueous solution). [d] In an aqueous solution and the solid state (^{31}P MAS NMR)

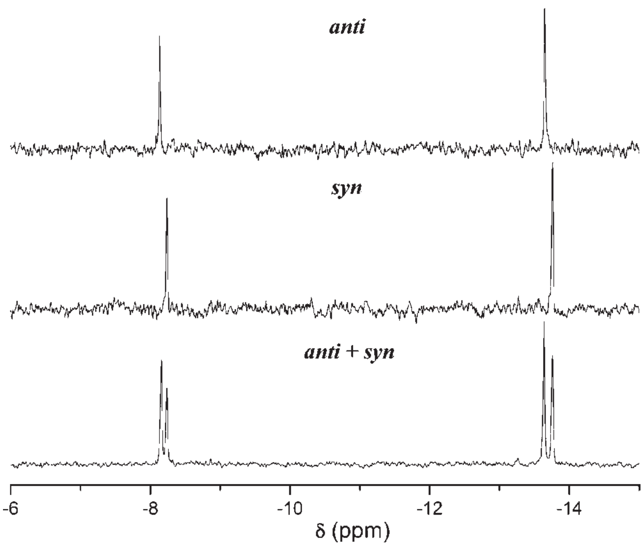

Figure 5. ^{31}P NMR spectra of **KLi-2** (top), **K-3** (middle) and a mixture of **KLi-2** and **K-3** (bottom) redissolved in H_2O/D_2O (room temperature).

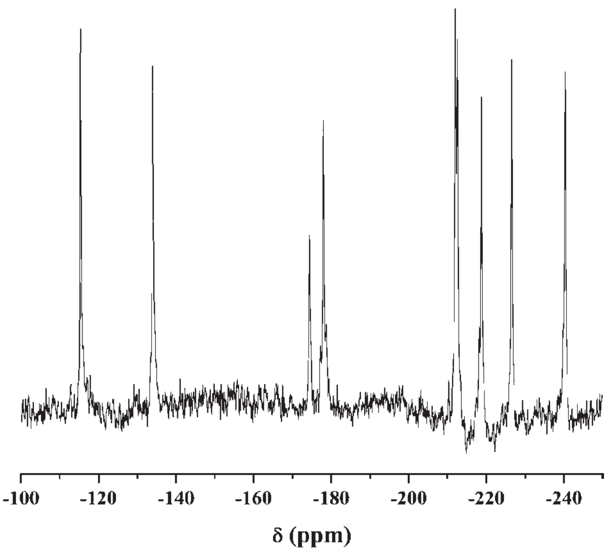

Figure 6. ^{183}W NMR spectrum of **KLi-2** redissolved in H_2O/D_2O (room temperature).

unique oxygen atom of the phosphate hetero group in each POM ligand with the Pd^{II} ions in **1**. The intense band at 955 cm^{-1} is assigned to the stretching vibrations of the terminal W═O bonds and the breathing vibrations of the inner PO_4 hetero groups. The bands corresponding to the W−O−W bending and stretching vibrations are observed at 483, 507, and 592 cm^{-1} and at 855 and 921 cm^{-1}, respectively.[20] The main differences between the IR spectra of **K-1** and $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 13H_2O$ appear in the range of 700−800 cm^{-1}, indicating that the bands at 708 and 774 cm^{-1} most likely correspond to the stretching vibrations of the W−O−Pd bonds.

Similarly, the IR spectrum of **KLi-2** resembles the spectrum of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 17H_2O$, exhibiting a set of ν(P−O) bands at 1019, 1052, and 1083 cm^{-1}, respectively (Figure S3 in the SI). The terminal W═O vibration appears at 944 cm^{-1}. The bands at 470, 528, 566, and 598 cm^{-1} correspond to W−O−W bending vibrations and that at 910 cm^{-1} to a W−O−W stretching vibration. The bands at 715, 760, and 792 cm^{-1} are attributed to Pd−O−W and W−O−W vibrations. The spectrum of **K-3** is almost identical with that of **KLi-2** with the following two minor differences: the lower intensity of the band at around 792 cm^{-1} and the splitting of the band at around 1019 cm^{-1} observed in the IR spectrum of **KLi-2** to two bands at 1028 and 1016 cm^{-1}.

^{31}P NMR Spectroscopy. The ^{31}P NMR spectra of **K-1**, **KLi-2**, and **K-3**, redissolved in water, are consistent with the solid-state structural data and hence prove the solution stability of polyanions **1**−**3**. The spectrum of **1** in H_2O/D_2O (Figure 4) exhibits a singlet at −12.56 ppm, while the signal of **TBA-1** redissolved in acetonitrile is slightly shifted upfield, appearing

Table 2. ^{183}W NMR Data for $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and Its Pd^{II}-Containing Derivatives[a]

polyanion	^{183}W NMR signals, ppm (relative intensity)	ref
$[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$	−127.9 (2), −140.8 (2), −159.6 (2), −175.8 (2), −179.6 (1), −218.9 (2), −222.7 (2), −225.0 (2), −242.3 (2)	21
$[anti\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_{0.5})_2]^{15-}$ (**2**)	−115.3 (2), −133.8 (2), −174.4 (1), −177.9 (2), −212.0 (2), −212.5 (2), −218.7 (2), −226.4 (2), −240.0 (2)	this work
$[\alpha\text{-}P_2W_{17}O_{61}Pd(H_2O)]^{8-}$[b]	−53.1, −85.0, −112.2, −121.3, −128.5, −155.8, −204.4	6

[a] Chemical shifts reported with respect to 1M Na_2WO_4 aqueous solution as external standard. 1 M Na_2WO_4 aqueous solution as the external standard. [b] In CH_3CN (all other entries in aqueous solution).

at −12.85 ppm (Figure S7 in the SI). It is noteworthy that these data are fully consistent with the ^{31}P NMR chemical shift previously reported by Maksimov et al. for the polyanion formulated as $[PW_{11}PdLO_{39}]^{6-}$ (L = Cl, OH; see Table 1).[1]

The ^{31}P NMR spectrum of **KLi-2**, redissolved in water (Figure 5, top), shows two singlets at −8.16 and −13.64 ppm, respectively, corresponding to two types of magnetically inequivalent phosphorus ions in the structure of **2**. The signal at −8.16 ppm can be assigned to the phosphorus atoms next to the lacunary site of the $\{P_2W_{17}\}$ ligand, while the signal at −13.64 ppm corresponds to the distant phosphorus centers. The aqueous solution ^{31}P NMR spectrum of **K-3** (Figure 5, middle) exhibits two singlets at −8.24 and −13.76 ppm, and thus the *anti* and *syn* isomers of $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ can be easily distinguished from each other by ^{31}P NMR spectroscopy. We did not observe *syn*-to-*anti* or *anti*-to-*syn* isomer conversion in an aqueous solution based on ^{31}P NMR because the spectra of the aqueous solutions for both isomers remained unchanged for at least 1−2 weeks. The ^{31}P NMR spectrum of a physical mixture of **KLi-2** and **K-3** redissolved in water (Figure 5, bottom) exhibits two pairs of signals, in full agreement with the coexistence of both conformers in solution, while the integration ratio between peaks corresponding to the *syn* and *anti* isomers does not change with time (for at least 1 week). On the other hand, the observation of just two signals (instead of the expected four) for polyanion **3** indicates that either it possesses C_{2v} symmetry in solution (in contrast to C_1 symmetry observed in the crystal structure of **K-3**) or there is fast exchange (on the NMR time scale) between the two enantiomers of $[syn\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$.

To further confirm the solution stability of the $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ polyanions, we performed ^{183}W NMR measurements on **KLi-2**, which is formed in higher yield. The room temperature ^{183}W NMR spectrum of **KLi-2** redissolved in H_2O/D_2O exhibits nine signals at −115.3, −133.8, −174.4, −177.9, −212.0, −212.5, −218.7, −226.4, and −240.0 ppm with relative intensities of 2:2:1:2:2:2:2:2:2, respectively (Figure 6). This result is fully consistent with the idealized C_{2h} symmetry of polyanion **2** in the solid state, while the observed chemical shifts are different from those for the noncoordinated $\{\alpha_2\text{-}P_2W_{17}\}$ POM precursor[21] and the hypothetical monomeric complex $[\alpha_2\text{-}P_2W_{17}O_{61}Pd(H_2O)]^{8-}$ reported by Liu and co-workers[6] (Table 2), thereby further supporting the structural integrity of **2** in an aqueous solution.

The ^{31}P NMR spectra of **TBA-2** in acetonitrile always contain several extra signals besides two main singlets at −9.29 and −12.81 ppm, which means that this polyanion is unstable in this solvent (Figure S8 in the SI). The same material redissolved in chloroform exhibits two singlets at −8.59 and −13.62 ppm (Figure S9 in the SI).

In order to determine the optimal synthetic conditions for **1**−**3**, we have also investigated reaction mixtures by ^{31}P NMR. By doing so, we discovered that polyanions **1**−**3** are formed in the entire pH range of 2.0−6.5, but the cleanest system with the largest concentration of **1**−**3** is obtained at pH 3.0−4.0. Importantly, for both systems (Pd^{II}/PW$_{11}$/H$_2$O and Pd^{II}/P$_2$W$_{17}$/H$_2$O), the pH of the reaction mixture without adjustment is around 3.4, at both the beginning and the end of the reaction. At pH >4.5, a significant amount of the POM precursor remains unreacted, most probably because of the loss of some Pd^{II} ions, which are consumed for the formation of colloidal $Pd_xO_yH_z$ species.[2,27] At pH <3.0, some of the POM precursor transforms to the plenary Keggin (in the case of $\{PW_{11}\}$) or Wells−Dawson (in the case of $\{P_2W_{17}\}$) ions, as shown by ^{31}P NMR signals at −14.0 (Keggin) or −12.9 (Wells−Dawson) ppm. The *anti*/*syn* isomer ratio of $[Pd_2(P_2W_{17}O_{61})_2]^{16-}$ in the reaction mixture of Pd^{II}/P$_2$W$_{17}$ is about 2:1 right after the reaction in all of the pH ranges studied, whereas the amount of the *syn* conformer increases with time, most likely because of precipitation of the less-soluble *anti* form. The main byproduct of polyanion **1** in the Pd^{II}/PW$_{11}$/H$_2$O system, which is present in the entire pH range studied, has a ^{31}P NMR signal at −12.23 ppm, which might correspond to $[Pd_3(PW_9O_{34})]^{12-}$ (see Table 1). Another presumably Pd^{II}-containing byproduct appears at pH <3 and has a ^{31}P NMR signal at −12.85 ppm, which might correspond to the polyanion observed by Maksimov et al. and formulated as $[PW_{11}O_{39}Pd(H_2O)]^{5-1}$ or the 20-tungsto-2-phosphate $[PdP_2W_{20}O_{70}(H_2O)_2]^{8-22}$ (see Table 1). The latter assignment would be in full agreement with the observation of Kuznetsova et al. for a noncoordinated $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ polyanion at pH 2.0 and low Pd^{II}/PW$_{11}$ ratios.[2]

In light of the above data, we cannot explain the results of Liu et al., who were unable to see any ^{31}P NMR signals for the TBA salts precipitated from the reaction mixture of Pd^{II} ions with $[PW_{11}O_{39}]^{7-}$.[4] Therefore, we performed ^{31}P NMR measurements on the Pd^{II}/PW$_{11}$ reaction mixture at exactly the conditions reported by Liu et al. (Pd:POM = 1:1, 90 °C for 30 min), and we observed the formation of three main species in the reaction mixture before precipitation of the TBA salt and right after redissolution of the TBA salt in acetonitrile: polyanion **1**, the tri-Pd^{II}-containing sandwich-type ion $[Pd_3(PW_9O_{34})_2]^{12-}$, and unreacted $[PW_{11}O_{39}]^{7-}$ (due to the lack of palladium, which precipitates at high temperature). Recrystallization of the TBA-precipitated material led to crystals of $(TBA)_{3-x}[PW_{12}O_{40}H_x]$, slightly contaminated with TBA salts of the above polyanions (see the spectra in Figure S10 in the SI). Very similar observations were also made very recently by Sokolov and co-workers for the Ir^{III} derivative $[PW_{11}O_{39}Ir(H_2O)]^{4-}$,[28] which was originally reported by Liu et al. in the same paper.[4] On the other hand, the Pd^{II}/$\{P_2W_{17}\}$ system seems to be more complicated and requires further study. We have discovered that the reaction between Pd^{II} and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ at 90 °C, as reported by Liu and coworkers,[6] actually does not lead to $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (which is only a very minor species), but rather to a mixture of some other products (see Figure S11 in the SI for the corresponding spectra). The main product of this reaction has a ^{31}P NMR signal at −12.7 ppm, corresponding to the TBA salt of $[\alpha\text{-}P_2W_{18}O_{61}]^{6-}$ (see Figure S12 in the SI). For some unknown reason, Liu et al. reported a slightly different chemical shift of −11.9 ppm.[6] However, our observation is fully consistent with the ^{183}W NMR spectrum provided in ref 6. It should be noted that two signals (those at −112.2 and −155.8 ppm) of the seven signals in the ^{183}W NMR spectrum reported by Liu et al. for $[\alpha_2\text{-}P_2W_{17}O_{61}Pd(H_2O)]^{8-}$ are much more intense than the others and also have an approximate 1:2 integration ratio, almost certainly corresponding to the plenary Wells−Dawson ion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. This assignment is further supported by the presence of two signals with the same chemical shifts and relative intensities as the ones above in the ^{183}W NMR spectra of some other noble-metal-containing derivatives formulated as $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)]^{n-}$, where M is Ru^{III}, Ir^{III},[6] or Pt^{IV} (claimed to be "paramagnetic" with octahedral coordination of the noble metal ion).[29] However, the minor products observed in this system (giving broad signals at −9.2 and −11.2 ppm in the ^{31}P NMR spectrum) could indeed correspond to some interesting species. We will hopefully report on this system in more detail in the future.

■ CONCLUSIONS

In summary, we have shown that the reaction of Pd^{II} ions with monolacunary tungstophosphates of the Keggin and Wells−Dawson types does not lead to incorporation of the Pd^{II} ion into the vacancy of the POM, which would result in a highly unusual octahedral or square-pyramidal coordination for this d^8 late-transition-metal ion. We would much rather observe the formation of the dimeric, sandwich-type polyanions **1** and $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_n)_2]^{(16-2n)-}$ (**2** and **3**), respectively, where two POM ligands are linked by two square-planar Pd^{II} centers, which interact in a side-on fashion at the lacunary sites coordinating to only two oxygen atoms of each POM unit. The $[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_n)_2]^{(16-2n)-}$ polyanion can exist in *anti* and *syn* conformations with respect to the relative orientation of the POM ligands. Both conformations were proven to exist (and also coexist) in solution for weeks. Polyanions **1**−**3** were isolated as potassium salts and thoroughly characterized in the solid state by single-crystal X-ray diffraction (XRD), elemental analysis, IR, and thermogravimetric analysis (TGA) and in solution by ^{31}P and ^{183}W (for **2**) NMR spectroscopy. Our NMR studies confirmed that the Pd^{II}-containing polyanions **1**−**3** are stable in aqueous and organic media.

■ EXPERIMENTAL SECTION

Reagents. $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 13H_2O$ and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 17H_2O$ were prepared according to the published procedures and identified by IR spectroscopy.[30,31] All other reagents were used as purchased without further purification. $PdCl_2$ and $Pd(NO_3)_2$ were obtained from Johnson Matthey PLC.

Instrumentation. Elemental analyses were performed by CNRS, Service Central d'Analyze, Solaize, France. IR spectra were recorded on KBr pellets using a Nicolet Avatar 370 spectrometer. The crystal water content was determined by TGA on a TA Instruments Q 600 device with 15−20 mg samples in 100 μL alumina pans, under a 100 mL min^{-1} N_2 flow and with a heating rate of 5 °C min^{-1}. ^{31}P NMR spectra were recorded in 5 mm tubes on a 400 MHz JEOL ECS instrument at room temperature with a resonance frequency of 161.834 MHz. Chemical shifts are reported with respect to 85% H_3PO_4; all chemical shifts downfield of the reference are reported as positive values. The ^{183}W NMR spectrum of **KLi-2** was recorded in 10 mm tube on a 400 MHz JEOL ECS instrument at room temperature with a resonance frequency of 16.688 MHz. All chemical shifts are reported with respect to 1 M $Na_2WO_4(aq)$ as a reference, and the signals downfield of the reference are reported as positive values. For the ^{183}W NMR measurements, about 1 g of **KLi-2** was dissolved in 3 mL of H_2O in the presence of a Li^+-loaded ion-exchange resin to increase the solubility of the POM salt, and then 0.5 mL of D_2O was added to the filtrate.

Synthesis of $K_9[Pd_2(\alpha\text{-}PW_{11}O_{39}H_{0.5})_2]\cdot 37H_2O$ (K-1). $K_7[\alpha\text{-}PW_{11}O_{39}]\cdot 13H_2O$ (0.320 g, 0.100 mmol) was dissolved in 5 mL of water with stirring and heating to 50 °C. After complete dissolution of the POM precursor, $PdCl_2$ (0.030 g, 0.169 mmol) was added to the obtained solution. The reaction mixture was stirred and heated at 50 °C for 30−40 min, then filtered, and cooled to room temperature. The pH of the deep-brown filtrate was 3.4. This solution was evaporated on a watch glass overnight, and then the obtained solid material was redissolved in a minimum amount of lukewarm water and put in a refrigerator (4 °C). Brown crystalline needles of **K-1** were filtered off the next day using a glass frit, washed with a small amount of ice-cold water, and dried in air. Yield: 0.092 g (28% based on W). Elem anal. Calcd for **K-1**: K, 5.34; P, 0.94; Pd, 3.23; W, 61.4. Found: K, 5.31; P, 0.92; Pd, 3.21; W, 61.5. IR (2% KBr pellets, ν/cm^{-1}): 1620 (m), 1102 (m), 1049 (m), 955 (s), 921 (sh), 774 (sh), 708 (s), 595 (w), 583 (w), 507 (m), 483 (w). ^{31}P NMR (H_2O/D_2O): δ −12.6.

Recrystallization of the dry material obtained after evaporation of the reaction mixture on a watch glass from a 0.5 M KNO_3 aqueous solution leads to the brown crystals of $K_{10}[Pd_2(PW_{11}O_{39})_2]\cdot 2KNO_3\cdot 19H_2O$ (**K-1N**; see structure CSD 423270).

Synthesis of $[(C_4H_9)_4N]_{10}[Pd_2(\alpha\text{-}PW_{11}O_{39})_2]$ (TBA-1). The crystals of **K-1** were dissolved in a small amount of water. The obtained solution was added dropwise to a saturated solution of tetrabutylammonium nitrate ($TBANO_3$; the molar ratio of **1** to TBA^+ was 1:15). The obtained precipitate of **TBA-1** was very fine and could not be filtered using a glass frit. Therefore, **TBA-1** was extracted to CH_2Cl_2. Slow evaporation of the obtained solution led to crystals of **TBA-1** after 1−3 days. The crystals were collected by filtration and washed with plenty of water to remove the $TBANO_3$ impurity. Unfortunately, the quality of crystals was not sufficient to perform X-ray structural analysis on **TBA-1**. Elem anal. Calcd for $[(C_4H_9)_4N]_{10}[Pd_2(\alpha\text{-}PW_{11}O_{39})_2]\cdot 2[(C_4H_9)_4N]NO_3$ (**TBA-1**·**2TBANO$_3$**): C, 26.81; H, 5.06; N, 2.28. Found: C, 26.92; H, 5.15; N, 2.43. IR (2% KBr pellets, ν/cm^{-1}): 1639 (m), 1484 (m), 1383 (m), 1099 (m), 1084 (w), 1044 (s), 951 (s), 912 (m), 889 (m), 837 (m), 785 (sh), 710 (m), 597 (w), 584 (w), 515 (m), 484 (w). ^{31}P NMR (CH_3CN/CD_3CN): δ −12.8.

Synthesis of $K_{14}Li[\textit{anti}\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_{0.5})_2]\cdot 50H_2O$ (KLi-2). $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 17H_2O$ (0.250 g, 0.051 mmol) was dissolved in 5 mL of water with stirring and heating to 50 °C. After complete dissolution of the POM precursor, $PdCl_2$ (0.020 g, 0.112 mmol) was added to the obtained solution. The reaction mixture was stirred and heated at 50 °C for 40 min, filtered while hot, and cooled to room temperature. Light-brown or yellowish precipitate of the product starts to form immediately after cooling. After 2−3 days, it was collected by filtration and recrystallized from a 0.2 M aqueous solution of LiCl. Evaporation of the obtained solution leads to large brown crystals of **KLi-2** within several days. The crystals were filtered using a glass frit, washed with a small amount of ice-cold water, and dried in air. Yield: 0.160 g (63% based on W). Elem anal. Calcd for $K_{14}Li[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_{0.5})_2]\cdot 50H_2O$ (**KLi-2**): K, 5.48; Li, 0.07; P, 1.24; Pd, 2.13; W, 62.5. Found: K, 5.33; Li, 0.07; P, 1.14; Pd, 2.07; W, 62.5. IR (2% KBr pellets, ν/cm^{-1}): 1618 (s), 1083 (m), 1052 (m), 1019 (w), 944 (s), 910 (m), 792 (sh), 760 (sh), 715 (s), 598 (w), 583 (w), 566 (w), 528 (m), 470 (w). ^{31}P NMR (H_2O/D_2O): δ −8.1 and −13.6. ^{183}W NMR (H_2O/D_2O): δ −115.3 (4 W), −133.8 (4 W), −174.4 (2 W), −177.9 (4 W), −212.0 (4 W), −212.5 (4 W), −218.7 (4 W), −226.4 (4 W), −240.3 (4 W).

Synthesis of $K_{10}[\textit{syn}\text{-}Pd_2(\alpha_2\text{-}P_2W_{17}O_{61}H_3)_2]\cdot 50H_2O$ (K-3). Evaporation of the filtrate obtained after removal of the precipitate of the *anti* isomer in the above-described synthesis of **KLi-2** leads to dark-brown crystals of **K-3** within 2−4 weeks. Yield: 0.050 g (20% based on W). IR (2% KBr pellets, ν/cm^{-1}): 1617 (s), 1086 (m), 1056 (m), 1028 (m), 1016 (m), 945 (s), 916 (m), 792 (m), 766 (sh), 715 (s), 608 (w), 600 (w), 583 (w), 566 (w), 529 (m), 473 (w). ^{31}P NMR (H_2O/D_2O): δ −8.2 and −13.7.

Synthesis of $[(C_4H_9)_4N]_{16}[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ (TBA-2). The crystals of **KLi-2** were dissolved in a small amount of water. The obtained solution was added dropwise to a saturated solution of $TBANO_3$ (the molar ratio of **2** to TBA^+ was 1:25). The obtained precipitate of **TBA-2** was filtered on a glass frit, washed with plenty of water, and air-dried. Elem anal. Calcd for $[(C_4H_9)_4N]_{16}[Pd_2(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ (**TBA-2**): C, 23.68; H, 4.62; N, 1.91. Found: C, 24.76; H, 4.67; N, 1.80. IR (2% KBr pellets, ν/cm^{-1}): 1631 (m), 1484 (s), 1488 (m), 1347 (w), 1152 (w), 1087 (s), 1052 (m), 1021 (w), 956 (s), 916 (m), 811 (sh), 788 (sh), 737 (s), 630 (w), 598 (w), 566 (w), 529 (m), 472 (w). ^{31}P NMR (CH_3CN/CD_3CN): δ −9.2 and −12.8 (main signals). ^{31}P NMR (CCl_3H/CCl_3D): δ −8.6 and −13.6.

X-ray Crystallography. Data for the structures of **K-1**, **K-1N**, **KLi-2**, and **K-3** were collected at 100 K on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed molybdenum tube and a graphite monochromator (λ = 0.71073 Å). The crystals were mounted in a Hampton cryoloop using light oil to prevent water loss. The *SHELX* software package (Bruker) was used to solve and refine the structure.[32] An empirical absorption correction was applied using the *SADABS* program.[33] The structures were solved by direct methods and refined by the full-matrix least-squares method minimization of $\Sigma w(F_o - F_c)^2$ with anisotropic thermal parameters for all heavy atoms (W, Pd, P, and K) except for the oxygen atoms of crystallization water molecules of highly disordered K^+ cations. The high value for R_{int} in the structure of **K-1** upon merging of the data compared to R_{sigma} (0.27 vs 0.12), together with several violations of systematic absences, is consistent with the crystal having at least one "friend", especially because structure solution and refinement in lower-symmetry space groups (even in $P1$) did not yield an improved model. Because we were unable to discern any pattern in the list of reflections for which $F(\text{obs}) \gg F(\text{calc})$, we were not able to systematically remove composite reflections. The relative site occupancy factors for disordered positions of potassium cations and oxygen atoms of crystallization water molecules were refined in an isotropic approximation and then fixed at the obtained values. The hydrogen atoms of the crystal water molecules in all four structures and the position of the lithium counteraction in the structure of **KLi-2** were not localized. Additional crystallographic data are summarized in Table S1 in the SI.

The exact number of countercations and the crystal water contents in the bulk material of **K-1** and **KLi-2** were determined by elemental analysis. In the both cases, the number of potassium atoms and water molecules obtained by elemental analysis was slightly higher than that determined by XRD, which can be explained by the disorder of potassium and oxygen atoms of crystallization water in the crystals. The obtained formulas were further used throughout the paper and in the CIF files for overall consistency because all further studies (e.g., electrochemistry, catalysis) will be performed on the bulk material.

Further details on the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49) 7247-808-666; e-mail crysdata@fiz-karlsruhe.de), upon quoting the depository numbers CSD 423269 (**K-1**), 423270 (**K-1N**), 423472 (**KLi-2**), and 423271 (**K-3**).

The TGA data for **K-1** and **KLi-2** (Figures S5 and S6 in the SI) showed a lower amount of crystal water compared to elemental analysis (18 vs 37 for **K-1** and 35 vs 50 for **KLi-2**). This can be explained by the fact that the materials used for the TGA measurements were apparently dried more than those used for elemental analysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data in CIF format, table of the main crystallographic and refinement parameters, IR spectra and TGA curves for **K-1**, **K-1N**, **KLi-2**, and **K-3**, ^{31}P NMR and IR spectra for **TBA-1** and **TBA-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: n.izarova@jacobs-university.de (N.V.I.); u.kortz@jacobs-university.de (U.K.).

Permanent Address

[†]Nikolaev Institute of Inorganic Chemistry, Prospekt Lavrentyeva 3, 630090 Novosibirsk, Russia.

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