

Organotin Derivatives of α -[X^{III}W₉O₃₃]⁹⁻ (X = As, Sb) Heteropolytungstates. Solution- and Solid-State Characterization of $[(C_6H_5Sn)_2O]_2H(\alpha-AsW_9O_{33})_2$ ⁹⁻ and $[(C_6H_5Sn)_3Na_3(\alpha-SbW_9O_{33})_2]$ ⁶⁻

Gerta Sazani, Michael H. Dickman, and Michael T. Pope*

Department of Chemistry, Georgetown University, Washington, D.C. 20057-1227

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The tris(phenyltin)-substituted tungstoantimonate(III) Cs₆[(PhSn)₃Na₃(α -SbW₉O₃₃)₂]·20H₂O (**1**) and the tetrakis(phenyltin)-substituted tungstoarsenate(III) Na₉[(PhSn)₂O]₂H(α -AsW₉O₃₃)₂]·20H₂O (**2**) have been prepared by reaction of phenyltin trichloride with Na₉[α -SbW₉O₃₃]·19.5H₂O and Na₉[α -AsW₉O₃₃]·19.5H₂O, respectively, in aqueous solution. The products were characterized by elemental analysis, X-ray crystallography, multinuclear NMR, and infrared spectroscopy. Crystals of **1** are monoclinic, space group *P*2₁/*n*, with *a* = 13.7952(1) Å, *b* = 22.3133(2) Å, *c* = 34.4493(2) Å, β = 90.933(1)°, and *Z* = 4. Anion **1** has nominal *D*_{3h} symmetry and contains three PhSn³⁺ groups and three sodium ions sandwiched between [α -SbW₉O₃₃]⁹⁻ units. Crystals of **2** are triclinic, space group *P*1, with *a* = 15.272(6) Å, *b* = 15.303(6) Å, *c* = 16.760(7) Å, α = 93.59(3)°, β = 106.187(19)°, γ = 112.23(3)°, and *Z* = 1. Anion **2** has nominal *C*_{2h} symmetry and contains four PhSn³⁺ groups sandwiched between two [α -AsW₉O₃₃]⁹⁻ units.

Introduction

The chemistry of polyoxometalates is of current interest due to the large range of applications of these complexes in many fields.¹ The covalent attachment of organic groups to polyoxometalates via linkages that are compatible with physiological conditions extends considerably their potential use as pharmaceuticals^{1d} and as phasing agents in the X-ray crystallography of proteins.²

Earlier work has demonstrated that the PhSn³⁺ group can be incorporated into Keggin and Dawson polytungstate structures.³ We report here the synthesis and structural characterization of two novel organotin complexes derived from the lacunary anions [α -SbW₉O₃₃]⁹⁻ and [α -AsW₉O₃₃]⁹⁻. Several inorganic complexes of [α -SbW₉O₃₃]⁹⁻ and [α -AsW₉O₃₃]⁹⁻ with metal ions have been reported previously.^{4–13}

Experimental Section

Synthesis. Na₉[α -SbW₉O₃₃]·19.5H₂O and Na₉[α -AsW₉O₃₃]·19.5H₂O were prepared by published methods^{4a,13} and were confirmed by infrared spectroscopy. Phenyltin trichloride (Aldrich, 98%) was used without any further purification.

Cs₆[(PhSn)₃Na₃(α -SbW₉O₃₃)₂]·20H₂O (1**).** PhSnCl₃ (0.60 g, 2.00 mmol) was dissolved in 10 mL of H₂O at room temperature. To this solution (pH ~ 1) was added 2.86 g (1.00 mmol) of powdered Na₉[α -SbW₉O₃₃]·19.5H₂O. The pH increased to 2.3 during the dissolution of the tungstate and the solution became yellow within 10–15 s. After 13–15 min the solution became turbid and remained so even after stirring overnight at room temperature. The undissolved white residue was filtered off. CsCl(s) (6 g) was added to the filtrate. The white precipitate obtained this way was recrystallized from a minimum amount of boiling water. Yield: 1.5 g (52%). Anal. Calcd (found) for Cs₆[(PhSn)₃Na₃(α -SbW₉O₃₃)₂]·20H₂O: Cs, 12.31 (12.75); Na, 1.07 (1.19); C, 3.34 (2.77); W, 51.10 (51.16). IR (metal oxygen stretching region, KBr disk, cm⁻¹): 958 (s), 904 (m), 875 (m), 844 (m), 735 (vs), 698 (s). ¹³C NMR (ppm): 132.1, 134.5, 134.9, 140.2. ¹H NMR (ppm): 7.4 (m), 8.1 (m).

Na₆[(PhSn)₃Na₃(α -SbW₉O₃₃)₂]·20H₂O (1a**).** This compound was prepared the same way as **1** by precipitating the product by means of 6 g of NaCl(s). The product was recrystallized from a minimum amount of boiling water. Due to the high solubility of the sodium salt, the yield is quite low (~25%). The IR spectra of **1** and **1a** are virtually identical.

Na₉[(PhSn)₂O]₂H(α -AsW₉O₃₃)₂]·20H₂O (2**).** PhSnCl₃ (1.13 g, 3.75 mmol) was dissolved in 10 mL of H₂O at room temperature. To this solution (pH ~ 0.8) was added 7.04 g (2.50 mmol) of powdered Na₉[α -AsW₉O₃₃]·19.5H₂O. The solution turned yellow immediately, and the pH increased to 1.7 when the dissolution of the tungstate was complete. The reaction mixture was stirred for 10 min at room

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temperature, and then 5.0 g of NaCl(s) was added to the clear yellow solution. A yellow precipitate formed, which was filtered off and recrystallized from a minimum amount of boiling water. Yield: 4.2 g (56%). Anal. Calcd (found) for $\text{Na}_9\{[(\text{PhSn})_2\text{O}]_2\text{H}(\alpha\text{-AsW}_9\text{O}_{33})_2\} \cdot 20\text{H}_2\text{O}$: Na, 3.51 (3.60); C, 4.89 (4.83); Sn, 8.05 (7.14); As, 2.54 (2.44); W, 56.11 (56.91). IR (metal oxygen stretching region, KBr disk, cm^{-1}): 962 (s), 908 (s), 883 (s), 761 (vs), 719 (vs). ^{13}C NMR (ppm): 131.9, 132.6, 138.5, 148.8. ^1H NMR (ppm): 7.5 (t), 7.6 (t), 8.3 (d).

Physical Measurements. All NMR data were recorded on a Bruker AM-300WB spectrometer. A sample of **1** was prepared by dissolving 1.0 g of the cesium salt in 2 mL of D_2O at room temperature and stirring with 0.5 g of LiClO_4 in order to obtain the soluble lithium salt. The supernatant liquid obtained upon centrifugation was used for NMR measurements. Another sample was prepared by dissolving 1.0 g of the water-soluble sodium salt of **1** in 2 mL of D_2O . The NMR spectra of both samples were identical. The NMR spectra of **2** were recorded on a solution obtained by dissolution of 1.5 g of sodium salt of **2** in 2 mL of D_2O . Resonance frequencies were 300.113 MHz for ^1H and 75.469 MHz for ^{13}C in 5 mm tubes and 111.925 MHz for ^{119}Sn and 12.505 MHz for ^{183}W in 10 mm tubes. Pulse widths (90°) were 2.2 μs for ^{13}C , 15 μs for ^{119}Sn , and 15 μs for ^{183}W . Chemical shifts are reported with respect to external standards: $(\text{CH}_3)_4\text{Sn}$ in D_2O (coaxial tubes) for ^{119}Sn , 2 M Na_2WO_4 in D_2O for ^{183}W , and TMS in D_2O (coaxial tubes) for ^1H and ^{13}C . All chemical shifts downfield of the references are reported as positive.

Thermogravimetric analyses were performed on a TA-Instruments TGA 2050; sample size was 18 mg for **1** and 22 mg for **2**.

Elemental analyses were performed by E & R Microanalytical Laboratory Inc., Corona, NY. Infrared spectra were recorded on a Nicolet FT-7000 spectrometer on KBr pellets.

X-ray Crystallography. Crystals of $\text{Na}_6[(\text{PhSn})_3\text{Na}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]$ were obtained upon methanol vapor diffusion into a water solution of the recrystallized compound. Data for **1** were taken on a Siemens SMART CCD single-crystal diffractometer using a Mo anode and graphite monochromator. A sphere of data (96.1% coverage to $\theta = 28.57^\circ$) was collected using ω scans. Routine Lorentz and polarization corrections were applied. A semiempirical absorption correction was applied, based on multiple scans of equivalent reflections at different ϕ and ω values.¹⁴ Programs used were SMART, SAINT, and SHELXTL.^{15,16}

Crystals of $\text{Na}_9\{[(\text{PhSn})_2\text{O}]_2\text{H}(\alpha\text{-AsW}_9\text{O}_{33})_2\}$ were obtained upon slow evaporation of an aqueous solution of the compound. A crystal of **2** was mounted on a glass fiber and placed on a Siemens P4 four-circle diffractometer equipped with a rotating Mo anode and graphite monochromator. Procedures for finding initial reflections, calculation of unit cell parameters, data collection, and data reduction have been described.¹⁷ The SHELXTL package of software was used to solve and refine the structures.¹⁵ A semiempirical absorption correction based on ψ scans was used.

Other experimental parameters and crystal data for **1** and **2** are presented in Table 1. Direct methods solutions were successful in both cases. W, Sb, As, and Sn atoms were refined anisotropically, Na, C, and O isotropically. Phenyl carbons were constrained to refine as a rigid ring with $\text{C}-\text{C} = 1.39 \text{ \AA}$ and $\text{C}-\text{C}-\text{C} = 120^\circ$. Hydrogen atoms were not included in the models. Refinements were full-matrix least-squares on F^2 using all data. The weighting scheme used throughout was $w = 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (F_o^2 - 2F_c^2)/3$. For **1**, $A = 0.0246$ and $B = 740$. For **2**, $A = 0.2$ and $B = 140$.

Results and Discussion

Synthesis. Slightly different synthetic approaches from the ones described above were attempted. Changing the order of

Table 1. Crystallographic Data for **1** and **2**

	compound	
	1	2
formula	$\text{C}_{18}\text{H}_{83}\text{Na}_6\text{O}_{102.50}\text{Sb}_2\text{Sn}_3\text{W}_{18}$	$\text{C}_{24}\text{As}_2\text{Na}_4\text{O}_{93.88}\text{Sn}_4\text{W}_{18}$
fw	5986.65	5816.18
space group, Z	$P2_1/n$ (No. 14), 4	$P\bar{1}$ (No. 2), 1
wavelength, \AA	0.710 73	0.710 73
a (\AA)	13.7952(1)	15.272(6)
b (\AA)	22.3133(2)	15.303(6)
c (\AA)	34.4393(2)	16.760(7)
α (deg)	90	93.59(3)
β (deg)	90.933(1)	106.19(2)
γ (deg)	90	112.23(3)
unit cell vol (\AA^3)	10 599.58(14)	3419(2)
ρ_{calc} (g cm^{-3})	3.752	2.825
μ (cm^{-1})	207.80	163.63
T ($^\circ\text{C}$)	-100(2)	-100(2)
final R^a	$R_1 = 0.0716$, $wR_2 = 0.1573$	$R_1 = 0.1062$, $wR_2 = 0.3187$

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ with } I > 2\sigma(I) \text{ and } wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

mixing the reagents (i.e adding the phenyltin trichloride to the solution of the heteropolyanion) resulted in both cases in mixtures of products; the title compounds, however, could be identified in the mixture. Carrying out the reactions at a higher temperature ($\sim 60^\circ\text{C}$) did not alter the products in either case. The pH of the solution, however, was found to be important. The synthetic procedure for **2** exhibits a higher tolerance toward pH changes in comparison to the one for **1**. If the pH of the solution in the synthesis of **1** is adjusted to 2 by means of 5% sodium borate solution prior to the addition of $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}]$, the final pH of the reaction after the dissolution of $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}]$ is ~ 7 . The result of this reaction is a mixture of products. ^{119}Sn NMR confirms the absence of **1**, and seven new peaks in the range -531 to -570 ppm were observed instead.

Changing the ratios of the starting materials (1:2 or 2:3) did not alter the products in either case.

That **2** is readily formed was made evident by an alternative synthesis. When $\text{Na}_{27}[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]$ was used as a starting material instead of $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}]$, in molar ratio 1:2 with respect to PhSnCl_3 , the crystals obtained upon addition of 1 M KCl to the reaction solution were identified by IR and X-ray analysis to be the same as **2**.

Structures. Selected bond lengths for **1** and **2** are compared in Table 2. Anion **1** (Figure 1) consists of two $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ anions linked by three PhSn^{3+} groups and three sodium cations into an assembly of virtual D_{3h} symmetry. The two $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ units are related by a noncrystallographic mirror plane; i.e., they are "eclipsed". Each Sn atom is coordinated to four oxygen atoms and a phenyl group in a square-pyramidal geometry. The Sn atoms are on average 0.720(15) \AA above the plane of the four equatorial oxygen atoms.

The structure of **2** (Figure 2) consists of two $[\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ anions linked by four PhSn^{3+} groups into an assembly of virtual C_{2h} symmetry. In contrast to **1**, the tin atoms in **2** are six-coordinate (Figure 3), with the Sn atom displaced 0.284-(13) \AA out of the equatorial plane toward the phenyl carbon atom. The Sn atoms are in pairs, each pair being bridged by one oxygen atom. The bridging oxygen atoms, O1S1 and its centrosymmetrically related counterpart, are only 2.33(5) \AA apart. This unusually short distance is significantly shorter than the sum of the oxygen van der Waals radii (2.8 \AA) and is among the shortest $\text{O}\cdots\text{O}$ contact distances observed, implying the presence of a strong hydrogen bond.¹⁸ A similar short $\text{O}\cdots\text{O}$

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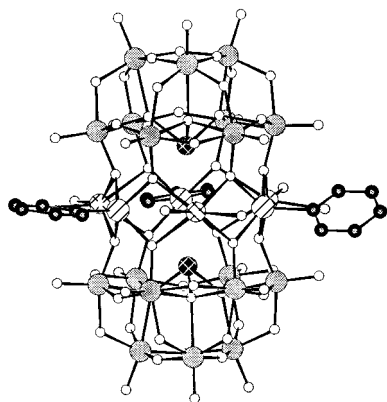
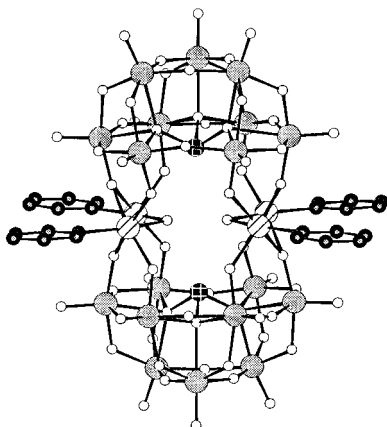
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Table 2. Selected Bond Lengths (Å) for [(PhSn)₃Na₃(α -SbW₉O₃₃)₂]⁶⁻ (Anion of **1**) and [{(PhSn)₂O}₂H(α -AsW₉O₃₃)₂]⁹⁻ (Anion of **2**)

anion of 1	bond length	av	anion of 2	bond length	av
W—O(W)	1.870(13)–1.979(13)	1.924(13)	W—O(W)	1.78(4)–2.00(3)	1.89(4)
W—O(Sn)	1.837(14)–1.871(13)	1.854(14)	W—O(Sn)	1.81(2)–1.93(2)	1.85(2)
W—O(Sb)	2.247(13)–2.352(12)	2.299(13)	W—O(As)	2.28(2)–2.42(2)	2.32(2)
W=O	1.690(13)–1.719(14)	1.703(14)	W=O	1.65(3)–1.75(3)	1.71(3)
Sn—O(W)	1.994(13)–2.064(12)	2.029(13)	Sn—O(W)	2.03(2)–2.20(2)	2.08(2)
Sn—C	2.097(5)–2.110(6)	2.102(6)	Sn—C	2.123(16)–2.120(16)	2.122(16)
Sb—O	1.961(12)–1.982(13)	1.973(13)	As—O	1.80(2)–1.85(2)	1.83(2)
Na—O(Sn)	2.432(14)–2.589(16)	2.478(16)	Sn—O(Sn)	2.04(2)–2.05(2)	2.05(2)

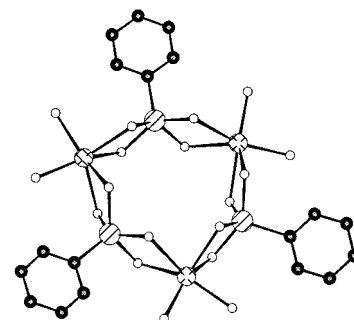
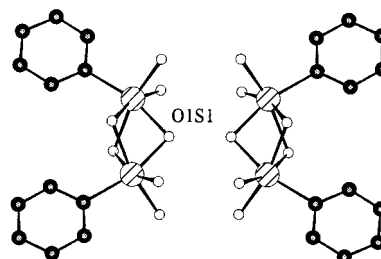
**Figure 1.** Ball-and-stick structural representation of [(PhSn)₃Na₃(α -SbW₉O₃₃)₂]⁶⁻. Oxygen atoms are represented by open circles, tungsten is solid gray, tin is diagonally hatched, sodium is white with black crosshatching, and antimony is black with diagonal white crosshatching.**Figure 2.** Ball-and-stick structural representation of [{(PhSn)₂O}₂H(α -AsW₉O₃₃)₂]⁹⁻. The representations of atoms are identical to Figure 1 except for arsenic which is black with vertical and horizontal white crosshatching.

contact (2.43 Å) has been observed previously in a polytungstate structure containing organophosphonyl groups.¹⁹ Protonation of O1S1 is also indicated by a bond valence (BV) sum calculation²⁰ which totals 1.33(6) valence units, compared with an average of 1.95(6) for the other oxygen atoms bound to Sn. The BV value of 1.33(6) is close to that expected for one proton (1.5), and this is consistent with the total anion charge on the basis of the sodium analysis. Hydrogen atoms could not be located due to the presence of W atoms; a neutron diffraction study would be necessary to resolve the question of hydrogen atom position.

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**a****b****Figure 3.** Coordination geometry of tin atoms in (a) [(PhSn)₃Na₃(α -SbW₉O₃₃)₂]⁶⁻ and (b) [{(PhSn)₂O}₂H(α -AsW₉O₃₃)₂]⁹⁻.

The overall structures of **1** and **2**, though obtained under essentially the same experimental conditions, are different. This may be a result of the differences in the sizes of As³⁺ and Sb³⁺ atoms, the lone electron pair on Sb³⁺ being more dispersed in space. The distance between the two Sb³⁺ atoms in **1** is shorter than the distance between the As³⁺ atoms in **2**: 4.782(2) compared with 5.691(8) Å. This arises in part from the longer Sb—O distances compared to the As—O distances. In addition, the distance between the planes of the “belt” tungsten atoms is different in the respective anions. (The belt tungstens are the six W atoms in each half of the anion which are closest to the center of the anion.) For **1** the belt planes are 6.14(3) Å apart while in **2** this distance is 6.47(3) Å.

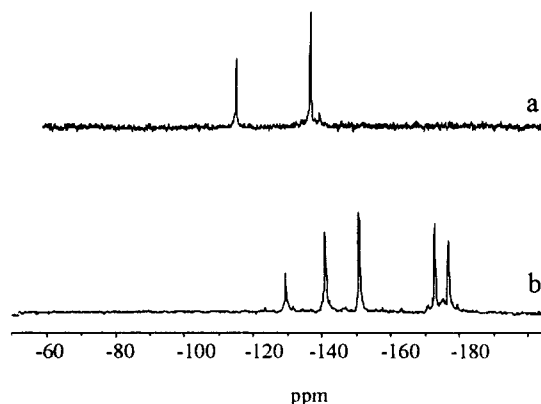
Structures of both **1** and **2** are different from the derivatives of A-XW₉O₃₄ (X = P^V, Si^{IV}), which contain three PhSn³⁺ groups sandwiched between the XW₉O₃₄ units.^{3a,b}

The incorporation of Na⁺ into the structure of **1** is reminiscent of a recent structure determination of Na₃[α -SbW₉O₃₃].^{4a} In the crystal network of this anion, two [α -SbW₉O₃₃]⁹⁻ units, related to each other by a center of inversion, are positioned with their lacunary sites facing each other. The structure is stabilized by a belt of six Na⁺ ions which connect both anions. In **1** the [SbW₉O₃₃]⁹⁻ units are eclipsed, and three out of six belt sodium ions are replaced by three PhSn³⁺ groups in alternate positions.

In contrast to **1** which is composed of two α -type [SbW₉O₃₃]⁹⁻, all the transition-metal-substituted tungstoantimonates [Sb₂W₂₀M₂O₇₀(H₂O)₆]⁽¹⁴⁻²ⁿ⁾⁻ (Mⁿ⁺ = Fe³⁺, Co²⁺, Zn²⁺) are composed of two β -type [SbW₉O₃₃]⁹⁻ structural building units.⁴

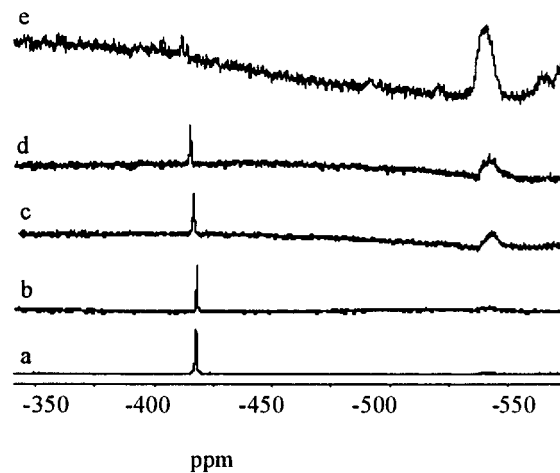
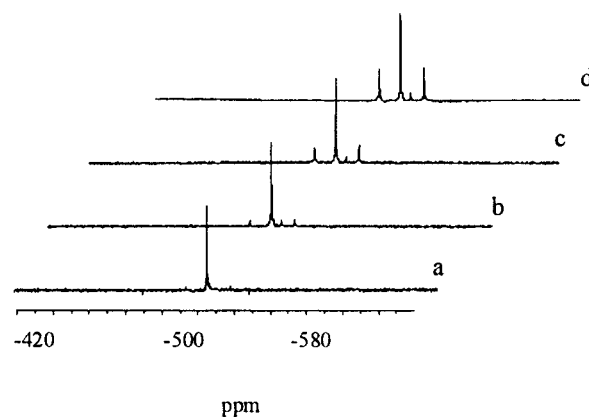
Table 3. Comparison of NMR Data for $\{(RSn)_n(XW_9)_2\}$ Sandwich-Type Anions

anion	$^{119}\text{Sn/ppm}$	$^{183}\text{W/ppm}$ (intensity)	ref
$[(\text{PhSn})_3\text{Na}_3(\text{B},\alpha\text{-SbW}_9\text{O}_{33})_2]^{6-}$	-417.8	-114.9(1), -136.7(2)	this work
$\{[(\text{PhSn})_2\text{O}]_2\text{H}(\text{B},\alpha\text{-AsW}_9\text{O}_{33})_2\}^{9-}$	-532.4	-129.0(1), -140.6(2), -150.6(2), -172.6(2), -176.4(2)	this work
$[(\text{PhSnOH})_3(\text{A},\alpha\text{-SiW}_9\text{O}_{34})_2]^{14-}$	-622.0	-150(1), -189(2)	3a
$[(\text{BuSnOH})_3(\text{A},\alpha\text{-SiW}_9\text{O}_{34})_2]^{14-}$	-576	-151(1), -190(2)	3a
$[(\text{PhSnOH})_3(\text{A},\alpha\text{-SiW}_9\text{O}_{34})_2]^{14-}$	-621	-126(1), -208(2)	3a
$[(\text{BuSnOH})_3(\text{A},\alpha\text{-SiW}_9\text{O}_{34})_2]^{14-}$	-575	-128(1), -211(2)	3a
$[(\text{PhSnOH})_3(\text{A},\alpha\text{-PW}_9\text{O}_{34})_2]^{12-}$	not reported	-138.6(1), -190.0(2)	3f

**Figure 4.** ^{183}W NMR spectra of (a) $\text{Li}_6[(\text{PhSn})_3\text{Na}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]$ and (b) $\text{Na}_9\{[(\text{PhSn})_2\text{O}]_2\text{H}(\alpha\text{-AsW}_9\text{O}_{33})_2\}$.

NMR Spectroscopy. Solutions of anion **1** exhibit a two-line ^{183}W NMR spectrum with relative intensity 1:2 corresponding to the cap- and belt-tungsten atoms, respectively, which is consistent with the solid state (D_{3h}) structure (Figure 4a). The pattern of the spectrum is consistent with the observation of Xin et al.^{3a} that for sandwich-type anions the line corresponding to the cap-tungsten atoms is situated downfield with respect to the one corresponding to the belt-tungsten atoms (see Table 3). The anion of **2** exhibits a five-line ^{183}W NMR spectrum (Figure 4b) which is consistent with solid state (C_{2h}) structure. The ^1H and ^{13}C NMR of both **1** and **2** show the characteristic pattern of a monosubstituted phenyl group. The tungsten and tin chemical shifts of both **1** and **2** are compared with those of other tungstostannates in Table 3. The 114-ppm chemical shift change of **2** compared to **1** in the ^{119}Sn NMR spectra can be explained in terms of the increase in the coordination number of tin. An increase in the coordination number of tin usually produces a large upfield chemical shift.^{21–23}

Solution Stability. $[(\text{PhSn})_3\text{Na}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]^{6-}$ is stable in aqueous solution only in a narrow pH interval around 1.7. Tin-NMR spectra of the unbuffered aqueous solution of the lithium salt of **1** (pH 1.7) were recorded several times during a 30 day period, and no sign of decomposition was observed. The stability of **1** with respect to pH was monitored by ^{119}Sn NMR; the pH of the solution was increased by means of $\text{Li}_2\text{CO}_3(\text{s})$. At pH 2.0 a broad peak at -540 ppm appeared and it increased in intensity as the pH increased. At pH 4.7 the intensity of the peak corresponding to **1** had diminished to noise level and the

**Figure 5.** ^{119}Sn NMR spectra of aqueous solutions of $\text{Li}_6[(\text{PhSn})_3\text{Na}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]$ at different pH values: (a) pH 1.7; (b) pH 2.0; (c) pH 2.7; (d) pH 3.0; (e) pH 4.7.**Figure 6.** Time dependence of ^{119}Sn NMR spectrum of $\text{Na}_9\{[(\text{PhSn})_2\text{O}]_2\text{H}(\alpha\text{-AsW}_9\text{O}_{33})_2\}$ in unbuffered aqueous solution: (a) 5 min; (b) 13 min; (c) 20 min; (d) 30 min. Spectrum d is unchanged after 1 year.

-540 ppm signal had become the major feature (Figure 5). These changes are irreversible as shown by ^{119}Sn NMR.

The anion of **2** displays a different reactivity pattern in aqueous solution. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of a fresh solution exhibits a single line at -532.4 ppm if recorded within 5–7 min. Later, two extra peaks with equal intensities appear at -520.5 and -545.7 ppm and increase until they reach an intensity of ~50% of the main peak each (Figure 6); this change is paralleled by the appearance of additional lines in the ^{183}W NMR spectrum. At this point the solution does not undergo any further change: the spectrum of a 1-year-old solution displays the same three-line pattern (1:2:1). The process is not reversible: cooling the solution to 0 °C does not restore the initial one-line pattern; neither does it cause any change in the relative intensities.²⁴ Addition of PhSnCl_3 and/or $\text{Na}_9[\alpha\text{-}$

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AsW₉O₃₃] to the NMR tube does not change the spectrum, which excludes the possibility of any equilibrium involving “dimers”.^{3a}

Conclusions

The synthesis and the single-crystal X-ray structural characterization of two novel tris(phenyltin)antimony(III) and tetrakis(phenyltin)arsenic(III) heteropolyanions are reported. Elemental analyses and multinuclear NMR spectroscopy of the complexes are fully consistent with the solid-state structures revealed by X-ray crystallography.

The overall structures of the complexes, although obtained under essentially the same experimental conditions, are different

and may reflect differences in the diffuseness of the lone-pair electron densities on As(III) and Sb(III). Both structures reported in this work are also different from sandwich complexes based on A-type polytungstates $\{(\text{RSn})_3(\alpha\text{-XW}_9\text{O}_{34})_2\}^{n-}$ (X = P⁵⁺, Si⁴⁺) which were shown to contain three RSn³⁺ groups sandwiched between the {XW₉} units.

The anion of **1** has been used to aid in the phasing of X-ray data for the large ribosomal subunit of *H. marismortui*; electron density maps were successfully calculated at resolutions between 20 and 9 Å.²⁵

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

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(24) The three-line Sn-NMR spectrum characterizing the mixture of complexes produced in solutions of **2** was not significantly affected by changes in pH. As the pH was decreased from 6.6 to 1.2, a new peak at -537.9 ppm appeared and grew in intensity at the expense of the -520.5-ppm peak which had disappeared at pH 1.2. These particular changes are reversible and suggest a protonation-deprotonation equilibrium involving *one* of the unidentified complexes present in solutions of **2**.

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