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The Bis-Phenyltin-Substituted, Lone-Pair-Containing Tungstoarsenate $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$

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The bis-phenyltin-substituted, lone-pair-containing tungstoarsenate $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) has been synthesized and characterized by multinuclear NMR, IR, and elemental analysis. Single-crystal X-ray analysis was carried out on $(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$ (**NH_4–1**), which crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 18.3127(17)$ Å, $b = 24.403(2)$ Å, $c = 22.965(2)$ Å, $\beta = 106.223(2)°$, and $Z = 4$. Polyanion **1** consists of two B-α-$(As^{III}W_9O_{33})$ Keggin moieties linked via a $WO(H_2O)$ fragment and two SnC_6H_5 groups leading to a sandwich-type structure with nominal C_{2v} symmetry. Polyanion **1** is stable in solution as indicated by the expected 6-line pattern (4:4:4:4:2:1) in ^{183}W NMR and the expected ^{119}Sn, ^{13}C, and ^{1}H NMR spectra. Synthesis of **1** was accomplished by reaction of $C_6H_5SnCl_3$ and $K_{14}[As_2W_{19}O_{67}(H_2O)]$ in a 2:1 molar ratio in aqueous acidic medium (pH 2). In the solid-state structure of **NH_4–1**, neighboring polyanions are weakly bound via W–O–Na bonds leading to chains which interact with each other via the phenyl rings resulting in a 2-D assembly.

Introduction

Polyoxometalates (POMs) are an important class of inorganic compounds, and they exhibit a diverse compositional range and significant structural versatility.[1,2] POMs are usually composed of early transition metal MO_6 ($M = W^{6+}$, Mo^{6+}, etc.) octahedra and main group XO_4 ($X = P$, Si, etc.) tetrahedra. The most famous POMs are probably the Keggin (e.g., $PW_{12}O_{40}^{3-}$) and the Wells–Dawson (e.g., $P_2W_{18}O_{62}^{6-}$) ions. Nevertheless, also lone-pair-containing main group elements (e.g., As^{III}) can act as hetero groups. There are numerous uses of POMs utilizing their specific molecular composition, size, shape, charge density, redox potentials, acidity, and solubility characteristics, which span a wide range of applications including homogeneous and heterogeneous catalysts, electrocatalysts, coatings, medicinal agents, pigments, recording materials, toners, precursors for oxide films, and sensors.[3–6] POMs have received particular attention in environmentally benign catalytic processes and in antiviral and antitumoral chemotherapy.[3–6] Nevertheless, the structure/composition–activity relationship of POMs in these and other applications is not yet fully understood, and therefore, the synthesis of new types of such polyanions remains an important research objective.

Hybrid organic–inorganic polyoxoanions are an extremely interesting class of compounds because they combine the unique properties of the metal–oxo fragment with those of the attached organic groups. Many of the reported products of this type are two- or three-dimensional in the solid state and therefore best described as materials.[7] There is only a small number of discrete hybrid organic–inorganic polyoxoanions, and almost all of these species belong to the class of organotin-substituted polyanions. The groups of Pope, Knoth, and Liu investigated the reactivity of mono- and polyvacant polyoxotungstate precursors with monoorganotin species. This work has led to several novel compounds (e.g., $[(PhSnOH_2)_2(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, $[(BuSn)_3P_2W_{15}O_{59}]^{9-}$).[8–10] It

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is apparent that the size of the monoorganotin fragment (RSn^{3+}) fits very well the lacunary sites of Keggin- and Dawson-based polyoxotungstates. Furthermore, the Sn−C bond is hydrolytically stable which allows us to envision applications of such polyoxoanion derivatives in medicine. The solid-state structures of these species have usually been obtained by single-crystal X-ray diffraction, but the diamagnetic nature of these compounds has also allowed for multinuclear NMR studies in solution. Especially the work of Pope et al. demonstrates nicely the powerful and complementary nature of single-crystal XRD and multinuclear NMR. In essentially all cases it was shown that the solid-state structure of the polyanion was preserved in solution.

Recently, Hasenknopf et al. used the same methodology to introduce peptide functions to monoorganotin units which were incorporated in the monolacunary Wells−Dawson derivatives $[x\text{-}P_2W_{17}O_{61}]^{10-}$ ($x = \alpha_1, \alpha_2$).[11] They grafted a pendant carboxylic acid on the organotin fragment which allowed for consecutive peptide or ester coupling reactions. For the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, they carried out coupling reactions using different amines leading to the corresponding amides.

Very recently, Kortz et al. reported on the first example of a diorganotin-substituted polyoxotungstate $[\{Sn(CH_3)_2(H_2O)_2\}_3(\beta\text{-}XW_9O_{33})]^{3-}$ ($X = As^{III}, Sb^{III}$). This polyanion self-condenses in the solid state leading to a hybrid organic−inorganic 2-D material $(CsNa_2[\{Sn(CH_3)_2\}_3(H_2O)_4(\beta\text{-}XW_9O_{33})]\cdot 7H_2O)_\infty$ ($X = As^{III}, Sb^{III}$).[12]

Here, we report on the solution and solid-state properties of a bis(monoorganotin) derivative of the dilacunary tungstoarsenate(III) $[As_2W_{19}O_{67}(H_2O)]^{14-}$.

Experimental Section

Synthesis. The precursor $K_{14}[As_2W_{19}O_{67}(H_2O)]$ was synthesized according to the published procedure of Kortz et al., and the purity was confirmed by infrared spectroscopy.[13] All other reagents were used as purchased without further purification.

Table 1. Crystal Data and Structure Refinement for $(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$ (**NH_4−1**)

emp formula	$As_2C_{12}H_{75}N_7NaO_{85.5}Sn_2W_{19}$
fw	5594.1
space group	$P2_1/c$ (No. 14)
a (Å)	18.3127(17)
b (Å)	24.403(2)
c (Å)	22.965(2)
β (deg)	106.223(2)
V (Å^3)	9854.0(16)
Z	4
T (°C)	−110
wavelength (Å)	0.71073
d_{calcd} (Mg m^{-3})	3.73
abs coeff (mm^{-1})	23.354
R [$I > 2\sigma(I)$][a]	0.075
R_w (all data)[b]	0.146

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

$(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$ (NH_4−1). The title compound was synthesized by dissolving 0.145 mL (0.88 mmols) of $C_6H_5SnCl_3$ in 40 mL H_2O followed by addition of 2.10 g (0.40 mmol) of $K_{14}[As_2W_{19}O_{67}(H_2O)]$. This solution (pH 1.6) was heated to 80 °C for 1 h and then cooled to room temperature. The solution was filtered, and a few drops of 0.1 M NH_4Cl and 0.1 M NaCl solution were added. Then, the solution was allowed to evaporate in an open vial at room temperature. A white crystalline product started to appear after a week. Evaporation was continued until the solvent approached the solid product (yield 1.6 g, 72%). IR for $(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$: 964(m), 905(m), 881(m), 860(m), 801(sh), 754(s), 736(s), 702(sh), 582(w), 518(sh), 486(w), 446(w) cm^{-1}. Anal. Calcd (Found) for $(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$: N 1.8 (1.6), Na 0.4 (0.2), Sn 4.2 (4.3), W 62.4 (61.6), As 2.7 (2.7), C 2.6 (2.7), H 1.6 (1.5). NMR of **1** at pH 1.6 (D_2O, 293 K) ^{183}W, δ −110.5, −120.7, −150.0, −159.6, −170.5, −196.9 ppm (all singlets with intensities 4:2:4:4:4:1); $^{119}Sn\{H\}$, δ −432.5 ppm (singlet); $^{13}C\{H\}$, δ 129.7, 132.0, 133.6, 137.3 ppm (singlets); ^1H, δ 7.6, 8.1 ppm (multiplets). Monophenyltrichloride ($C_6H_5SnCl_3$) in H_2O at pH 1.6: $^{119}Sn\{H\}$, δ −536.5 ppm (singlet); $^{13}C\{H\}$, δ 128.9, 130.4, 133.1, 134.3 ppm (singlets); ^1H, δ 7.3, 7.5 ppm (multiplets).

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 400 MHz JEOL ECX instrument at room temperature using D_2O as a solvent.

X-ray Crystallography. A crystal of compound **NH_4−1** 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 ($\lambda = 0.71073$ 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.[14] Crystallographic data are summarized in Table 1.

Results and Discussion

Synthesis and Structure. The novel bis-phenyltin-substituted, dimeric tungstoarsenate(III) $[(C_6H_5Sn)_2As_2W_{19}O_{67}$-

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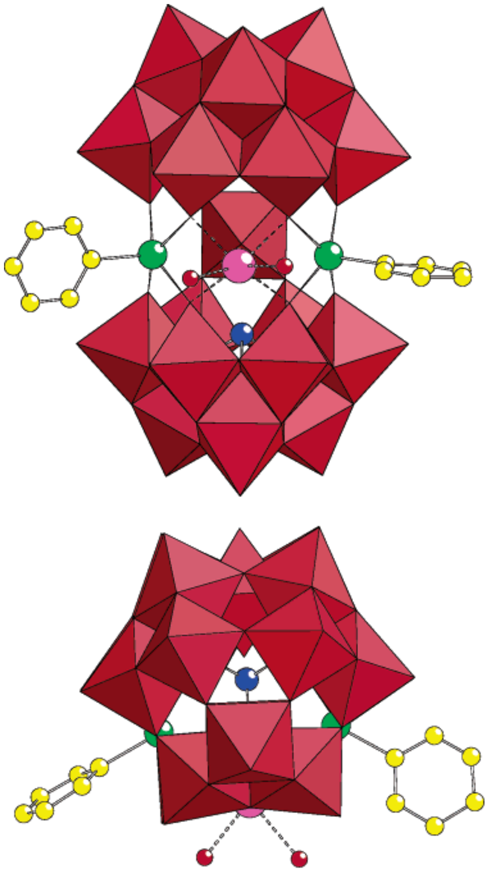

Figure 1. Combined polyhedral/ball-and-stick representation of $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) as a side-view (upper) and a top-view (lower). The red octahedra represent WO_6, and the color code of the balls is tin (green), arsenic (blue), sodium (purple), oxygen (red), and carbon (yellow). Hydrogen atoms are omitted for clarity.

$(H_2O)]^{8-}$ (**1**) consists of two lacunary B-α-$[AsW_9O_{33}]^{9-}$ Keggin fragments linked via two $(C_6H_5Sn)^{3+}$ groups and a $\{WO(H_2O)\}^{4+}$ moiety leading to a structure with nominal C_{2v} symmetry (see Figure 1). Alternatively, **1** can be described as a dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14-}$ fragment which has taken up two organotin units. It can be noticed that the tin atoms are situated well above the plane of the four equatorial μ_2-oxo ligands. Therefore, the tin atoms are displaced toward the terminal phenyl ligand, i.e., toward the exterior of the equator of **1**. This resembles the displacement of all tungsten sites of **1** toward the external, terminal oxo groups. On the other hand, the unique tungsten atom in the central belt of **1** is displaced toward the interior of the equator of **1**. As a result of this symmetry breaking, polyanion **1** exhibits a surface with both positive and negative curvature.

Bond-valence-sum (BVS) calculations for **1** indicated that no oxygen of the two (AsW_9O_{33}) caps is protonated.[15] However, the central tungsten atom has two *trans* related ligands which are a water molecule and an oxo group. The latter is inside the central cavity of **1** whereas the former is on the outside. This is in complete agreement with the single-crystal XRD data of related structures that contain one or three central tungsten atoms linking two (α-AsW_9O_{33}) fragments (e.g., $[As_2W_{19}O_{67}(H_2O)]^{14-}$, $[As_2W_{21}O_{69}(H_2O)]^{6-}$).[13,16b,17]

The title polyanion **1** was synthesized rationally and in a one-pot reaction by interaction of $C_6H_5SnCl_3$ with $K_{14}[As_2W_{19}O_{67}(H_2O)]$ in aqueous, acidic medium (pH 2). However, we obtained **1** for the first time accidentally during our efforts to discover novel diphenyltin-substituted species. Interaction of $(C_6H_5)_2SnCl_2$ with Na_9[α-AsW_9O_{33}] and Na_2WO_4 in a molar ratio of 3:1:3 in aqueous medium at pH 2 resulted in **1**. This means that the diphenyltin precursor underwent partial hydrolysis resulting in the loss of one phenyl group. Then, we decided to reproduce this compound via a more rational synthetic procedure using the dilacunary polyoxotungstate precursor $[As_2W_{19}O_{67}(H_2O)]^{14-}$ and $(C_6H_5)SnCl_3$ (see Experimental Section). The tungstoarsenate $[As_2W_{19}O_{67}(H_2O)]^{14-}$ was synthesized for the first time about 30 years ago by Tourné et al., and recently, Kortz et al. confirmed the proposed structure by X-ray diffraction.[13,16] Interestingly, to date only a few polyoxoanions have been synthesized using $[As_2W_{19}O_{67}(H_2O)]^{14-}$ as a precursor.[13,18]

Polyanion **1** represents a novel member in the class of monoorganotin-substituted polyoxotungstates in general and the subclass of tungstoarsenates(III) in particular. Pope et al. have synthesized and characterized several monomeric and dimeric polyoxotungstates substituted by monoorganotin functions.[8] Among them the tetrakis(monophenyltin)-substituted tungstoarsenate(III) $[\{(C_6H_5Sn)_2O\}_2H(\alpha\text{-}AsW_9O_{33})_2]^{9-}$ and the tris(monophenyltin)-substituted tungstoantimonate(III) $[(C_6H_5Sn)_3Na_3(H_2O)_6(\alpha\text{-}SbW_9O_{33})_2]^{6-}$ are related to **1**.[8e] These species were synthesized by reaction of $C_6H_5SnCl_3$ with Na_9[α-AsW_9O_{33}] and Na_9[α-SbW_9O_{33}], respectively, in aqueous acidic medium (pH 2). The antimony derivative $[(C_6H_5Sn)_3Na_3(H_2O)_6(\alpha\text{-}SbW_9O_{33})_2]^{6-}$ and **1** exhibit both a dimeric sandwich-type structure with square pyramidal organotin groups, whereas $[\{(C_6H_5Sn)_2O\}_2H(\alpha\text{-}AsW_9O_{33})_2]^{9-}$ contains four monoorganotin units which are all octahedral.

The solid-state structure of **NH_4−1** indicates that the title polyanion contains a sodium atom in the central belt between the two tin atoms ($d_{Na\cdots Sn} = 3.52-3.55(1)$ Å, see Figure 1). The sodium ion is six-coordinated by four bridging oxo-groups of **1** and two terminal water molecules resulting in an octahedral coordination sphere and typical bond lengths ($d_{Na-O} = 2.29-2.46(2)$ Å). The presence of a sodium ion in the belt of **1** is not all that surprising, as crystal structures of several derivatives of **1** have also revealed the presence of sodium ions in analogous positions. In $[(C_6H_5Sn)_3Na_3(H_2O)_6(\alpha\text{-}SbW_9O_{33})_2]^{6-}$, three sodium ions are located in the central belt in addition to the three C_6H_5Sn groups.[8e] This is analogous to the di- and tri-transition-metal-substituted derivatives of this structural type, $[M_2(H_2O)_2WO(H_2O)Na_3(H_2O)_6(\alpha\text{-}AsW_9O_{33})_2]^{7-}$ (M = Co^{2+}, Zn^{2+}, Mn^{2+}) and

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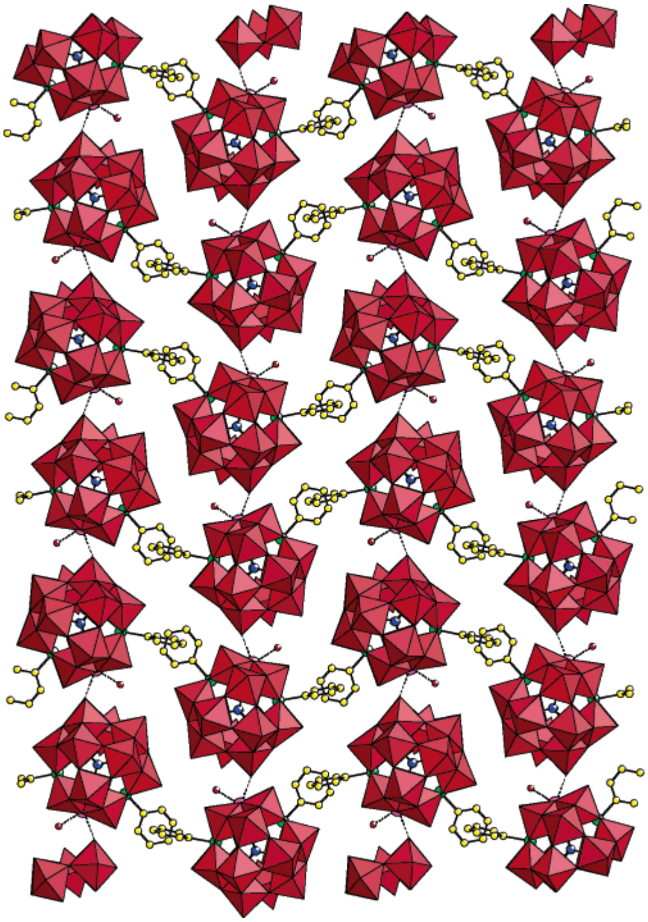

Figure 2. Packing diagram of $(NH_4)_7Na[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]\cdot 17.5H_2O$ (**NH₄−1**) in the *bc* plane. This representation indicates (a) that neighboring polyanions are weakly bound via W−O−Na bonds leading to chains in the *c* direction and (b) that the phenyl rings of adjacent polyanion chains interact in an orthogonal fashion. The color code is the same as in Figure 1. The ammonium ions and waters of hydration are omitted for clarity.

$[M_3(H_2O)_3Na_3(H_2O)_6(\alpha\text{-}XW_9O_{33})_2]^{9-}$ (X = As^{III}, M = Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}; X = Sb^{III}, M = Cu^{2+}, Zn^{2+}).[19]

The −8 charge of the title polyanion is balanced by the unique sodium ion in the belt of **1** and seven ammonium ions which surround the polyanion. The exact positions of the ammonium ions could not be identified by X-ray diffraction as they could not be distinguished from water molecules. However, the result of elemental analysis is in complete agreement with the formula of **NH_4−1**.

The solid-state arrangement of **1** deserves special attention (see Figure 2). The title polyanions exhibit 2-D packing in the *bc* plane, and additional intermolecular connectivities in the *c* direction via W−O−Na bonds lead to the formation of chains. Interestingly, the phenyl rings of adjacent polyanions interact in an orthogonal fashion. Nevertheless, the respective Na−O−W bond lengths (Na1−O12T = 2.401(14) Å; W12−O12T = 1.698(13) Å) indicate that this intermolecular interaction is rather weak and mostly a result of crystal packing. It can be expected that redissolution of **NH_4−1** leads to a complete breakdown of the entire lattice, resulting in the presence of individual polyanions **1** in solution. In order to verify this assumption, we decided to perform multinuclear NMR spectroscopy.

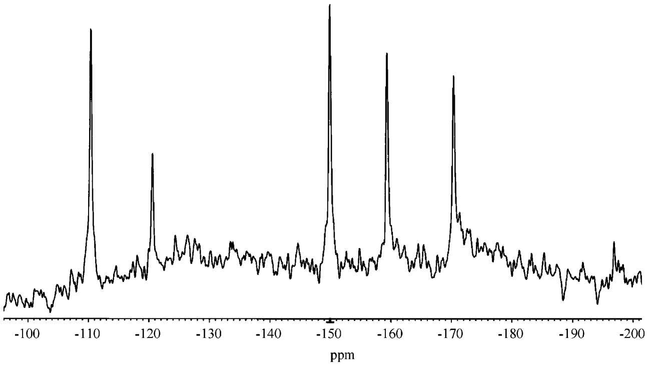

Figure 3. ^{183}W NMR spectrum of $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) at 293 K. The sample preparation was as follows: synthesis of **1** as described in the Experimental Section but with a four times higher concentration. Solid $LiClO_4$ was added during the reaction in order to prevent precipitation of **1**.

NMR Studies. 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. The ^{1}H and ^{13}C NMR spectra of **1** are consistent with two equivalent phenyl groups. Especially, ^{183}W NMR is a very sensitive technique which allows us to verify if the solid-state structure of a polyoxotungstate is preserved in solution. However, the low natural abundance of the ^{183}W nucleus requires preparation of very concentrated solutions. In order to accomplish this, we synthesized **1** as described in the Experimental Section but with a concentration that is four times higher. During the reaction, solid $LiClO_4$ was added in order to prevent precipitation of **1**. The solid $KClO_4$ was filtered off before running the NMR measurements, which means that essentially all potassium ions were removed from the solution.

For **1**, a six line pattern with relative intensities 4:4:4:4:2:1 is expected, and indeed, this is what we observed, confirming the C_{2v} symmetry of **1** (see Figure 3). This conclusion is based on the assumption that the two phenyl groups can rotate freely in solution, which is most likely the case. The smallest peak in the ^{183}W NMR spectrum (δ −196.9 ppm) is somewhat hard to identify, but we performed several experiments to confirm our assignment. The ^{119}Sn NMR spectrum of **1** is expected to show a single peak, if the two Sn atoms are equivalent. Indeed a single resonance at −432.5 ppm is observed, but in addition, we see a pair of fairly intense satellites which most likely result from coupling of a ^{119}Sn nucleus to an adjacent ^{183}W nucleus (see Figure 4). Pope et al. observed a singlet in ^{119}Sn NMR for $[(C_6H_5Sn)_3Na_3(H_2O)_6(\alpha\text{-}SbW_9O_{33})_2]^{6-}$ of almost identical chemical shift (−417.8 ppm) to **1** and a pair of satellites with similar intensity.[8e] In his polyanion, the tin atoms are in a square-pyramidal coordination geometry, in complete analogy to **1**.

Although single-crystal X-ray diffraction of **NH_4−1** clearly indicated the presence of a sodium ion in the central belt of the title polyanion, it must be remembered that we synthesized **1** in the absence of sodium ions (see Experimental

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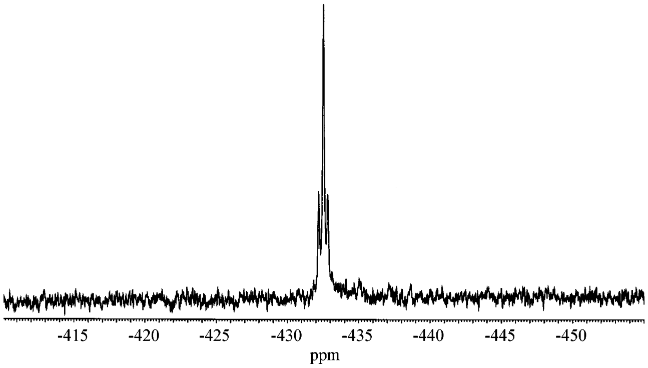

Figure 4. ^{119}Sn NMR spectrum of $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) at 293 K using the same solution as for the measurement shown in Figure 3.

Section). Furthermore, we eliminated the potassium ions by precipitation as $KClO_4$ as described above. Sodium ions were only added after the synthesis of **1** in order to obtain better quality crystals. On the basis of our observation that in the solid-state structure a sodium ion is located in the central belt of **1**, we decided to investigate by ^{119}Sn NMR if sodium ions also play an important role in solution. We discovered that in the absence of sodium ions only one signal is observed at −432.5 ppm together with a pair of satellites (see above). Addition of solid NaCl to this solution or alternatively the presence of sodium ions already during the synthesis of **1** resulted in both cases in the appearance of a second ^{119}Sn NMR signal at −434.9 ppm with the expected pair of satellites ($^2J_{\mathrm{Sn-W}} = 100$ Hz). This peak increased with the concentration of sodium ions in solution, but never reached the same intensity as the −432.5 ppm peak.

Our conclusion is that the peak at −434.9 ppm almost certainly represents **1** with a sodium ion in the vacancy. We could not identify any two-bond ^{119}Sn−^{23}Na coupling in this peak pattern, most likely for the following reasons: (a) the ^{23}Na nucleus is quadrupolar ($I = {}^3/_2$), and the satellite signal would be a quartet; (b) the Na−O bond lengths are rather long (2.44−2.46(2) Å) so that any coupling would be expected to be rather weak. On the other hand, we believe that the peak at −432.5 ppm indicates a vacancy in the title polyanion **1** between the two tin atoms. The fact that the ^{119}Sn NMR signal for the sodium-substituted species at −434.9 ppm is always smaller than the signal at −432.5 ppm (even for high Na^+ concentrations) indicates that the latter represents almost certainly a species with a “vacant” belt. The two freely rotating phenyl groups probably exhibit a steric effect which makes incorporation of an alkali cation in the belt of **1** more difficult. We also performed ^{23}Na NMR on solutions of **1** with added sodium chloride. For such solutions, a single peak is observed at around −1.5 ppm, which is very similar to the chemical shift of our 1 M NaCl reference solution. No satellite peaks could be observed, but we noticed that the peak of the polyanion solution is significantly broader than that of the NaCl reference solution.

The observed Sn−O−W coupling constant for **1** ($^2J_{\mathrm{Sn-W}} = 96$ Hz) is even larger than the largest values reported by Pope et al. for $[(C_6H_5Sn)_3P_2W_{15}O_{59}]^{9-}$ ($^2J_{\mathrm{Sn-W}} = 78$ Hz), $[(C_4H_9Sn)_3P_2W_{15}O_{59}]^{9-}$ ($^2J_{\mathrm{Sn-W}} = 49$ Hz), $[(C_6H_5SnOH)_3(\alpha\text{-}SiW_9O_{34})_2]^{14-}$ ($^2J_{\mathrm{Sn-W}} = 35$ Hz), and $[(C_6H_5SnOH)_3(PW_9O_{34})_2]^{12-}$ ($^2J_{\mathrm{Sn-W}} = 33$ Hz).[8] Pope et al. have identified that an increase in the Sn−O−W bond angle is accompanied by an increasing Sn−O−W coupling constant for $[(C_6H_5Sn)_3P_2W_{15}O_{59}]^{9-}$ ($^2J_{\mathrm{Sn-W}} = 78$ Hz, Sn−O−W = 147−158°) and $[(C_6H_5SnOH)_3(PW_9O_{34})_2]^{12-}$ ($^2J_{\mathrm{Sn-W}} = 33$ Hz, Sn−O−W = 139−142°).[8b] However, this bond angle argument alone does not explain the very large coupling constant observed for **1**, as the Sn−O−W bond angle ranges from 135° to 140°. Most likely, the coordination geometries of the tin atoms play also an important role. In all of Pope’s polyanions above (with the exception of $[(C_6H_5Sn)_3Na_3(H_2O)_6(\alpha\text{-}SbW_9O_{33})_2]^{6-}$), the Sn atoms are six-coordinated (octahedral), whereas they are five-coordinated (square-pyramidal) in **1**. Perhaps the overall charge of the polyanion also affects the Sn−O−W coupling constant. It can be noticed that **1** has the smallest charge (−8) and the largest Sn−O−W coupling constant ($^2J_{\mathrm{Sn-W}} = 96$ Hz). For Pope’s polyanions above, the species with large negative charges have smaller coupling constants than those with smaller charges (e.g., $[(C_6H_5Sn)_3P_2W_{15}O_{59}]^{9-}$, $^2J_{\mathrm{Sn-W}} = 78$ Hz vs $[(C_6H_5SnOH)_3(\alpha\text{-}SiW_9O_{34})_2]^{14-}$, $^2J_{\mathrm{Sn-W}} = 35$ Hz). Nevertheless, NMR data of more polyanions containing square pyramidal organotin groups are needed in order to be able to draw definitive conclusions. The ^{183}W, ^{119}Sn, ^{13}C, and ^{1}H NMR spectra of **1** remain the same even if the same solution is measured again after several weeks, indicating that **1** does not undergo structural transformations in aqueous acidic medium.

Conclusions

We have synthesized the bis-phenyltin-substituted, lone-pair-containing tungstoarsenate $[(C_6H_5Sn)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**). Polyanion **1** was characterized by several solution (multinuclear NMR) and solid state (IR, elemental analysis, single-crystal XRD) techniques. This polyanion adds a new member to the class of mono-phenyltin-substituted polyoyotungstates. Our work re-emphasizes (a) the facile synthesis of polyoxoanions by one-pot reactions, (b) the structural variety of polyoxoanion chemistry, (c) the stability of polyoxoanions in solution, (d) the complementary nature of XRD and multinuclear NMR, (e) easy incorporation of monoorganotin fragments in polyoxotungstate precursors, and (f) the strong attachment of organotin fragments to polyoxoanions. Nevertheless, the work of Pope and also our work shows that interaction of monoorganotin groups with lacunary polyoxoanions almost inevitably leads to monomeric or dimeric products. Currently, we investigate the reactivity of diorganotin groups with lacunary polyoxotungstates in order to synthesize discrete polyoxometalates with fundamentally novel architectures of large size.

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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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