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Organoantimony-Containing Polyoxometalate: $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$

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The dimeric, sandwich-type tungstophosphate $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**1**) has idealized D_{3h} symmetry and represents the first organoantimony-containing polyoxometalate. Polyanion **1** was synthesized in an aqueous, acidic medium via three different routes and was fully characterized in the solid state by X-ray diffraction, IR, and thermogravimetric analysis and in solution by multinuclear NMR (^1H, ^{13}C, ^{31}P, and ^{183}W).

Polyoxometalates (POMs) are anionic, discrete molecular metal−oxygen clusters with a vast structural variety and interesting properties resulting in potential applications in various fields such as catalysis, medicine, and materials science.[1] Covalent attachment of organic or organometallic groups to POMs can be a strategy for improving selectivity to specific targets, e.g., in medicinal applications.[2] This approach has been very successful for the synthesis of mono- and diorganotin-containing, hydrolytically stable POMs.[3,4] To date, there are no reports on analogous organoantimony polyanions. In 1989, the group of Liu reported on the solid-state structure of $(Bu^n{}_4N)_2[Ph_2SbO(MoO_4)]_2$, in which two separated MoO_4 tetrahedra bridge two octahedrally coordinated antimony atoms.[5] A few years later, Krebs and coworkers prepared the isostructural tungsten analogue.[6] Recently, Winpenny's group synthesized a reverse Keggin ion comprising 12 PhSb units in the addenda positions and a central MO_4 (M = Mn, Zn) tetrahedron.[7]

Now we report on the synthesis and structural characterization of the phenylantimony-containing tungstophosphate $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**1**; see Figure 1). The title polyanion has a dimeric, sandwich-type structure with two $\{PW_9\}$ Keggin units capping three octahedral {PhSbOH} fragments resulting in an assembly with idealized D_{3h} symmetry. The hydroxo groups all point inside the structure

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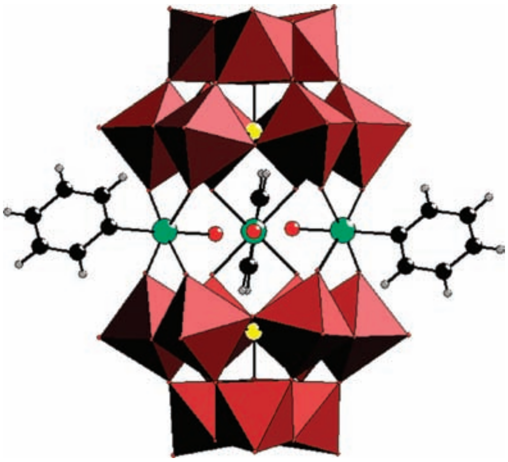

Figure 1. Combined polyhedral/ball-and-stick representation of **1**. Color code: WO_6 octahedra, dark red; antimony, olive green; oxygen, red; phosphorus, yellow; carbon, black; hydrogen, gray.

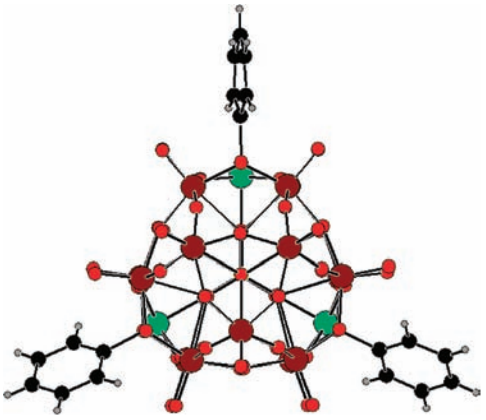

Figure 2. View of polyanion **1** along the idealized 3-fold rotation axis. Tungsten atoms are represented as dark-red balls; otherwise, the color code is the same as that in Figure 1.

and the phenyl groups away from it (see Figure 2). We isolated the title polyanion as a hydrated cesium salt, $Cs_9[\{PhSb(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 24H_2O$ (**Cs-1**). **Cs-1** was synthesized by the hydrothermal reaction of Ph_2SbCl_3[8] and $Na_9[(A\text{-}PW_9O_{34}]\cdot 7H_2O$[9] in a 3:2 ratio at 140 °C in a lithium acetate buffer at pH 4 for a total of 5 h.[10] This result indicates that one phenyl group has been lost during the reaction.

Single-crystal X-ray diffraction (XRD) indicated that **Cs-1** crystallizes in the monoclinic space group *C*2/*c*.[11] Each antimony atom exhibits a very regular octahedral coordination with C−Sb−O angles within 7 degrees of 90 or 180. The axial Sb−OH (trans to phenyl) distances range from 1.926(15) to 1.935(18) Å, whereas the four equatorial Sb−O bonds are in the range of 1.986(12)−2.036(13) Å. Bond valence sum calculations[12] confirmed that the axial oxygen atom attached to the antimony is indeed monoprotonated.

Polyanion **1** is structurally related to Pope's organotin polyanion $[(PhSnOH)_3(A\text{-}\beta\text{-}PW_9O_{34})_2]^{12-}$,[4f] but there is a charge difference of three units (9− vs 12−, due to Sb^{5+} vs Sn^{4+}) and Pope's ion contains $\{A\text{-}\beta\text{-}PW_9\}$ Keggin units rather than $\{A\text{-}\alpha\text{-}PW_9\}$ in **1**. Considering that we used hydrothermal conditions for the synthesis of **1**, it is not surprising that any $[A\text{-}\beta\text{-}PW_9O_{34}]^{9-}$ present was transformed to $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ in the course of the reaction.[4e,f]

Fourier transform infrared (FT-IR) spectra of **Cs-1** showed a weak band at 461 cm^{-1}, which we assign to the $PhSb^{4+}$ moiety.[13] The two peaks at 1479 and 1431 cm^{-1} are assigned to C−C stretching vibrations of the aromatic rings, while those found at 894 and 763 cm^{-1} correspond to aromatic C−H out-of-plane vibrations.[14] The bands at 1088 and 1018 cm^{-1} correspond to P−O antisymmetric stretching modes, whereas the peaks below 1000 cm^{-1} are assigned to terminal W═O as well as bridging W−O−W stretching modes.[15]

Thermogravimetric analysis (TGA) of **Cs-1** under a nitrogen atmosphere reveals a dehydration process up to around 240 °C resulting in a loss of the 24 waters of crystallization (see the Supporting Information). Between 240 and 700 °C, a gradual decomposition of the title compound is observed.

We also performed multinuclear NMR studies on solutions of **1** after having replaced the Cs^+ counterions by Li^+ via ion exchange.[16] ^{183}W NMR revealed the expected two singlets of relative intensity 1:2 at −115.5 and −202.9 ppm, respectively (see Figure 3), confirming the nominal D_{3h} symmetry of **1**. The ^{31}P NMR spectrum of **1** showed a singlet at −14.7 ppm, and the ^{13}C and ^{1}H NMR spectra are as expected for phenyl groups (see the Supporting Information).

It is of interest to compare the ^{183}W NMR parameters of **1** with structurally related phenyltin derivatives such as

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(10) Synthesis of $Cs_9[\{PhSb(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]\cdot 24H_2O$ (**Cs-1**): **Method 1:** $Na_9[A\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.75 g, 0.29 mmol) was dissolved in 25 mL of a 0.5 M lithium acetate buffer solution at pH 4, whereas 0.17 g (0.44 mmol) of Ph_2SbCl_3 was dissolved in a separate beaker in a minimum amount of ethanol. Then both solutions were mixed in a beaker, transferred into a hydrothermal bomb, and placed in an oven at 140 °C for 5 h. When the solution had cooled down to room temperature, it was filtered and layered with a few drops of 1 M CsCl. Slow evaporation at room temperature led to colorless, rodlike crystals suitable for XRD measurements after approximately 3 days (yield: 0.19 g, 19% based on $\{PW_9\}$). FT-IR (KBr pellets, cm^{-1}): 1621 (s), 1479 (m), 1431 (m), 1384 (m), 1088 (s), 1024 (m), 954 (s), 930 (w), 901 (w), 763 (vs), 691 (w), 664 (w), 614 (w), 524 (m). **Method 2:** $K_7[PW_{11}O_{39}]\cdot 14H_2O$ (0.64 g, 0.20 mmol) and 0.09 g (0.20 mmol) of Ph_2SbCl_3 were used, but otherwise the synthesis procedure was identical with method 1. **Method 3:** $K_{10}[P_2W_{20}O_{70}(H_2O)_2]\cdot 24H_2O$ (1.00 g, 0.18 mmol) and 0.08 g (0.21 mmol) of Ph_2SbCl_3 were used, but otherwise the synthesis procedure was identical with method 1. All three methods described above resulted in exactly the same product, **Cs-1**, based on FT-IR and single-crystal XRD, and the yields were also about the same in all cases.

(11) Crystallographic data of **Cs-1**: $C_{18}H_{58}Cs_9O_{91}P_2Sb_3W_{18}$, $M = 6663.10$, monoclinic, space group *C*2/*c* with $a = 33.899(2)$ Å, $b = 13.6814(9)$ Å, $c = 21.6122(13)$ Å, $\beta = 103.999(3)°$, $V = 9725.8(11)$ Å^3, $Z = 4$, $T = 173$ K, $D_{calc} = 4.551$ Mg/m^3, $\mu = 25.479$ mm^{-1}, 181 375 total reflections, 11 991 unique [R(int) = 0.17], final R1 = 0.059 for 8338 observations with $F_0 > 4\sigma(F_0)$, and wR2 = 0.174 for all data.

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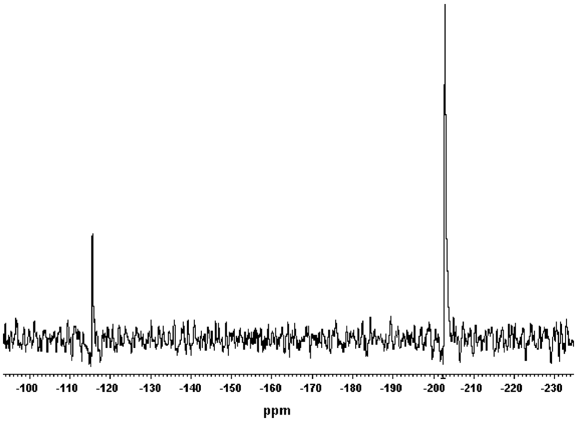

Figure 3. ^{183}W NMR spectrum of **1** recorded at room temperature in H_2O/D_2O. The lithium salt of **1** was prepared by ion exchange in order to increase the concentration of **1**. See the text for more details.

Table 1. Comparison of ^{183}W NMR Chemical Shifts for **1** and Structurally Related Phenyltin Derivatives

polyanion	δ_{cap}	δ_{belt}	$\delta_{cap} - \delta_{belt}$	ref
1	−115.5	−202.9	87.4	this work
$[(PhSnOH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$	−138.6	−190.0	51.4	4e
$[(PhSnOH)_3(A\text{-}\beta\text{-}PW_9O_{34})_2]^{12-}$	−123.4	−202.2	78.8	4f
$[(PhSnOH)_3(A\text{-}\alpha\text{-}SiW_9O_{34})_2]^{14-}$	−150.0	−189.0	39.0	4g
$[(PhSnOH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{14-}$	−126.0	−208.0	82.0	4g

Knoth's $[(PhSnOH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$ and Pope's $[(PhSnOH)_3(A\text{-}\beta\text{-}PW_9O_{34})_2]^{12-}$, $[(PhSnOH)_3(A\text{-}\alpha\text{-}SiW_9O_{34})_2]^{14-}$, and $[(PhSnOH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{14-}$ (see Table 1).[4e−g] In all cases, the signal for the belt tungstens is upfield with respect to the cap tungstens. Also, we can notice that the chemical shift for the belt tungstens (δ_{belt}) is always in a narrow range of around −190 to −210 ppm, whereas the chemical shift for the cap tungstens (δ_{cap}) ranges from −115 to −150 ppm. This can be explained by the presence of α-Keggin vs β-Keggin rotational isomers, which affects the cap tungstens more than the belt tungstens. We can also see that for the phenyltin species the chemical shift difference between δ_{cap} and δ_{belt} is consistently larger (~80 ppm) for structures containing the β-Keggin isomers than for those with the α-Keggin isomers (40−50 ppm). On the basis of these NMR parameters, our title polyanion **1** seems to follow the trend for the β-Keggin phenyltin isomers, but it clearly contains α-Keggin units (see Figure 1). We believe that this must be due to the presence of antimony rather than tin. The preparation and NMR study of other phenylantimony sandwich POMs could perhaps shed more light on this issue.

In summary, we have reported on the synthesis of the first organoantimony-containing POM. Polyanion **1** has been structurally characterized in the solid state and in solution by several techniques. The title polyanion can be prepared by the direct interaction of Ph_2SbCl_3 with three different lacunary tungstophospate precursors, $Na_9[(A\text{-}\alpha\text{-}PW_9O_{34}]$, $K_7[PW_{11}O_{39}]$, or $K_{10}[P_2W_{20}O_{70}(H_2O)_2]$, in an aqueous acidic medium. Hydrothermal conditions were required because of the poor solubility of Ph_2SbCl_3 in water and the need to cleave a phenyl group. Nevertheless, after polyanion **1** has been synthesized, it remains stable in the presence of air and moisture. In fact, NMR spectra of **1** in aqueous solution remain unchanged for weeks. Our results most likely open the door for a new subfamily of organoantimony polyanions. We have extended the well-known monoorganotin POM chemistry to main group V, and most likely other RSb analogues of **1** exist (e.g., R = methyl, ethyl, *n*-butyl, *tert*-butyl, R′COOH, R′COOR″, R′CONHR″). Furthermore, the entire arsenal of lacunary POM precursors can be reacted with Ph_2SbCl_3, and our preliminary results in this direction are promising. We will also explore whether diorganoantimony POMs can be prepared. Organoantimony POMs have a smaller charge compared to their organotin analogues because of the presence of Sb^{5+} vs Sn^{4+}, which could have important consequences for their reactivity, stability, toxicity, etc. For example, it is possible that organoantimony POMs could be more useful for antifouling applications than their organotin analogues.

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Supporting Information Available: FT-IR and NMR spectra, TGA curve, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) All NMR spectra were recorded on a JEOL ECP400H instrument at room temperature using freshly prepared solutions of **1** and H_2O/D_2O as the solvent. In order to increase the solubility of **Cs-1**, we performed ion exchange using a lithium-charged resin (Dowex 50W X8, AppliChem). The ^{183}W NMR measurements were performed in 10 mm tubes at 16.656 MHz, whereas ^{31}P (161.923 MHz), ^{13}C (100.525 MHz), and ^{1}H (399.782 MHz) NMR measurements were done in 5 mm tubes, and the chemical shifts are reported with respect to the standard references of 2 M Na_2WO_4, 85% H_3PO_4, and tetramethylsilane, respectively.