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Article

Tetrakis(dimethyltin)-Containing Tungstophosphate $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$: First Evidence for a Lacunary Preyssler Ion

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We demonstrate for the first time that the superlacunary polyanion $[H_2P_4W_{24}O_{94}]^{22-}$ reacts with electrophiles. One-pot reaction of this precursor polyanion with dimethyltin dichloride in aqueous acidic medium results in the hybrid organic–inorganic $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$ (**1**). Single-crystal X-ray analysis was carried out on $K_{17}Li_{11}[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]\cdot 51H_2O$ (**1a**), which crystallizes in the tetragonal system, space group $P4_2/nmc$, $a = b = 21.5112(17)$ and $c = 27.171(3)$ Å, and $Z = 2$. Polyanion **1** is composed of two $(P_4W_{24}O_{92})$ fragments that are linked by four equivalent diorganotin groups. The unprecedented assembly **1** has D_{2d} symmetry and contains a hydrophobic pocket in the center of the molecule. The cyclic voltammetry pattern of **1** is constituted by a first broad, 16-electron reduction wave followed by a second large current intensity wave. No splitting of the first reduction wave could be obtained at moderate scan rate values, even though two well-separated oxidation processes are associated with it. The characteristics of the first wave are clearly different from those obtained for the polyanion precursor $[H_2P_4W_{24}O_{94}]^{22-}$ and the related, wheel-shaped $[H_7P_8W_{48}O_{184}]^{33-}$, which is due to the $\{Sn(CH_3)_2\}$ fragments in **1**. However, no feature was observed in the voltammogram which could be associated with reduction of the Sn centers.

Introduction

The class of polyoxometalates is unique in inorganic chemistry due to the enormous structural variety combined with interesting properties.[1−6] The first polyanion was reported by Berzelius a long time ago, and since then, the global interest in polyoxometalates and the rate of discovery of novel species has steadily increased.[7,8] Nevertheless, the mechanism of formation of polyoxoanions is still poorly understood and usually described as self-assembly. Lately, there have been increasing efforts worldwide toward the functionalization of polyoxometalates via incorporation of organo or organometallic moieties.[9,10] Reaction of mono-organotin species (e.g. $C_6H_5SnCl_3$) with lacunary polyoxotungstates has been thoroughly investigated over the years. This work has led to several monomeric (e.g. $[(BuSn)_3P_2W_{15}O_{59}]^{9-}$) and also dimeric (e.g. $[(PhSnOH_2)_2$-

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(γ-$SiW_{10}O_{36})_2]^{10-}$) polyanions.[11−13] These species are very stable, diamagnetic, and water soluble, which is attractive for potential medicinal applications.[14] Recently, the groups of Pope and Hasenknopf showed independently that monoorganotin-containing polyanions can be further derivatized by peptide or ester functions.[15,16]

Very recently we introduced the first examples of diorganotin-containing polyoxotungstates.[17] We showed that the *trans*-dimethyltin group represents a highly efficient linker of lacunary polyanion fragments (e.g. $As^{III}W_9O_{33}{}^{9-}$, $PW_9O_{34}{}^{9-}$). To date we have isolated monomeric,[17a] trimeric,[17b] tetrameric,[17c] and dodecameric[17d] assemblies. All these molecular, hybrid organic−inorganic polyanions exhibit unprecedented architectures and some (e.g. $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A\text{-}PW_9O_{34})_{12}]^{36-}$) are among the largest (∼1000 atoms) and heaviest (∼33 000 g/mol) polyoxotungstates ever reported with central, hydrophobic cavities of up to 7 Å in diameter allowing for extensive host−guest chemistry studies.

Now we decided to investigate interaction of the dimethyltin linker with other, larger polyoxoanion precursors with an emphasis on tungstophosphates. The polyanion $[H_2P_4W_{24}O_{94}]^{22-}$ was discovered in 1986 by Contant and Tézé, but its structure has remained elusive until today. These authors had proposed two possible linkages of the two $(H_2P_2W_{12}O_{48})$ fragments, one resulting in an orthogonal C_{2v} polyanion and the other in a linear C_{2h} species. On the basis of ^{31}P NMR, they suggested in fact that both forms are present in solution.[18]

Here we report on interaction of $[H_2P_4W_{24}O_{94}]^{22-}$ with $(CH_3)_2SnCl_2$ in aqueous, acidic medium.

Experimental Section

Synthesis. The precursor $K_{16}Li_2[H_6P_4W_{24}O_{94}]$ was synthesized according to the published procedure of Contant and Tézé, and the purity was confirmed by infrared spectroscopy.[18] All other reagents were used as purchased without further purification.

Table 1. Crystal Data and Structure Refinement for $K_{17}Li_{11}[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]\cdot 51H_2O$ (**1a**)

emp formula	$C_8H_{130}K_{17}Li_{11}O_{235}P_8Sn_4W_{48}$
fw	14275.8
space group (No.)	$P4_2/nmc$ (14)
a (Å)	21.5112(17)
b (Å)	21.5112(17)
c (Å)	27.171(3)
V (Å^3)	12573(2)
Z	2
temp (°C)	−120
wavelength (Å)	0.710 73
d_{calcd} (Mg m^{-3})	3.72
abs coeff. (mm^{-1})	22.69
R [$I > 2\sigma(I)$][a]	0.045
R_w (all data)[b]	0.109

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

$K_{17}Li_{11}[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]\cdot 51H_2O$ (1a). Polyanion **1** was synthesized by interaction of 0.072 g (0.30 mmol) of $(CH_3)_2SnCl_2$ with 0.728 g (0.10 mmol) of $K_{16}Li_2[H_6P_4W_{24}O_{94}]$ in 20 mL of LiAc buffer at pH 4.1. The solution was heated to 50 °C for 1 h and filtered after it had cooled. Addition of 0.5 mL of 1.0 M KCl solution to the colorless filtrate and slow evaporation at room temperature led to a white, crystalline product after about 2 weeks (yield 0.39 g, 54%). Anal. Calcd (found) for **1a**: K, 4.7 (4.8); Li, 0.5 (0.8); W, 61.8 (61.1); P, 1.7 (1.5); Sn, 3.3 (3.5); C, 0.7 (0.8); H, 0.9 (1.0). IR for **1a**: 1136, 1086, 1018, 981, 952, 928, 915, 812, 693, 573, 525, 462 cm^{-1}. Elemental analysis was performed by Kanti Labs Ltd. in Mississauga, Canada. The IR spectrum was recorded on a Nicolet Avatar FTIR spectrophotometer in a KBr pellet. All NMR spectra were recorded on a JEOL Eclipse 400 instrument at room temperature using D_2O as a solvent.

X-ray Crystallography. A crystal of compound **1a** was mounted on a glass fiber for indexing and intensity data collection at 163 K on a Bruker D8 SMART APEX CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Direct methods were used to solve the structure and to locate the heavy atoms (SHELXS97). Then the remaining atoms were found from successive difference maps (SHELXL97). Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[19] Crystallographic data are summarized in Table 1.

Electrochemistry. General Methods and Materials. Pure water was used throughout. It was obtained by passing through a RiOs 8 unit followed by a Millipore-Q Academic purification set. All reagents were of high-purity grade and were used as purchased without further purification. The pH = 4 medium was made of 1 M $CH_3COOLi + CH_3COOH$.

Electrochemical Experiments. The concentration of polyanion **1** was 2×10^{-4} M. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The source, mounting, and polishing of the glassy carbon (GC, Tokai, Japan) electrodes has been described.[20] The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. All experiments were performed at room temperature.

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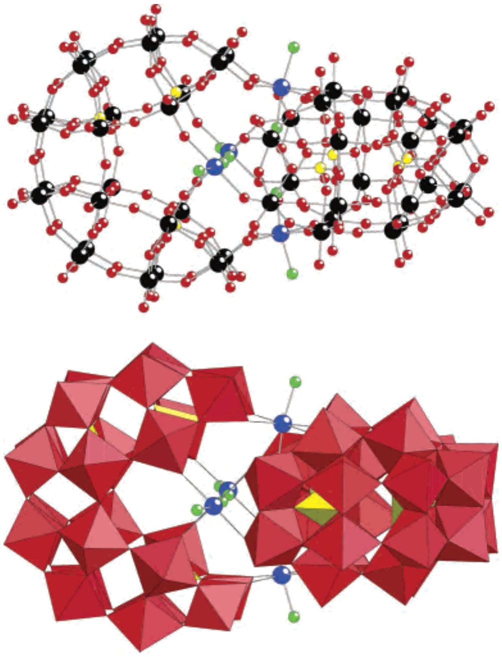

Figure 1. Ball and stick (top) and polyhedral (bottom) representations of $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$ (**1**). The color code is as follows: tungsten (black); oxygen (red); phosphorus (yellow); tin (blue); carbon (green).

Results and Discussion

Synthesis and Structure. Reaction of $(CH_3)_2SnCl_2$ with $K_{16}Li_2[H_6P_4W_{24}O_{94}]$ in aqueous, acidic (pH 4.1) medium at 50 °C resulted in $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$ (**1**). Single-crystal X-ray analysis on $K_{17}Li_{11}[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]\cdot 51H_2O$ (**1a**) revealed that the title polyanion **1** is composed of two $(P_4W_{24}O_{92})$ fragments that are linked by four equivalent diorganotin groups. The unprecedented assembly **1** has D_{2d} symmetry and contains an empty, hydrophobic pocket (diameter around 2 Å) in the center of the molecule (see Figure 1). The two $(P_4W_{24}O_{92})$ fragments of **1** are orthogonal to each other and are held together by four structurally equivalent dimethyltin groups. Interestingly, the two $(P_2W_{12}O_{48})$ subunits of each $(P_4W_{24}O_{92})$ fragment are fused via four W−O−W′ bridges involving cap and belt tungsten centers. It remains to be seen if the "free" $[H_6P_4W_{24}O_{94}]^{18-}$ precursor has the same connectivity or only two W−O−W′ bridges involving the caps as originally suggested by Contant and Tézé.[18] We are currently trying to obtain single crystals of $K_{16}Li_2[H_6P_4W_{24}O_{94}]$ to resolve this open question. It is highly likely that the presence of the four $(CH_3)_2Sn^{2+}$ groups causes the small angle (∼45°) of the fused $(P_2W_{12}O_{48})$ groups.

In agreement with our previously reported diorganotin-containing polyoxotungstates, the two methyl groups of each tin atom in **1** are in relative trans positions (C1−Sn−C2 = 169.6(11)°); see Figure 2.[17] The Sn−C bond lengths in **1** are 2.12(3) and 2.19(3) Å, respectively, and the equatorial Sn−O bond lengths are 2.230(13) and 2.254(12) Å, respectively. The bond lengths of the tungstophosphate framework are not unusual.

Bond valence sum calculations indicate that polyanion **1** contains only one type of protonated oxygen (O1A, s = 1.44).[21] There is a total of eight O1A atoms in **1**, and they are all μ_2-oxo bridges (W1−O1A−Sn1) linking the four cap-tungstens of each $(P_2W_{12}O_{48})$ fragment with tin centers. The intermediate bond valence sum for O1A indicates that only 50% of all eight atoms are actually protonated. This probably means that at each cap of the two $(P_2W_{12}O_{48})$ units in **1** only one of the two W−O−Sn bridges is actually protonated. Interestingly, this is in complete agreement with the conclusions of Contant and Tézé in their studies of the $[H_2P_2W_{12}O_{48}]^{12-}$ and $[H_2P_4W_{24}O_{94}]^{22-}$ precursors.[18]

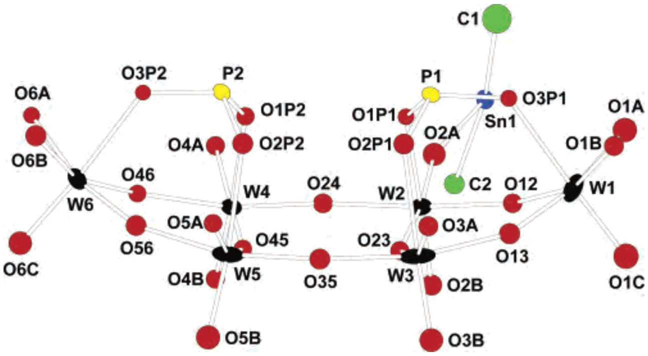

Figure 2. Ball and stick representation of **1** showing thermal ellipsoids (50%) and the labeling scheme.

All potassium ions could be identified crystallographically (K_4 with half occupancy) but none of the lithium ions. Nevertheless, their presence and therefore the complete molecular formula of **1a** were determined by elemental analysis.

Polyanion **1** is diamagnetic and contains four spin 1/2 nuclei (^{183}W, ^{119}Sn, ^{13}C, ^{1}H) and therefore represents a good candidate for solution NMR studies at room temperature. Our ^{31}P NMR measurements resulted in two singlets (−7.1, −8.7 ppm) of equal intensity, and ^{1}H NMR showed a singlet at 0.7 ppm. For ^{119}Sn and ^{13}C NMR (both ^{1}H decoupled) we observed singlets at −243.2 and 8.6 ppm, respectively. The above results are in good agreement with the solid-state structure of **1** and with our previous compounds of this class.[17] Although we used the lithium salt of **1** we were unable to observe any signals in ^{183}W NMR, which indicates that the concentration of the polyanion was too small due to very poor solubility.

Close inspection of the structure of each $(P_4W_{24}O_{92})$ fragment in **1** indicates that it may be considered as a lacunary derivative of the well-known Preyssler ion $[NaP_5W_{30}O_{110}]$.[14−22a] This plenary polyanion has approximate D_{5h} symmetry and consists of a cyclic assembly of five (PW_6O_{22}) units. The $(P_4W_{24}O_{92})$ fragments in **1** may be considered as being composed of a cyclic assembly of four (PW_6O_{22}) units with a linkage pattern of the individual units identical to the Preyssler ion. However, due to one missing (PW_6O_{22}) unit in each $(P_4W_{24}O_{92})$ fragment the latter is best described as a lacunary Preyssler ion.

Electrochemistry Studies. The title polyanion **1** was also studied by cyclic voltammetry in 1 M (CH_3COOLi + CH_3COOH) pH 4 buffer corresponding essentially to its

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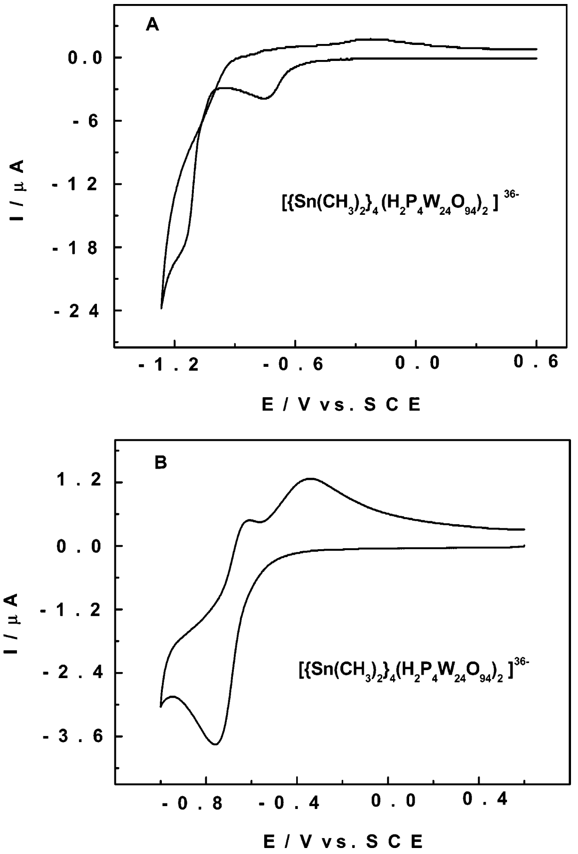

Figure 3. Cyclic voltammogram of 2×10^{-4} M **1** in a pH 4 medium (1 M $CH_3COOLi + CH_3COOH$). The scan rate was 10 mV·s^{-1}, the working electrode was glassy carbon, and the reference electrode was SCE. The whole voltammetric pattern and the voltammetric pattern (A) and the voltammetric pattern restricted to the first redox processes (B) are shown.

synthesis medium. Figure 3A shows the features of interest in the overall CV of **1** in the above pH 4 medium. This CV is constituted by a broad first wave, followed by a large current intensity second wave which peaks close to the electrolyte discharge. Actually, the second multielectron reduction process is a combination of two very closely spaced waves. The decomposition products generated at this combined wave deposit on the electrode surface upon continuous cycling of the potential up to the cathodic limit shown in Figure 3A. The efficiency of the deposition process increases when the potential scan rate decreases. Specifically, a very faint reversibility can be detected for this combined second wave at a scan rate of 200 mV s^{-1}. Such reductive deposition phenomena at fairly negative potentials are known and have been described for a large variety of heteropolyanions.[23] The complex phenomena associated with the second combined wave will not be considered further here.

The behavior of the first wave is more characteristic of **1** and is shown in Figure 3B. In the following, the CV pattern is restricted to this process. The cathodic part features a broad electrochemical wave which remains composite if the potential scan rate is lower than the 200 mV s^{-1} explored here. In contrast, two well-separated oxidation processes are observed on potential reversal, at −0.612 and −0.356 V vs SCE, respectively, thus confirming the composite nature of the cathodic scan.

Table 2. Reduction Peak Potentials Measured from CVs and Number (n_1 or n_2) of Electrons Corresponding to Each Wave of **1**, $[H_2P_4W_{24}O_{94}]^{22-}$, and $[H_7P_8W_{48}O_{184}]^{33-}$ [a]

polyoxometalate	n_1	$-E_{pc1}$/V vs SCE	n_2	$-E_{pc2}$/V vs SCE
1	16	0.755		
$[H_2P_4W_{24}O_{94}]^{22-}$	4	0.802	4	~1.110
$[H_7P_8W_{48}O_{184}]^{33-}$	8	0.610	8	0.728

[a] The scan rate was 10 mV s^{-1}, the working electrode was glassy carbon, and the reference electrode was SCE.

The detailed molecular structure of the polyanion precursor $[H_2P_4W_{24}O_{94}]^{22-}$ before its engagement in the self-assembly process resulting in formation of **1** remains unknown. Nevertheless, comparison of the first wave system of **1** with the cyclic voltammograms of $[H_2P_4W_{24}O_{94}]^{22-}$ and the wheel-shaped $[H_7P_8W_{48}O_{184}]^{33-}$ in the same medium is expected to be useful. This study might allow us to extract some distinct features of **1** which are due to the incorporated dimethyltin units. All three polyanions can be considered as lacunary species, and thus, their electrochemistry should be carried out in a well-buffered electrolyte.[24] The comparisons between **1** and $[H_2P_4W_{24}O_{94}]^{22-}$ on one hand and between **1** and $[H_7P_8W_{48}O_{184}]^{33-}$ on the other hand are shown in Figures 4A and 4B, respectively. The potential locations of the reduction peaks and the number of electrons consumed by each wave are gathered in Table 2. The number of electrons for the waves of $[H_7P_8W_{48}O_{184}]^{33-}$ (three equal 8-electron waves)[18,25] and $[H_2P_4W_{24}O_{94}]^{22-}$ (three equal 4-electron waves)[18] were known from previous works. For the first wave of **1** the corresponding number of electrons was evaluated in two different ways. A first rough estimate was performed by determining the area delimited by the relevant voltammograms and comparing the charges corresponding to each wave. This method was used to compare **1** and $[H_2P_4W_{24}O_{94}]^{22-}$, which shows suitable, well-separated waves. The charge ratio was 4.07 in favor of **1**, thus indicating roughly 16 electrons/molecule for the first wave of this complex. As a second method, controlled-potential coulometry was carried out at −0.780 V vs SCE, but the number of electrons consumed/molecule exceeds 16, due to a nonidentified catalytic and/or decomposition process. Such behavior was also observed previously during coulometric studies on $[H_7P_8W_{48}O_{184}]^{33-}$, albeit to a smaller extent.[25] Finally, it can be concluded that the result of the second method supports the value of roughly 16 electrons/molecule of **1** obtained by the first method. Further coulometric study of the catalytic process as a function of electrolyte composition might help to accurately determine electron numbers but is beyond the scope of this work.

Figure 4 and Table 2 indicate unambiguously that the three polyanion species **1**, $[H_2P_4W_{24}O_{94}]^{22-}$, and $[H_7P_8W_{48}O_{184}]^{33-}$ have distinct electrochemical properties. During these studies, we also observed that the stability of $[H_2P_4W_{24}O_{94}]^{22-}$ in solution is enhanced by formation of **1**.

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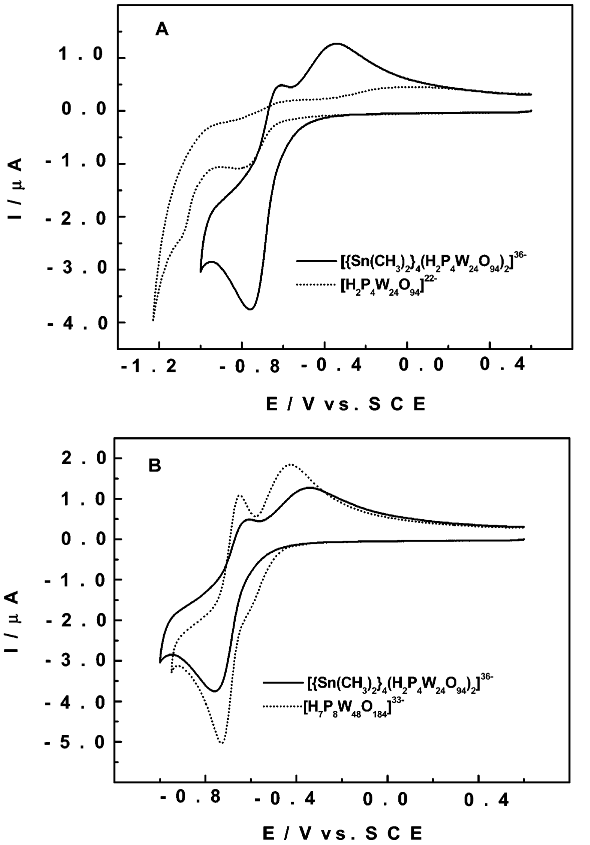

Figure 4. Comparison of the cyclic voltammograms of 2×10^{-4} M solution of **1** in a pH 4 medium (1 M CH_3COOLi + CH_3COOH). The scan rate was 10 mV·s^{-1}, the working electrode was glassy carbon, and the reference electrode was SCE. Comparison of the voltammetric patterns of **1** and $[H_2P_4W_{24}O_{94}]^{22-}$ and comparison of the voltammetric patterns of **1** and $[H_7P_8W_{48}O_{184}]^{33-}$ are shown.

In fact, the combined results from present and previous[18,25] work allow to establish the following order of stability: $[H_7P_8W_{48}O_{184}]^{33-} \gg$ **1** $>$ $[H_2P_4W_{24}O_{94}].^{22-}$

In agreement with the literature, the CV pattern of $[H_2P_4W_{24}O_{94}]^{22-}$ is constituted by three separated 4-electron waves, two of which are shown in Figure 4A.[18] In Figure 4A and Table 2, these waves are located at more negative potentials than the sole wave considered for **1**. In contrast, Figure 4B and Table 2 show the first two 8-electron waves of $[H_7P_8W_{48}O_{184}]^{33-}$ (already described previously)[18,25] to be located at more positive potentials than that of **1**. In the present case, these results might be interpreted on the basis of the assumption that **1** is composed of two identical, mostly noninteracting moieties, a feature that would support the existence of a composite reduction wave. Then, the following reduction trends should be expected for the tungsten−oxo frameworks of the three polyoxometalates discussed here: In comparison of a substituted polyoxometalate and its lacunary precursor, binding of one or more cationic moieties to the latter will diminish the overall negative charge of the product polyanion. As a consequence, the reduction potential of the tungsten−oxo framework will be driven in the positive direction compared to that of the lacunary precursor complex. One assumption behind this conclusion is that no specific complicating influences appear in the overall reduction schemes of the two polyanions. In short, the cation-substituted polyanion will behave much like a "saturated" complex, with a reduction potential intermediate between those of the plenary and lacunary parents,[1] a feature well-illustrated by the reduction patterns of Keggin and Dawson-type tungstostannates.[26] However, this conclusion must be applied with caution in the general case because such a reasoning would not take into account any specific modification, e.g. a change in acid−base properties of the polyanion as a result of cation incorporation. Detailed parameters of the cation like size, electronic configuration, and coordination geometry including possible distortions (e.g. Jahn−Teller) may also contribute to the specificity.[27]

Interestingly, $[H_7P_8W_{48}O_{184}]^{33-}$ appears to behave as if it were more saturated than **1**. However, the comparison is not straightforward as the linkage pattern of the $(P_2W_{12}O_{48})$ subunits is different in $[H_7P_8W_{48}O_{184}]^{33-}$ and **1** and for free $[H_2P_4W_{24}O_{94}]^{22-}$ it is not yet known.[18] As a consequence, the acidities of $[H_7P_8W_{48}O_{184}]$,$^{33-18}$ $[H_2P_4W_{24}O_{94}]^{22-}$, and **1** might also be different from each other. Such an assumption is supported by the splitting of the CV pattern of $[H_7P_8W_{48}O_{184}]^{33-}$ in two 8-electron waves at pH 4, without any possibility to make them merge until pH = 7.3. Even then the merging is incomplete, as a slight decrease of the potential scan rate favors splitting of the waves.

Finally, it is worth noting that for **1** no wave was observed which could be associated with reduction of the Sn centers. This result is reminiscent of that obtained by Chorghade and Pope for Keggin and Dawson-type tungstostannates.[26]

Conclusions

The title polyanion **1** is of interest for several reasons: (i) It represents the first example of a polyanion synthesized from the $[H_6P_4W_{24}O_{94}]^{18-}$ precursor. (ii) It represents the first example of a polyoxoanion containing the $(P_4W_{24}O_{92})$ fragment. (iii) It reveals that the $(P_4W_{24}O_{92})$ fragment is a lacunary derivative of the Preyssler ion $[NaP_5W_{30}O_{110}]^{14-}$. (iv) It represents a novel polyanion architecture. (v) It has a central, hydrophobic pocket. (vi) It adds a new member to our series of monomeric, trimeric, and dodecameric dimethyltin-containing polyoxotungstates. The structure of **1** allows for a multitude of studies including host/guest chemistry, catalysis, and medicine. Some of this work is currently in progress, and the results will be reported in due time.

The first reduction wave in the CV pattern of **1** was studied in detail because it contains the main features useful for a characterization of this complex. This 16-electron, broad reduction wave is associated on potential reversal with two well-separated oxidation processes. As judged from the potential locations and current intensities, the voltammetric pattern is unambiguously different from those of $[H_7P_8W_{48}O_{184}]^{33-}$ and $[H_2P_4W_{24}O_{94}]^{22-}$, even though no feature was observed that could be traced to the reduction of Sn centers.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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