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# New Organotin and Organosilicon Derivatives of P/ As/Sb/Bi-Polyoxotungstates

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# NEW ORGANOTIN AND ORGANOSILICON DERIVATIVES OF P/As/Sb/Bi-POLYOXOTUNGSTATES

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# **ABSTRACT**

Mono- or bis(organoelement)-substituted Keggin molybdotungstophosphates  $K_4[C_4H_9SnPMo_2W_9O_{39}]$ ·14H<sub>2</sub>O,  $K_4[C_6H_5SnPMo_2W_9O_{39}] \cdot 14H_2O_{39}$  $K_3[(C_2H_3Si)_2$ PMo2W9O40] 17H2O, tris(organoelement)-substituted Keggin tungstophosphates and tungstoarsenates  $Cs_{12}[(C_4H_9SnOH)_3(PW_9O_{34})_2] \cdot 19H_2O, K_{11}H[(C_2H_3SiOH)_3(PW_9O_{34})_2]$  $Cs_{12}[(C_4H_9SnOH)_3(AsW_9O_{33})_2] \cdot 43H_2O_1$  $Cs_{12}[(C_2H_3SiOH)_3(AsW_9O_{33})_2]$ ·14H<sub>2</sub>O. bis(organoelement)-substituted  $\cdot 12H_2O_1$ and monoor pseudo-Keggin and tungstobismutates K4[(C4H9SnOH)SbW11O38H]-12H2O, tungstoantimonates  $K_4[(C_4H_9SnOH)BiW_{11}O_{38}H] \cdot 10H_2O)$  $K_2[(C_2H_3Si)_2SbW_{11}O_{39}H] \cdot 16H_2O_{39}$ and K<sub>2</sub>[(C<sub>2</sub>H<sub>3</sub>Si)<sub>2</sub>BiW<sub>11</sub>O<sub>39</sub>H]·14H<sub>2</sub>O, have been prepared by reaction of organoelement trichlorides with  $[PMo_2W_9O_{39}]^{7}$ ,  $[PW_9O_{34}]^{9}$ ,  $[HAsW_9O_{33}]^{8}$ ,  $[HSbW_{11}O_{38}]^{6}$  and  $[HBiW_{11}O_{38}]^{6}$ , respectively. The products were characterized by elemental and thermal analyses, UV, IR and <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectroscopy. The results of these studies suggest that the compounds obtained from Keggin trilacunary anions are 2:3 sandwichtype complexes, and those obtained from monolacunary Keggin anions are 1:1 opentype complexes.

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#### **INTRODUCTION**

Polyoxometallates are typical examples of supramolecular inorganic compounds.<sup>1</sup> Their versatility for applications in environmentally benign catalytic processes, in medicine and in many other fields, stimulates the continuous interest of many laboratories in their study and sustained activity was observed in recent years. Currently, areas of particular interest are the biological activity exhibited by polyoxometallates and potential chemotherapy involving such species, as well as their versatility as catalysts. In each of these fields it is desirable to modify the polyoxoanion surface in order to develop specific anion-substrate recognition, and, in the area of polyoxometallates with organometallic fragments<sup>2-7</sup> seem to be promising from this point of view.

Among the great diversity of polyoxometallate structures, the so-called cubeoctahedral  $XW_{12}O_{40}^{n}$  (X = B, Si, Ge, P, As, Sb, Bi) Keggin-type is the best known<sup>8</sup> and by derivatization can give rise to "lacunary" anions of various compositions in which one or more octahedral units of the parent anion were lost. Examples are the monolacunary  $XW_{11}O_{39}^{n}$  and trilacunary  $XW_9O_{34}^{n}$  anions. The structural vacancies of these anions can be filled with a broad variety of heteroatoms resulting in the formation of novel types. Organometallic fragments can serve for this purpose.

The reaction of Keggin and pseudo-Keggin type polyoxometallates with organometallic chlorides  $\text{RECl}_3$  (E = Sn, R = Bu, Ph and E = Si, R = vinyl) in aqueous media leads to complexes of the type [{P}ER]<sup>n</sup> where {P} are [PMo<sub>2</sub>W<sub>9</sub>O<sub>39</sub>]<sup>7</sup> (P<sup>1</sup>),  $\alpha$ -A-[PW<sub>9</sub>O<sub>34</sub>]<sup>9</sup> (P<sup>2</sup>),  $\alpha$ -B-[HAsW<sub>9</sub>O<sub>33</sub>]<sup>6</sup> (P<sup>3</sup>) ( $\alpha$ -XM<sub>12</sub> is the  $\alpha$ -isomer of the Keggin anion; the A-XM<sub>9</sub> lacunary structure corresponds to loss of a corner-shared group of {MO<sub>6</sub>} octahedra; the B-XM<sub>9</sub> lacunary structure corresponds to loss of an edge-shared group. Note that in the B-type anion, in contrast to the A-XM<sub>9</sub> type anion, the central tetrahedrally coordinated heteroatom has an unshared terminal oxygen atom<sup>9</sup>, [HSbW<sub>11</sub>O<sub>38</sub>]<sup>6</sup> (P<sup>4</sup>), and [HBiW<sub>11</sub>O<sub>38</sub>]<sup>6</sup> (P<sup>5</sup>). Elemental analyses, thermal analyses, IR, UV and <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectra were used to characterise the new compounds.

#### **RESULTS AND DISCUSSION**

Monolacunary Keggin and pseudo-Keggin polyoxometallate anions and organotin trichlorides react in 1:1 molar ratio and with organotrichlorosilanes in 1:2 ratio, while the trilacunary Keggin polyoxometallate anions react with organotin and organosilicon trichlorides in 2:3 molar ratio conform to the following equations:

$$P^{p^{*}} + nRECl_{3} \rightarrow [(RE)_{n}(O)_{x}P]^{(p^{*}+2x+3)*} + 3nCl^{*}$$

$$P = P^{1}, P^{4}, P^{5}; E = Si; R = vinyl; n = 2; x = 1.$$

$$P = P^{1}, P^{4}, P^{5}; E = Sn; R = Bu, Ph; n = 1; x = 0.$$

$$2P^{p^{*}} + 3RECl_{3} + 3H_{2}O \rightarrow [(REOH)_{3}(P)_{2}]^{(2p+6)*} + 3HCl + 6Cl^{*}$$

$$P = P^{2}, P^{3}; E = Si; R = vinyl.$$

$$P = P^{2}, P^{3}; E = Sn; R = Bu, Ph$$

The stoichiometric amounts of solid polyoxometallate were added to the aquoues solution of organometallic compounds under vigorous stirring for obtaining compounds (1), (2), (3), (8), (9), (10) and (11). The compounds (4), (5), (6) and (7) were synthesized in an "one-pot reaction" from commercially available reagents.

The following compounds were obtained:

 $K_{4}[C_{6}H_{5}SnPMo_{2}W_{9}O_{39}] \cdot 14H_{2}O(1),$   $K_{4}[C_{4}H_{0}SnPMo_{2}W_{9}O_{39}] \cdot 14H_{2}O(2),$   $K_{2}[(C_{2}H_{3}Si)_{2}PMo_{2}W_{9}O_{40}] \cdot 17H_{2}O(3),$   $C_{512}[(C_{4}H_{0}SnOH)_{3}(PW_{9}O_{34})_{2}] \cdot 19H_{2}O(4),$   $K_{11}H[(C_{2}H_{3}SiOH)_{3}(PW_{9}O_{34})_{2}] \cdot 14H_{2}O(5),$   $C_{512}[(C_{4}H_{0}SnOH)_{3}(AsW_{9}O_{33})_{2}] \cdot 43H_{2}O(6),$   $C_{512}[(C_{2}H_{3}SiOH)_{3}(AsW_{9}O_{33})_{2}] \cdot 12H_{2}O(7),$   $K_{4}[(C_{4}H_{9}SnOH)SbW_{11}O_{38}H] \cdot 12H_{2}O(8),$   $K_{2}[(C_{2}H_{3}Si)_{2}SbW_{11}O_{39}H] \cdot 10H_{2}O)(10),$   $K_{4}[(C_{4}H_{9}SnOH)BiW_{11}O_{38}H] \cdot 10H_{2}O)(10),$ 

The organometallic derivatives were separated as cesium and potassium salts.

The compositions of the new compounds was establised on the basis of chemical and thermal analyses and is in agreement with the suggested formulae (see EXPERIMENTAL).

Thermogravimetric curves were recorded for all of the new polyoxometallates prepared. The first important process is the weight loss accompanied by an endothermal effect at temperatures in the range 40-240° C. This corresponds to the elimination of water molecules, with the loss of lattice water and the loss of structural water, without the possibility to evaluate in a quantitative way their individual contribution. Therefore, the weight loss noticed in this part of the curves was used to calculate the total water content.

The next important process observed at 200-350° C is related to changes in the polyanionic architecture, as reported for other representatives of this class of compounds. Above 380° C in all cases, after the combustion of the organic components, the inorganic residue exhibits some minor exothermal effect probably due to a polymorphic transformation.

All of the prepared compounds present characteristic IR spectral bands for the polyoxometallates<sup>10</sup> in the range 700-1000 cm<sup>-1</sup>. These bands are shifted by comparison with lacunary polyoxometallates because of the structural changes caused by the coordination of the organometallic fragments (see Fig. 1.). Also, new bands assigned to the vibrations of C-E-O and E-O-E bonds (E = Sn, Si) can be observed.

The chemical individuality of the newly-formed species is supported by UV spectra in solutions containing both the ligands and the complexes. Thus UV-electronic spectra exibit two characteristic bands at ~46,000 cm<sup>-1</sup> and ~38,000 cm<sup>-1</sup>, respectively<sup>11,12</sup> (see Fig. 2). In both "sandwich" and "open" polyoxometallates these bands are shifted by comparison with the ligand bands, but in the first case the shift is to lower frequencies, while in the second case the shift is to higher frequencies.

NMR spectra were recorded only in the case of (<u>n</u>-Bu)tin derivatives of  $[PMo_2W_9O_{39}]^{7}$ ,  $\alpha$ -A- $[PW_9O_{34}]^{9}$ , and  $\alpha$ -B- $[HAsW_9O_{33}]^{8}$  because of the low solubily of



Fig. 1. IR Spectra of Compounds (1)-(11) Compared with those of the Ligands (P<sup>1</sup>)-(P<sup>5</sup>).



Fig. 2. UV Spectra of Compounds (1)-(11) Compared with those of the Ligands (P<sup>1</sup>)-(P<sup>5</sup>).

- --- -

the other derivatives. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra show four signals typical for the butyl group but these signals are shifted relative to <u>n</u>-BuSnCl<sub>3</sub> (see Tables I and II.).

The <sup>31</sup>P NMR spectra may be explained in terms of changes in electron density surrounding the phosphorus atom. The oxygen atoms of the central PO<sub>4</sub> tetrahedron may be assumed to have the highest influence on this electron density. The occurrence of a vacancy leads to a weakening of the P-O bond, as shown by the change of mean v(PO) frequencies, and induces a decrease of the  $\delta$  value.

The <sup>31</sup>P NMR spectrum of K<sub>4</sub>[C<sub>4</sub>H<sub>9</sub>SnPMo<sub>2</sub>W<sub>9</sub>O<sub>39</sub>]·14H<sub>2</sub>O shows two peaks ( $\delta = 9.67$  ppm and  $\delta = 10.65$  ppm) suggesting the presence of two isomers. The <sup>31</sup>P NMR spectrum of Cs<sub>12</sub>[(C<sub>4</sub>H<sub>9</sub>SnOH)<sub>3</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·19H<sub>2</sub>O shows one signal upfield relativ to the free ligands (from  $\delta = -9.45$  to  $\delta = -10.11$ ).

The proposed structures for monolacunary Keggin polyoxometallates with organoelement frameworks are "open"-type. The structures of the anions (1), (2) and (3) are based on the well-known monolacunary Keggin anion  $[XM_{11}O_{39}]^p$  with one of the "cap" WO<sup>4+</sup> group replaced by  $\{SnR\}^{3+}$  or  $\{(RSi)_2O\}^{4+}$  groups (Fig. 3).

The proposed structures for the trilacunary Keggin polyoxometallates with organoelement frameworks are "sandwich"-type. In the structures of (4), (5), (6) and (7) anions the tin or silicon atoms act as the filling in a two XW<sub>9</sub> sandwich (Fig. 4).

Because the structure of  $XW_{11}O_{38}H^{6-}$  (X = Sb, Bi) polyoxometallates are not yet known we can't suggest the structures of these complexeses with organoelements, but, in many respects these anions resemble lacunary Keggin species<sup>13</sup>.

# **EXPERIMENTAL**

The polyoxometallates  $K_7[PMo_2W_9O_{39}] \cdot 13H_2O$ ,  $Na_6[SbW_{11}O_{38}H] \cdot 14H_2O$  and  $Na_6[BiW_{11}O_{38}H] \cdot 14H_2O$ , were prepared according to literature data<sup>14,15</sup> and were identified by infrared spectroscopy. Organotin chlorides, organotrichlorosilanes,  $Na_2WO_4 \cdot 2H_2O$ ,  $NaHPO_4 \cdot 7H_2O$  and  $As_2O_3$  were commercial samples (Aldrich).

Thermal analyses were performed using a Paulik-Erdely OD-102 system derivatograph, UV spectra were recorded on a SPECORD UV/VIS-75 in aqueous

Table L. <sup>1</sup>H NMR Chemical Shifts (ppm) of K<sub>4</sub>[BuSnPMo<sub>2</sub>W<sub>9</sub>O<sub>39</sub>]·14H<sub>2</sub>O (2), Cs<sub>12</sub>[(BuSnOH)<sub>3</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·19H<sub>2</sub>O (4), Cs<sub>12</sub>[(BuSnOH)<sub>3</sub>(AsW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]·43H<sub>2</sub>O (6).

	BuSnCl <sub>3</sub>	(2)	(4)	(6)
$C\underline{H}_{2}(\alpha)$	2.41	1.62	1.60	2.12
C <u>H</u> <sub>2</sub> (β)	1.90	1.96	1.96	2.12
C <u>H</u> <sub>2</sub> (γ)	1.50	1.55	1.55	1 47
C <u>H</u> ₃ (δ)	0.98	0.97	0.97	0.90

Table II <sup>13</sup>C NMR Chemical Shifts (ppm) of K<sub>4</sub>[BuSnPMo<sub>2</sub>W<sub>9</sub>O<sub>39</sub>]·14H<sub>2</sub>O (2),  $Cs_{12}[(BuSnOH)_3(PW_9O_{34})_2]\cdot19H_2O$  (4),  $Cs_{12}[(BuSnOH)_3(AsW_9O_{33})_2]\cdot43H_2O$ (6).

	BuSnCl <sub>3</sub>	(2)	(4)	(6)
$\underline{C}H_{2}(\alpha)$	33.54	-	30.09	32.07
$\underline{C}H_{2}(\beta)$	26 93	-	27.38	27.80
$\underline{C}H_{2}(\gamma)$	25.74	-	25.47	26.25
$\underline{C}H_{3}(\delta)$	13.44	-	13.34	13.48

solution, IR spectra using a SPECORD IR-75 spectrophotometer on KBr pellets and multinuclear NMR spectra using a Varian Gemini 300 spectrophotometer. Atomic absorption was used to determine the composition of synthesized compounds (Cs, K, Mo, W, P, Si, Sn). The water content was determined on the basis of thermal analysis

The new polyoxometallate derivatives with organometallic fragments were prepared as described below.



Fig. 3. The Probable Structures of  $[RSnPMo_2W_9O_{39}]^{4-}$  (a),  $[(RSi)_2PMo_2W_9O_{40}]^{3-}$  (b)



Fig. 4. The Probable Structure of  $[(\text{REOH})_3(\text{P})_2]^{(2p-6)-}$  (E = Sn, Si) Anions.

#### Synthesis of K4[C6H5SnPM02W9O39]·14H2O(1)

To a solution of 0.2 mL (1 mmol) of  $C_6H_5SnCl_3$  in 50 mL of water at room temperature was added sodium acetate to adjust the pH to 1.5. At this stage the solution is slightly turbid. Powdered  $K_7[PMo_2W_9O_{39}] \cdot 13H_2O$  (3 g, 1 mmol) was added quickly to this solution under stirring. Within a few seconds most of the dimolybdo-9 tungstophosphate had dissolved and the solution had clarified. The final pH was 5.0. Traces of unreacted molybdotungstophosphate were filtered out after 10 min. Potassium chloride was added to the filtrate in small portions until no more precipitation was observed. The precipitate was collected on a fine glass frit, dried under water aspirator vacuum for 1 h, washed with saturated KCl solution and dried overnight under vacuum to give a yield of 1.79 g (62%). White crystals of this solid were obtained by the method of vapor diffusion with ethanol.

Calcd. for  $C_6H_{33}K_4Mo_2O_{53}PW_9Sn$  (M 3106.6): K, 5.02; W, 53.28; Mo, 6.18; P, 0.99; Sn, 3.82; H<sub>2</sub>O, 8.18. Found: K, 5.20; W, 50.45; Mo, 5.89; P, 0.68; Sn, 3.86; H<sub>2</sub>O, 8.02.%.

#### Synthesis of K4[C4H9SnPM02W9O39]·14H2O (2)

 $K_4[C_4H_9SnPM_02W_9O_{39}] \cdot 14H_2O$  was prepared analogously to (1) using n-C\_4H\_9SnCl<sub>3</sub> instead of C\_6H\_5SnCl<sub>3</sub> and the same quantities of the other reactants. Yield, 1.9 g (62%). Calcd. for C\_4H\_{37}K\_4Mo\_2O\_{53}PW\_9Sn (M 3086.6): K, 5.06; W, 53.63; Mo, 6.22; P, 1.00; Sn, 3.25; H\_2O, 8.23. Found: K, 5.15; W, 51.10; Mo, 6.02; P, 0.89; Sn, 3.90; H\_2O, 8.10%.

# Synthesis of K3[(C2H3Si)2PM02W9O40]-17H2O (3)

 $K_3[(C_2H_3Si)_2PMo_2W_9O_{40}] \cdot 17H_2O$  was obtained analogously to (1) using the same quantities as above except vinyltrichlorosilane (0.3 mL; 0.2 mmol) instead of C<sub>6</sub>H<sub>5</sub>SnCl<sub>3</sub>. Yield, 1.86 g (61%). Calcd. for C<sub>4</sub>H<sub>40</sub>K<sub>3</sub>Mo<sub>2</sub>O<sub>57</sub>PW<sub>9</sub>Si<sub>2</sub> (M 3051.9): K, 4.27; W, 60.28; Mo, 6.99; P, 1.13; Si, 2.04; H<sub>2</sub>O, 11.15. Found: K, 4.40; W, 58.26; Mo, 6.80; P, 1.06; Si, 1.98; H<sub>2</sub>O, 11.00 %.

#### Synthesis of Cs12[(C4H9SnOH)3(PW9O34)2].19H2O (4)

To a solution of 1.04 g (2.5 mmol) Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O in 10 mL of water at 60-70 °C was added 15 g (45.5 mmol) Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in 50 mL of water and 5 mL conc. HCl under stirring at this temperature for 15 min. Then 1.5 mL (7.6 mmol) C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub> was added quickly to this solution under stirring. The final pH was adjusted to 5 with conc. HCl. The traces of unreacted tungstophosphate were filtered after 10 min. Finely powdered CsCl was added to the filtrate until no more precipitation was observed. The precipitate was collected on a fine glass frit, dried under water aspirator vacuum for 2 hours, washed with saturated CsCl solution and dried overnight under vacuum to give a yield of 12.7 g (72%). Recrystallization from warm water gave white microcrystals.Yield, 10.2 g.(57%). Calcd. for  $C_{12}H_{68}Cs_{12}O_{90}P_2W_{18}Sn_3$  (M 6974.8): P, 0.89; Sn, 5.11; Cs, 22.87; W, 47.45; H<sub>2</sub>O, 4.90. Found: P, 0.67; Sn, 5.24; Cs, 22.90; W, 46.97; H<sub>2</sub>O, 5.00 %.

#### <u>Synthesis of $K_{11}H[(C_2H_3SiOH)_3(PW_9O_{34})_2] \cdot 14H_2O(5)</u></u>$

 $K_{11}H[(C_2H_3SiOH)_3(PW_9O_{34})_2]$ ·14H<sub>2</sub>O was prepared analogously using the same quantities as above except vinyltrichlorosilane (0.96 mL, 7.6 mmol). It was precipitated by adding KCl instead of CsCl because this compound was less soluble than the butyltin analog. Yield, 9.34 g (69%). Calcd. for C<sub>6</sub>H<sub>41</sub>K<sub>11</sub>O<sub>85</sub>P<sub>2</sub>W<sub>18</sub>Si<sub>3</sub> (M 5358.5): Si, 1.57; P, 1.16; K, 8.00; W, 61.79; H<sub>2</sub>O, 4.77. Found: Si, 1.47; P. 1.07; K, 8.33; W, 62.52; H<sub>2</sub>O, 5.00 %.

#### Synthesis of Cs12 (C4H9SnOH)3(AsW9O33)2 +43H2O (6)

To a solution of 0.5 g (2.5 mmol)  $As_2O_3$  in 10 mL of water and 5 mL conc. HCl was added 15 g (45.5 mmol)  $Na_2WO_4$ ·2H<sub>2</sub>O in 50 mL of water warmed at 60-70 °C,

under stirring at this temperature for 30 min. Then 1.5 mL (7.6 mmol) C<sub>4</sub>H<sub>9</sub>SnCl<sub>3</sub> was added quickly to this solution with stirring. The final pH was adjusted to 5 with conc. HCl. Traces of unreacted tungstoarsenate were filtered after 10 min. Finely powdered CsCl was added to the filtrate until no more precipitation was observed. The precipitate was collected on a fine glass frit, dried under a water aspirator vacuum for 2 h, washed with saturated CsCl solution and dried overnight under vacuum, to give a yield of 13.38 g (71%).Calcd. for  $C_{12}H_{89}Cs_{12}O_{112}As_2W_{18}Sn_3$  (M 7463.1): As, 2.01; Sn, 4.77; Cs, 21.37; W, 44.34; H<sub>2</sub>O, 10.37. Found: As, 1.98; Sn, 4.94; Cs, 21.15; W, 44.08; H<sub>2</sub>O, 10.5 %.

# Synthesis of Cs12[(C2H3SiOH)3(AsW9O33)2]·12H2O (7)

 $Cs_{12}[(C_2H_3SiOH)_3(AsW_9O_{33})_2]$ ·12H<sub>2</sub>O was prepared analogously using the same quantities as above except vinyltrichlorosilane, (0.96 mL, 7.6 mmol). It was precipitated by adding CsCl. Yield, 11.96 g (73%) Calcd. for C<sub>6</sub>H<sub>36</sub>Cs<sub>12</sub>O<sub>81</sub>As<sub>2</sub>W<sub>18</sub>Si<sub>3</sub> (M 6486.4): Si, 0.43; As, 2.31; Cs, 24.59; W, 51.02; H<sub>2</sub>O, 3.33. Found: Si, 0.38; As, 2.52; Cs, 24.29; W, 50.98; H<sub>2</sub>O, 3.5%.

#### Synthesis of K4[(C4H9SnOH)SbW11O38H]+12H2O (8)

To a solution of 0.2 mL (1 mmol) of  $C_4H_9SnCl_3$  was added sodium acetate to adjust the pH to 1.5. At this stage the solution is slightly turbid. Powdered Na<sub>6</sub>[SbW<sub>11</sub>O<sub>38</sub>H]·14H<sub>2</sub>O (3.1 g; 1 mmol) was added quickly to this solution under stirring. Within a few seconds most of the tungstoantimonate had dissolved and the solution became clear. The final pH was 5.0. Traces of unreacted tungstoantimonate were filtered out after 10 min. KCl was added to the filtrate in small portions until no more precipitation was observed. The precipitate was collected on a fine glass frit, dried under water aspirator vacuum for 1 h, washed with saturated KCl solution and dried overnight under vacuum, to give a yield of 2.2 g (65 %) Long, needle-like yellow crystals of this solid were obtained by the method of vapor diffusion with ethanol; yield, 1.8 g.(53 %). Calcd. for C<sub>4</sub>H<sub>35</sub>K<sub>4</sub>O<sub>51</sub>SbW<sub>11</sub>Sn (M 3302.5): K, 4.74; Sn, 3.59; Sb, 3.69; W, 61.24; H<sub>2</sub>O, 6.05. Found: K, 4.54; Sn, 3.75; Sb, 3.50; W, 61.07; H<sub>2</sub>O, 6.75 %.

#### Synthesis of K2[(C2H3Si)2SbW11O39H].16H2O (9)

 $K_2[(C_2H_3Si)_2SbW_{11}O_{39}H]$ ·16H<sub>2</sub>O was prepared analogously using the same quantities as above except vinyltrichlorosilane,  $C_2H_3SiCl_3$  (0.3 mL; 2 mmol). It was precipitated by adding KCl. Yield, 1.98 g (60%). Calcd. for  $C_4H_{39}K_2O_{55}SbW_{11}Sn$  (M 3245.8): Si, 1.73; K, 2.41; Sb, 3.75; W, 62.31; H<sub>2</sub>O, 8.87. Found: Si, 1.67; K, 2.52; Sb, 3.65; W, 62.14; H<sub>2</sub>O, 9.00 %.

#### Synthesis of K4 (C4H9SnOH)BiW11O38H ·10H2O (10)

To a solution of 0.2 mL (1 mmol) of  $C_4H_9SnCl_3$  was added sodium acetate to adjust the pH to 1.5. At this stage the solution is slightly turbid. Powdered Na<sub>6</sub>[BiW<sub>11</sub>O<sub>38</sub>H]·14H<sub>2</sub>O (3.1 g; 1 mmol) was added quickly to this solution under stirring. Within a few seconds most of the tungstobismutate had dissolved and the solution became clear. The final pH was 5.0. Traces of unreacted tungstobismutate were filtered out after 10 min. KCl was added to the filtrate in small portions until no more precipitation was observed. The precipitate was collected on a fine glass frit, dried under water aspirator vacuum for 1 h, washed with saturated KCl solution and dried overnight under vacuum to give a yield of 2.27 g (68%). A white powder of this solid was obtained by the method of vapor diffusion with ethanol; yield, 1.9 g.(59%). Calcd. for C<sub>4</sub>H<sub>31</sub>K<sub>4</sub>O<sub>49</sub>BiW<sub>11</sub>Sn (M 3369.7): K, 4.64: Sn. 3.52; W, 60.02; Bi, 6.20; H<sub>2</sub>O, 5.34. Found: K, 4.64; Sn, 3.52; W, 60.02; Bi, 6.20; H<sub>2</sub>O, 5.34 %.

#### Synthesis of K2[(C2H3Si)2BiW11O39H]·14H2O (11)

 $K_2[(C_2H_3Si)_2BiW_{11}O_{39}H] \cdot 14H_2O$  was prepared analogously to (10) using the same quantities as above except vinyltrichlorosilane (0.3 mL, 2 mmol), instead of

C<sub>4</sub>H<sub>9</sub>SnCl. It was precipitated by adding KCl. Yield, 2 g (62%) Calcd. for  $C_4H_{35}K_2O_{55}BiW_{11}Si_2$  (M 3296.9): Si, 1.70; K, 2.36; W, 61.37; Bi, 6.34; H<sub>2</sub>O, 7.64. Found: Si, 1.56; K, 2.48; W, 61.05; Bi, 6.04; H<sub>2</sub>O, 7.64 %.

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