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Synthesis and Biological Activity of Organoantimony(III)-Containing Heteropolytungstates

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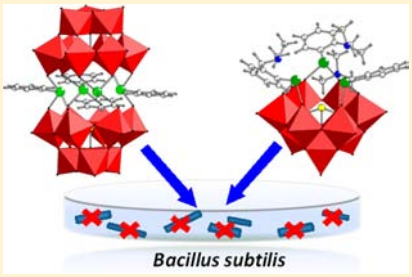
Supporting Information

ABSTRACT: Three discrete organoantimony(III)-containing heteropolytungstates $[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]^{12-}$ (**1**), $[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]^{10-}$ (**2**), and $[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$ (**3**) have been synthesized in one-pot reactions in aqueous medium using the appropriate lacunary heteropolyanion precursor and organoantimony(III) source. Polyanions **1**−**3** were isolated as hydrated salts, $(NH_4)_{12}[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]\cdot 20H_2O$ (**1a**), $Rb_9Na[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]\cdot 20H_2O$ (**2a**), and $Rb_3[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]\cdot 7H_2O$ (**3a**). The compounds **1a**−**3a** were fully characterized in the solid state using infrared (IR) spectroscopy, single-crystal XRD, and thermogravimetric and elemental analyses. The stability of **1**−**3** in aqueous solution was confirmed by multinuclear NMR (^1H, ^{13}C, ^{31}P, and ^{183}W) spectroscopy. Preliminary studies on the biological activity of **1**−**3** showed that all three compounds might act as potent antimicrobial agents.



INTRODUCTION

Polyoxometalates (POMs) represent a large class of discrete polynuclear metal-oxo anions usually formed by early d-block elements (e.g., W^{VI}, Mo^{VI}, V^{V}) in high oxidation states.[1] Organic POM derivatives are of particular interest, as they combine the features of both, the inorganic polyanion and the covalently bound organic units, in one discrete, molecular assembly. The functionalization of POMs with organometallic moieties allows in particular for tuning of shape, size, lipophilicity, solubility, stability, as well as redox and acid−base properties, and hence such derivatives are very interesting for medicinal applications.[2] Hybrid organic−inorganic POMs may also combine several interesting features, such as chirality,[2b,3] magnetic and electrical properties,[1j,4] as well as catalytic properties.[5]

Several successful attempts were made in order to prepare suitable POMs and study their biological and pharmacological activity as potential inhibitors of viral enzymes such as the protease and reverse transcriptase of HIV, mammalian histone deacetylase, or various cholinesterases.[6] Inhibition of the latter two types of enzymes by POMs is of interest for the treatment of cancer and neurodegenerative disorders, such as Alzheimer's disease.[6e,f]

In particular, organotin-POMs have been of wide interest due to the stability of the Sn−C bond and also the fact that Sn^{IV} has the right size to occupy addenda sites in POM skeletons.[6c,7−9] Our group has already reported a variety of such organotin-containing polyoxoanions, namely, $[\{Me_2Sn^{IV}(H_2O)_2\}_3(\beta\text{-}X^{III}W_9O_{33})]^{3-}$ (X = As, Sb),[9a] $[(PhSn^{IV})_2As^{III}{}_2W_{19}O_{67}(H_2O)]^{8-}$,[9b] $[\{Me_2Sn^{IV}(H_2O)\}_{24}(Me_2Sn^{IV})_{12}(A\text{-}\alpha\text{-}X^{V}W_9O_{34})_{12}]^{36-}$ (X = P, As),[9d] $[\{PhSn^{IV}(OH)\}_3(A\text{-}\alpha\text{-}X^{IV}W_9O_{34})]^{4-}$ (X = Ge, Si),[9j] $[\{PhSn^{IV}(OH)\}_3(A\text{-}\beta\text{-}X^{IV}W_9O_{34})]^{4-}$ (X = Ge, Si), as well as $[\{PhSn^{IV}(A\text{-}\beta\text{-}H_3SiW_9Sn^{IV}{}_2O_{37})\}_2O_2]^{8-}$.[9n]

In contrast, only a few POMs functionalized by organoantimony fragments are known. In 1989, the Liu group reported the solid-state structure of $[(Ph_2Sb^{V})_2(\mu\text{-}O)_2(\mu\text{-}MoO_4)_2]^{2-}$, in which two separated $\{MoO_4\}$ tetrahedra bridge two octahedrally coordinated Sb^{V} ions.[10] The analogous tungsten species was also reported.[1d] Recently, Winpenny's group prepared a reverse Keggin ion comprising 12 $\{PhSb^{V}\}$ units in addenda positions and a central $\{M^{II}O_4\}$ (M = Mn, Zn) group.[11] The reactivity of organostibonic acids toward the formation of polyoxostibonates is also being intensively studied these days, and several representatives of POMs built exclusively by organoantimony units have already been obtained.[12]

In 2009, our group prepared the first organoantimony(V)-containing polyoxotungstate, $[\{PhSb^{V}(OH)\}_3(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]^{9-}$, synthesized in a hydrothermal reaction of

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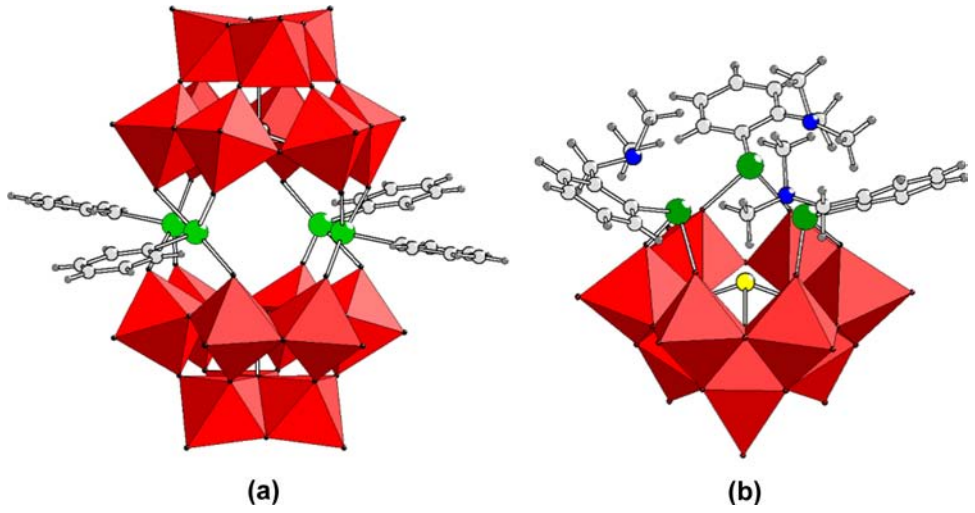

Figure 1. Combined polyhedral/ball-and-stick representation of (a) $[(PhSb^{III})_4(A\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$ (X = Ge^{IV} (**1**), P^V (**2**)) and (b) $[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$ (**3**). Color code: WO_6 red octahedra; X and As, yellow; Sb, green; C, light gray; N, blue; H, dark gray balls.

Table 1. Selected Bond Lengths for 1, 2, and $[\{PhSb^V(OH)\}_3(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]^{9-}$ (Data for the Latter Taken from ref 13)

	Bond Lengths [Å]		
	1	**2**	$[\{PhSb^V(OH)\}_3(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]^{9-}$
W−O_t	1.708(18)−1.750(17)	1.719(12)−1.746(12)	1.698(13)−1.734(13)
W−O(X)	2.196(15)−2.309(15)	2.365(11)−2.427(10)	2.350(11)−2.411(11)
W−O(W)	1.813(17)−2.095(17)	1.816(12)−2.061(12)	1.849(12)−1.982(12)
W−O(Sb)	1.792(17)−1.900(16)	1.793(11)−1.883(12)	1.831(13)−1.862(13)
Sb−O	1.993(15)−2.380(18)	2.000(12)−2.335(11)	1.986(12)−2.036(13)
Sb−C	2.134(12)−2.157(12)	2.152(8)−2.174(8)	2.096(16)−2.140(13)
X−O	1.728(15)−1.793(16)	1.527(11)−1.576(11)	1.523(12)−1.584(12)
Sb−OH			1.926(15)−1.935(18)

$Ph_2Sb^VCl_3$ with $Na_9[A\text{-}\alpha\text{-}P^VW_9O_{34}]\cdot 13H_2O$ in aqueous, acidic medium.[13]

Here, we report the synthesis and structural characterization of three novel organoantimony(III)-containing POMs, isolated as hydrated ammonium and alkali-metal salts, $(NH_4)_{12}[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]\cdot 20H_2O$ (**1a**), $Rb_9Na[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]\cdot 20H_2O$ (**2a**), and $Rb_3[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]\cdot 7H_2O$ (**3a**). Preliminary studies on the biological activity of these compounds are also presented. Because of the results of previous studies on the bioactivities of POMs related to the inhibition of viral or mammalian enzymes, and since the internalization of metals via POMs into bacterial cells might efficiently kill those cells,[14] the growth inhibition of bacteria with different types of cell wall was assessed.

RESULTS AND DISCUSSION

Synthesis and Structure. The polyanions $[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]^{12-}$ (**1**), $[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]^{10-}$ (**2**), and $[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$ (**3**) have been prepared in a facile self-assembly reaction of $PhSbCl_2$ or $[2\text{-}(Me_2NCH_2C_6H_4)]SbCl_2$ with the sodium salt of the respective POM precursor $Na_{10}[A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34}]\cdot 18H_2O$, $Na_9[A\text{-}\alpha\text{-}P^VW_9O_{34}]\cdot 13H_2O$, or $Na_9[B\text{-}\alpha\text{-}As^{III}W_9O_{33}]\cdot 27H_2O$ in water, and crystallized in yields of 73%, 68%, and 46% for **1a**, **2a**, and **3a**, respectively. It should be noted that the Sb^{III} sources were dissolved in a minimum amount of ethanol and then added dropwise. All three compounds are stable toward air and light in the solid state, and they are also stable in solution, at least for a week, as shown by multinuclear NMR spectroscopy (vide infra).

Single-crystal X-ray analysis showed that **1a** and **2a** are isostructural and crystallize in the triclinic crystal system, space group $P\bar{1}$. The two respective polyanions $[(PhSb^{III})_4(A\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$ (X = Ge^{IV} (**1**), P^V (**2**)) have a dimeric, sandwich-type structure with two $\{A\text{-}\alpha\text{-}XW_9O_{34}\}$ units capping four $\{PhSb^{III}\}$ groups (see Figure 1a). Each antimony(III) center is tetra-coordinated and exhibits a seesaw geometry, with the bulky phenyl group and the lone pair of Sb^{III} in equatorial positions. The three remaining positions are occupied by oxo-bridges at the lacunary sites of the $\{A\text{-}\alpha\text{-}XW_9O_{34}\}$ units, bridging to two edge-shared WO_6 octahedra from one unit and one WO_6 octahedron from the other, having two of the three oxo-ligands located in an axial position (O−Sb^{III}−O ca. 169°−172°) and the third oxo-group in an equatorial position *cis* to the phenyl group. This is in contrast to the reported polyanion $[\{PhSb^V(OH)\}_3(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]^{9-}$ containing three organoantimony(V) units, where each antimony(V) has an octahedral coordination, being in the oxidation state +5 with no lone pair of electrons, with four oxo-ligands from the sandwiching $[A\text{-}\alpha\text{-}P^VW_9O_{34}]^{9-}$ units and a hydroxo-ligand *trans* to the phenyl group.[13] The bond lengths in **1**, **2**, and $[\{PhSb^V(OH)\}_3(A\text{-}\alpha\text{-}P^VW_9O_{34})_2]^{9-}$ are very similar (see Table 1), except for the Sb−O bonds, which are longer for **1** and **2**, because of the lower oxidation state of the Sb centers. Moreover, in comparison with $[\{PhSb^V(OH)\}_3(A\text{-}\alpha\text{-}$

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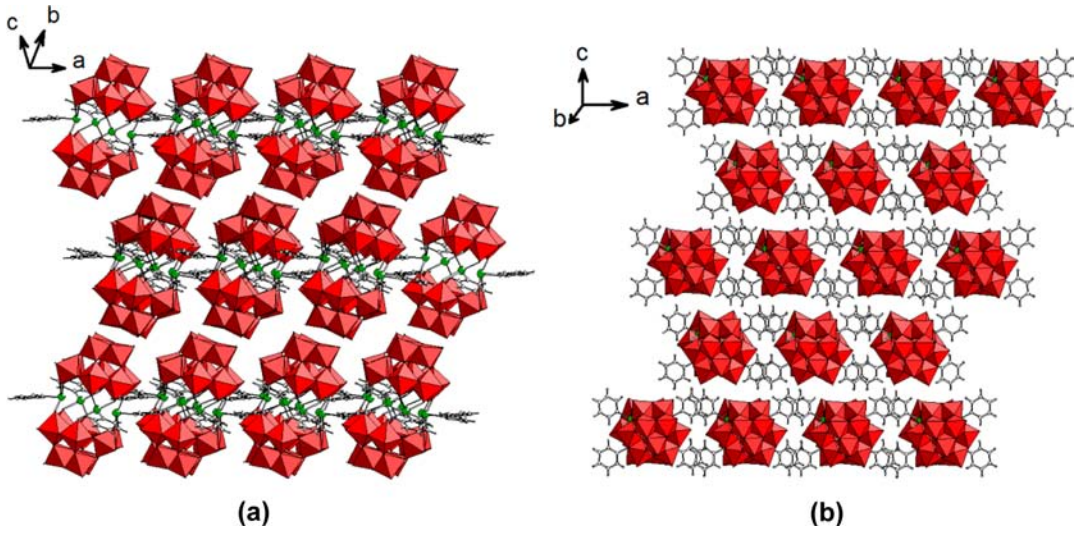

Figure 2. Crystal packing arrangement of **1a**: (a) view of a layer and (b) top view of a layer. Counter cations and crystal waters omitted for clarity. Color code is the same as in Figure 1.

$P^{V}W_9O_{34})_2]^{9-}$, the synthetic procedures for **1** and **2** are easier and more straightforward. This is not surprising, as the starting material for antimony(V) (Ph_2SbCl_3) contains two phenyl groups bonded to antimony, requiring hydrothermal conditions to release one of them, in order to reduce the steric hindrance and allow the Sb^{V} atom to coordinate to the lacunary site of the POM. On the other hand, for **1** and **2**, the Sb^{III} center can directly coordinate to the {*A*-*α*-XW_9O_{34}} units.

The four Sb^{III} atoms in **1** and **2** are coplanar with the coordinated phenyl rings, which are arranged in an up−up−down−down fashion. Interestingly, the up−up and down−down ring pairs are adjacent to each other. Such arrangement results in idealized C_{2v} point group symmetry for **1** and **2**.

In the solid-state, polyanions **1** and **2** form two-dimensional (2D) layers parallel to the *a*-axis, with the phenyl rings of adjacent polyanions along the *a*-axis exhibiting *π*−*π* stacking (Figure 2 shows the solid state arrangement of polyanions in **1a**).

Very recently our group reported on three Sb^{III}-containing heteropolytungstates, $[Sb_3(A\text{-}\alpha\text{-}XW_9O_{34})_2]^{11-}$ (X = Si^{IV}, Ge^{IV}) and $[Sb_6O_2(A\text{-}PW_6O_{26})(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{15-}$, which represent the first examples of sandwich-type POMs with trigonal-pyramidal $Sb^{III}O_3$ linkers. All three polyanions are stable in solution, as shown by multinuclear (^{183}W, ^{31}P) NMR and UV-vis spectroscopy.[15]

The polyanion $[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$ (**3**) comprises a $[B\text{-}\alpha\text{-}As^{III}W_9O_{33}]^{9-}$ lacunary fragment to which three $\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}^{2+}$ moieties are coordinated, resulting in an assembly with C_3 symmetry (see Figure 1b). Each Sb^{III} ion in **3** coordinates two oxygens of the vacant site of the $[B\text{-}\alpha\text{-}AsW_9O_{33}]^{9-}$ unit, associated with W^{VI} centers of two adjacent triads, as well as the C atom of the organic moiety (see Table 2 for bond lengths). The resulting $\{CSb^{III}O_2\}$ core possesses a trigonal-pyramidal geometry with a lone pair on the Sb^{III} center directed to the center of the polyanion. The nitrogen atom in each $\{2\text{-}(Me_2NCH_2C_6H_4)\text{-}Sb^{III}\}^{2+}$ unit forms an additional bond (bond valence is ∼0.5)[16] with the Sb atom *trans* to one of the Sb−O bonds. The N−Sb distances (2.360(11)−2.390(11) Å) lie between the sums of the corresponding covalent (Σr_{cov}(Sb,N) 2.11 Å) and van der Waals radii (Σr_{vdW}(Sb,N) 3.74 Å).[17] These N→Sb interactions are of the same strength as observed in the dichloride $[2\text{-}(Me_2NCH_2C_6H_4)]SbCl_2$ used as a starting material (2.407(5) Å),[18] but considerably stronger than in *cyclo*-$[\{2\text{-}(Me_2NCH_2C_6H_4)\}SbO]_3$ in which the N → Sb interaction (2.613(4)−2.660(4) Å) is also *trans* to a Sb−O bond.[19] Taking into account the N−Sb bond, the overall coordination geometry around the Sb^{III} ions can be described as a distorted seesaw, with the N atom and one of the O atoms in axial positions (N−Sb−O 157.2(3)−158.3(4) Å). In addition, the N−Sb interactions play an important structure-directing role, as they determine the relative orientation of the three organic ligands.

Table 2. Selected Bond Lengths for Polyanion 3

bond	bond length [Å]
W−O_t	1.690(14)−1.735(13)
W−O(As)	2.298(12)−2.380(12)
W−O(W)	1.901(12)−1.926(12)
Sb−O(W)	1.950(13)−2.144(12)
Sb−C	2.100(19)−2.144(12)
Sb−N	2.360(11)−2.390(11)
As−O	1.770(12)−1.789(12)

Overall, the structure of polyanion **3** resembles that of the previously reported flower pot-shaped organotin-containing polyanions $[\{Me_2Sn^{IV}(H_2O)_2\}_3(\beta\text{-}X^{III}W_9O_{33})]^{3-}$ (X = As, Sb)[9a] and allows to draw some analogies for the reactivity of organotin *vs* organoantimony species toward lacunary POM ligands. Nevertheless, the structure of polyanion **3** is unique considering the seesaw coordination geometry of the Sb^{III} ions *vs* the octahedral coordination of the Sn^{IV} centers in the above-mentioned flower pot-shaped POMs.

In the solid-state, polyanions **3** is connected via intermolecular $C{-}H_{(aromatic\ ring)}{-}\pi$ bonds directed along diagonals between the crystallographic *a*- and *b*-axes, as well as −*a* and *b*, to form pseudo-layers in the *ab*-plane (Figure 3a). These pseudo-layers alternate in an ABAB sequence along the crystallographic *c*-axis being connected by C−H−*π* interactions between the CH_2 group of one POM with the *π*-system of a polyanion phenyl group in the adjacent pseudo-layer (Figure 3b).

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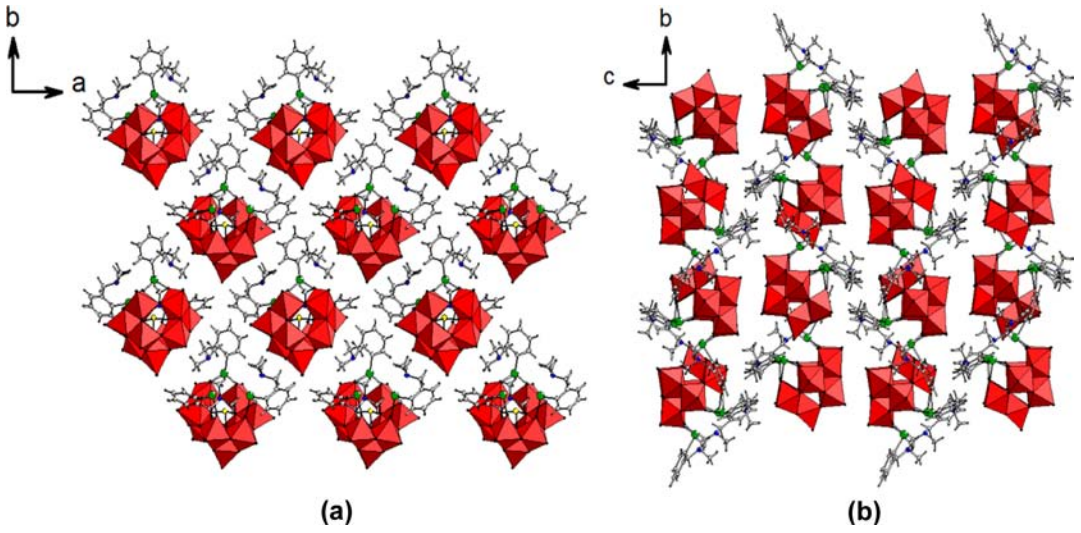

Figure 3. Crystal packing arrangement of **3a**: (a) view along the *c*-axis; (b) view along the *a*-axis. Counter cations and crystal water molecules omitted for clarity. Color code is the same as in Figure 1.

Infrared (IR) Spectroscopy. Fourier transform infrared (FT-IR) spectra recorded on **1a**, **2a**, and **3a** are shown in the Supporting Information (Figures S1, S2 and S3, respectively). The stretching and bending vibrations of the C−H and C−C bonds of the organic groups appear at 1184, 1065, 721, and 618 cm^{-1} for **1a**, in the range of 1480−1060 cm^{-1}, and at 721 and 618 cm^{-1} for **2a**, and between 3060−2790 cm^{-1} and 1440−1030 cm^{-1}, and at 749 and 692 cm^{-1} for **3a**.[20] The band at 780 cm^{-1} corresponds to Ge−O vibrations in **1a**. For **2a**, the band at 1013 cm^{-1} corresponds to P−O stretching modes. The band at 854 cm^{-1} corresponds to As−O stretching modes for **3a**. The other peaks below 1000 cm^{-1} are assigned to terminal W═O, as well as bridging W−O−W stretching modes for all three compounds.[21] The bands at 3142, 3020, 2834, and 1401 cm^{-1} correspond to NH_4^+ ions for **1a**. The broad bands at 1625 cm^{-1} for **1**, at 1619 cm^{-1} for **2a** and at 1618 cm^{-1} for **3a** belong to asymmetric vibrations of crystal water molecules.[22]

Thermogravimetric Analysis (TGA). The thermogram of **1a** revealed several weight-loss steps (see Figure S4 in the Supporting Information). The first step occurs between 25 °C and 160 °C and corresponds to the loss of 20 crystal water molecules per formula unit (6.2% found versus 6.1% calculated). Several consecutive weight loss steps covering the temperature range of 160−480 °C are attributed to the release of 4 phenyl groups and 12 NH_3 molecules per formula unit (8.0% found versus 8.7% calculated). The experimental weight loss percentage for the organic groups is less than the calculated one, probably due to incomplete decomposition. The total observed weight loss for **1a** at 1000 °C is 17.9%.

The thermogram of **2a** also showed several weight-loss steps (see Figure S5 in the Supporting Information). The first step occurs between 25 °C and 170 °C and corresponds to the loss of 16 crystal water molecules per formula unit (4.5% found versus 4.6% calculated). The number of crystal water molecules determined by TGA is slightly lower than that obtained by crystallography (16 molecules versus 20 molecules). This fact can be easily explained by a partial loss of crystal water molecules during sample drying. Single crystals for XRD measurements were taken directly from the mother liquid, placed in oil, and then placed on the diffractometer under a liquid nitrogen flow, whereas the samples for TGA were air-dried for at least one day. The combustion of four phenyl groups per formula unit proceeds in the temperature range of 380−600 °C (5.0% found versus 4.9% calculated). The total observed weight loss for **2a** at 1000 °C is 10.8%.

In case of **3a**, the first step on the thermogram occurs between 25 °C and 200 °C and corresponds to the loss of nine water molecules per formula unit of **3a** (4.5% found versus 4.7% calculated; see Figure S6 in the Supporting Information). In this case, the number of waters determined by TGA is slightly higher than that obtained by crystallography (seven molecules), because of high disorder of the crystallization waters in the crystal structure of **3a**. Dehydration step is followed by the release of the organic moieties confirmed by the series of steps between 200 °C and 590 °C (11.5% found versus 11.7% calculated). The total observed weight loss for **3a** at 1000 °C is 28.7%.

Nuclear Magnetic Resonance (NMR) Studies. The solution stability of **1**, **2**, and **3** was investigated by multinuclear NMR spectroscopy after redissolution of the compounds in H_2O/D_2O. It should be noted that the final pH values of such solutions were ∼7. The ^{183}W NMR spectra of isomorphous **1** and **2** showed the expected five peaks for each polyanion (at −78, −93, −102, −148, −195 ppm for **1** and at −105, −112, −115, −168, −178 ppm for **2**) with intensity ratios of 2:1:2:2:2, fully consistent with the C_{2v} symmetry of polyanions seen in the solid state (see Figure 4). The ^{13}C NMR spectra of **1a** and **2a** are as expected for coordinated phenyl groups (see Figure S7 in the Supporting Information). The ^1H NMR spectra of **1a** and **2a** also prove the presence of coordinated phenyl groups, as well as NH_4^+ ions in the case of **1a** (see Figure S8 in the Supporting Information). The ^{31}P NMR spectra of **2a** revealed one signal at −11.1 ppm (see Figure 5). Because of the low solubility of **3a**, we were not able to carry out a solution ^{183}W NMR study on this compound. However, the ^1H NMR spectrum of **3a** shows the presence of the $\{Me_2NCH_2C_6H_4\}$ groups (see Figure S9 in the Supporting Information).

Based on the results of the multinuclear NMR study, we conclude that polyanions **1**−**3** are stable at physiological pH, and could hence be used for biological studies.

Biological Activity—Determination of Minimal Inhibitory Concentrations (MIC). Since we have shown the

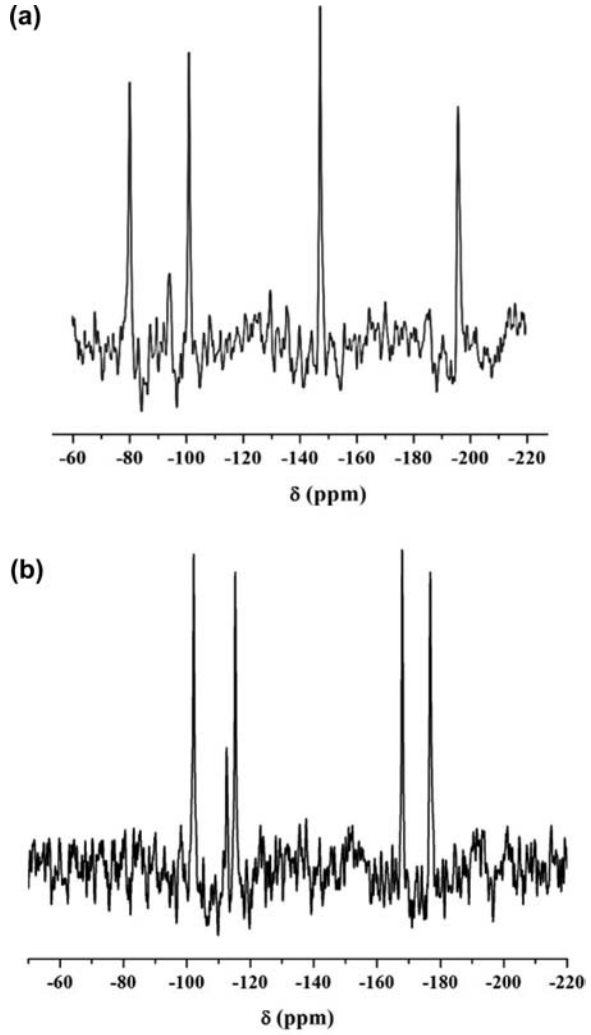

Figure 4. ^{183}W NMR spectra of (a) **1a** and (b) **2a** recorded in H_2O/D_2O at room temperature.

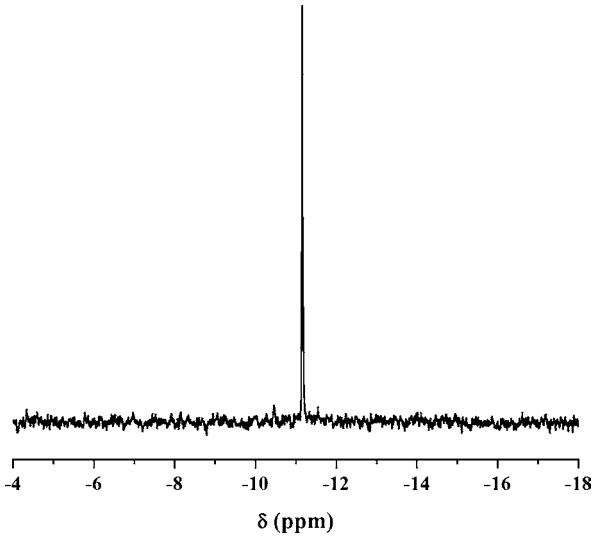

Figure 5. ^{31}P NMR spectrum of **2a** recorded in H_2O/D_2O at room temperature.

stability of polyanions **1**–**3** in aqueous media at physiological pH value (~7.0), we decided to study their antimicrobial activity. Results of the MIC assays showed that all three polyanions very efficiently inhibit the growth of the used indicator bacterial strains, which represent gram-negative and gram-positive bacteria. The MICs for each compound are summarized in Table 3. Use of the two different media did not reveal any significant differences. The Mueller–Hinton–Bouillon (MHB) medium was used as a standard medium for MIC determination, and the Luria–Bertani (LB) medium was used as a complex growth medium. Comparative growth in either medium might indicate metabolic differences in susceptibility or tolerance toward the tested antimicrobials. Interestingly, polyanions **2** and **3** have a slightly stronger activity against the gram-positive *B. subtilis*, compared to the gram-negative organism, *E. coli*. Polyanion **1** showed this increased activity against gram-positive microbes only when *B. subtilis* was grown in an LB medium. These results indicate that all three polyanions **1**–**3** have the potential to act as antibacterial agents, despite structural/compositional differences. Our results also showed a delayed uptake of these polyanions into bacteria possessing an outer membrane, suggesting that internalization of the metal ions might lead to cell toxicity, as described earlier for mammalian cells.[14]

Table 3. MIC Determination of the Different Polyanions in *Escherichia coli* DH5α and *Bacillus subtilis*[a]

	MIC Determination (μg/mL)					
	1		**2**		**3**	
microorganism	MHB	LB	MHB	LB	MHB	LB
E. coli	80	80	110	110	130	130
B. subtilis	80	40	50	50	60	60

[a]MHB = Mueller–Hinton–Bouillon medium; LB = Luria–Bertani medium.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All reagents were purchased from commercial sources and used without further purification. The infrared (IR) spectra for the solid samples were obtained on KBr pellets using a Nicolet Avatar 370 FTIR spectrophotometer. Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 thermobalance, using 10–30 mg of sample in 100-μL alumina pans under a 100 mL/min flow of nitrogen; the temperature was ramped from 20 °C to 1000 °C at a rate of 5 °C/min. The NMR spectra of the obtained compounds were recorded on a 400 MHz JEOL ECX instrument at room temperature, using 5-mm tubes for ^{1}H, ^{13}C, and ^{31}P NMR, and 10-mm tubes for ^{183}W NMR. The respective resonance frequencies were 399.78 MHz (^{1}H), 100.71 MHz (^{13}C), 162.14 MHz (^{31}P), and 16.69 MHz (^{183}W). The chemical shifts are reported with respect to the references $Si(CH_3)_4$ (^{1}H and ^{13}C), 85% H_3PO_4 (^{31}P), and 1 M Na_2WO_4(aq) (^{183}W). Elemental analyses were performed by Kanti Laboratories (Tirupathi, India) for **1a**, Analytische Laboratorien (Lindlar, Germany) for **2a**, and Service Central d'Analyze (Solaize, France) for **3a**.

$(NH_4)_{12}[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]\cdot 20H_2O$ (1a). The trilacunary precursor salt $Na_{10}[A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34}]\cdot 18H_2O$ (0.417 g, 0.145 mmol), synthesized according to a previously published procedure,[23] was dissolved in 20 mL of water, whereas 0.078 g (0.290 mmol) of $PhSbCl_2$[24] was dissolved in a separate beaker in a minimum amount of ethanol. The solution of $PhSbCl_2$ was

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added dropwise to the POM precursor solution under vigorous stirring. The resulting solution was stirred for 30 min and then filtered. Several drops of 1 M NH_4Cl were added to the final solution, and then it was cooled to 4−5 °C. After 1 day, yellow crystals suitable for XRD measurements were obtained. Yield: 0.315 g (73%, based on W). Elemental analysis (%) calcd: N 2.84, H 1.84, C 4.87, Sb 8.23, Ge 2.46, W 56.0; Found: N 2.91, H 1.92, C 4.77, Sb 8.12, Ge 2.48, W 55.9. IR (2% KBr pellet, ν/cm^{-1}): 3142 (s), 3020 (sh), 2834 (sh), 1625 (m), 1401 (s), 1184 (w), 1065 (w), 926 (s), 879 (s), 780 (s), 721 (s), 618 (sh), 533 (m), 479 (m).

$Rb_9Na[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]\cdot 20H_2O$ (2a). $Na_9[A\text{-}\alpha\text{-}P^{V}W_9O_{34}]\cdot 13H_2O$ (0.417 g, 0.145 mmol), prepared as described previously,[25] was dissolved in 20 mL of water, whereas 0.078 g (0.290 mmol) of $PhSbCl_2$[24] was dissolved in a separate beaker in a minimum amount of ethanol. The solution of $PhSbCl_2$ was added dropwise to the POM precursor solution under vigorous stirring. The resulting solution was stirred for 30 min, filtered, and several drops of 0.5 M RbCl were added. The final solution was cooled to 4−5 °C. After 1 day, yellow crystals were obtained. Yield: 0.345 g (68%, based on W). Elemental analysis (%) calcd: Rb 12.01, Na 0.36, H 0.94, C 4.50, Sb 7.60, P 0.97, W 51.65; Found: Rb 11.53, Na 0.30, H 1.05, C 4.73, Sb 9.34, P 1.10, W 51.25. IR (2% KBr pellet, ν/cm^{-1}): 1619 (m), 1478 (w), 1428 (w), 1185 (w), 1066 (s), 1013 (m), 942 (s), 913 (s), 892 (sh), 822 (sh), 741 (s), 592 (w), 516 (m), 459 (m).

$Rb_3[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]\cdot 7H_2O$ (3a). $Na_9[B\text{-}\alpha\text{-}As^{III}W_9O_{33}]\cdot 27H_2O$ (0.134 g, 0.05 mmol), obtained following a published procedure,[26] was dissolved in 10 mL of water. 0.047 g (0.15 mmol) of $[2\text{-}(Me_2NCH_2C_6H_4)]SbCl_2$[18] was dissolved in ethanol with heating at 40 °C. The solution of the organoantimony dichloride was added dropwise to the POM precursor solution under vigorous stirring. The mixture was stirred for 30 min at room temperature and filtered off. One milliliter of 0.5 M RbCl was added to the resulting solution. Yellow crystals were obtained after several days, filtered off, and air-dried. Yield: 0.080 g (46%, based on W). Elemental analysis (%) calcd: Rb 7.45, N 1.22, H 1.58, C 9.42, Sb 10.61, As 2.18, W 48.0; Found: Rb 7.09, N 1.19, H 1.45, C 9.55, Sb 10.30, As 2.11, W 47.6. IR (2% KBr pellet, ν/cm^{-1}): 3056 (m), 2998 (m), 2968 (m), 2906 (m), 2835 (m), 2797 (m), 1618 (m), 1437 (m), 1360 (w), 1287 (w), 1208 (w), 1113 (w), 1031 (w), 997 (s), 955 (s), 854 (s), 790 (s), 749 (s), 692 (s), 655 (s), 481 (m), 447 (m).

X-ray Crystallography. XRD data for the structures of **1a**−**3a** were collected at 173 K on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo tube and graphite monochromator (λ = 0.71073 Å). Crystals were mounted in a Hampton cryoloop with light oil to prevent water loss. The SHELX software package (Bruker) was used to solve and refine the structures.[27] Absorption corrections were applied empirically using the SADABS program.[28] 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. The H atoms of the organic groups in **1**−**3** were introduced in geometrically calculated positions and refined using the riding model. Additional crystallographic data are summarized in Table S1 in the Supporting Information. Further details of the crystal structure investigation are available free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif on quoting the depository numbers CCDC 891299 (**1a**), CCDC 891300 (**2a**), and CCDC 891301 (**3a**).

Biological Activity—Determination of Minimal Inhibitory Concentrations (MIC). *Escherichia coli* DH5α and *Bacillus subtilis* were used to test the antimicrobial activity of solutions of the compounds **1a**−**3a** in deionized water (Table 4). The MIC of the polyanions against the microorganisms was

Table 4. Polyanions and Their Concentrations Used in the MIC Assay

polyanion	molecular formula	POM concentration in deionized water (mM)
1	$[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]^{12-}$	4.2
2	$[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]^{10-}$	2.7
3	$[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$	2.9

assayed in microtiter plates using a standard method.[29] For the generation of the MIC assay plates, two bacterial growth media—Mueller−Hinton−Bouillon (MHB) and Luria−Bertani (LB)—were used. Aliquots of 180 μL of media were added into row A of the microtiter plate, and 100 μL aliquots were added to rows B−H. Twenty microliters (20 μL) of the antimicrobial compounds at the concentrations indicated in Table 4 were added into row A. Dilution series (1/2) were made from rows A−H by transferring 100 μL from well to well, using a multichannel pipetman. Next, 100 μL of the bacterial suspension (~2 × 10^6 bacteria/mL) were added into each well of the microtiter plate. All MIC assay plates were incubated overnight for *E. coli* at 37 °C and for *B. subtilis* at 30 °C. For each compound, the MIC assay was performed in triplicate with deionized water used as a negative control.

CONCLUSIONS

In summary, we have synthesized the three first examples of polyoxotungstates functionalized by organoantimony(III) units—$[(PhSb^{III})_4(A\text{-}\alpha\text{-}Ge^{IV}W_9O_{34})_2]^{12-}$ (**1**), $[(PhSb^{III})_4(A\text{-}\alpha\text{-}P^{V}W_9O_{34})_2]^{10-}$ (**2**), and $[\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B\text{-}\alpha\text{-}As^{III}W_9O_{33})]^{3-}$ (**3**)—via facile reactions of $PhSbCl_2$ or $[2\text{-}(Me_2NCH_2C_6H_4)]SbCl_2$ with the sodium salt of the respective POM precursor in aqueous medium. Single-crystal X-ray analysis revealed that polyanions **1** and **2** have a sandwich-type structure with two $\{A\text{-}\alpha\text{-}XW_9O_{34}\}$ (X = Ge^{IV}, P^{V}) moieties capping four $\{PhSb^{III}\}$ groups, whereas polyanion **3** is a flower-pot-shaped species with three $\{2\text{-}(Me_2NCH_2C_6H_4)Sb^{III}\}^{2+}$ units coordinated to a $[B\text{-}\alpha\text{-}As^{III}W_9O_{33}]^{9-}$ fragment. Multinuclear NMR studies (^1H, ^{13}C, ^{31}P, ^{183}W) of polyanions **1**−**3** in H_2O/D_2O indicated that they are stable in solution.

Our biological studies revealed that the gram-positive bacterium *B. subtilis*, has a slightly higher sensitivity toward **1**−**3**, as compared to the gram-negative organism *E. coli*. This difference may be due to differences in the composition of the cell envelopes of gram-positive and gram-negative bacteria.[30] Since gram-negative bacteria are surrounded by a hydrophobic outer membrane, our results might indicate that the hydrophilic character or specific hydrophilic residues of the tested polyanions could prevent an efficient entry into gram-negative bacterial cells. Alternatively, structural features of polyanions could potentially facilitate a more efficient entry into gram-positive bacterial cells and thus make those organisms more susceptible. However, it should be noted that the differences in MIC values are rather small, allowing the conclusion that all

three polyanions might act as potent antimicrobial agents, possibly via internalization of the contained metal ions into the cells. Since this cellular uptake of POMs can be further promoted by encapsulating them in chitosan,[14] and since chitosan has been considered to be an effective wound-healing cover component,[31] a combination of the POMs described herein with chitosan fibers might represent an interesting alternative material for antibacterial wound-covering devices.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, a table with the main crystallographic and refinement parameters (Table S1), IR spectra (Figures S1−S3), and thermograms (Figures S4−S6), ^{13}C and ^{1}H NMR spectra of **1a**−**3a** (Figures S7−S9), are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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