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Richard Villanneau, Aïcha Ben Djamâa, Lise-marie Chamoreau, Geoffrey Gontard, Anna Proust. Bisorganophosphonyl and -Organoarsenyl Derivatives of Heteropolytungstates as Hard Ligands for Early-Transition-Metal and Lanthanide Cations. *European Journal of Inorganic Chemistry*, 2013, 2013 (10-11), pp.1815-1820. 10.1002/ejic.201201257 . hal-04564842

**HAL Id: hal-04564842**

**<https://hal.science/hal-04564842>**

Submitted on 30 Apr 2024

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## Bis-organophosphonyle and -organoarsonyle derivatives of heteropolytungstates as hard ligands for early-transition metal cations and lanthanides

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Anna Proust<sup>[a]</sup>

*Dedicated to Professor Michael T. Pope on the occasion of his 80<sup>th</sup> birthday.*

**Keywords:** polyoxometalates hybrids / phosphonate / coordination chemistry / lanthanum / early-transition cations

Coordination properties of bis-organophosphonyle and -organoarsonyle derivatives of heteropolytungstates were studied in organic medium towards lanthanides and early-transition metal cations. This new class of vacant polyoxometalates (POMs) hybrids proved to conserve coordination sites after the grafting of the {RP=O}<sup>2+</sup> or {RAs=O}<sup>2+</sup> groups onto the trivacant A, $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> and B, $\alpha$ -[AsW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> platforms. The consequence of the presence respectively free {P=O} or {As=O} groups is an increase of the hardness (according to Pearson's HSAB theory) of the coordination site in these anions.

While soft divalent transition metal cations were hardly coordinated with these hybrid monovacant POMs, complexes with hard cations from s group (Ca<sup>2+</sup>), lanthanides (La<sup>3+</sup>, Ce<sup>3+</sup>) and d<sup>0</sup> early-transition metal were obtained and studied, in particular by single crystal X-Ray diffraction. Due to the possibility to modify the trivacant platform, the type of the grafted function (phosphonyle or arsonyle) or the organic function R at once, these systems offer a unique possibility to finely modulate the coordination sphere of the cation.

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Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

### Introduction

The covalent incorporation of organic derivatives of *p*-block elements (such as {SiR}, {SnR}, {PR} or {AsR}) into polyoxometalate (POM) frameworks has been well documented in the past fifteen years.<sup>[1-2]</sup> These organically-derivatized POMs are referenced as class II organic/inorganic POMs hybrids, compared to class I compounds obtained through electrostatic or weak interactions between the organic and inorganic partners.<sup>[3]</sup> They have found numerous applications either in reactivity studies - in particular in the field of catalytic oxidation reactions<sup>[4]</sup> - or in molecular nanosciences. Recent examples include the covalent immobilization of POMs on various surfaces, being porous<sup>[5,6]</sup> or planar metallic and semi-conductive materials.<sup>[7-9]</sup> A step beyond may correspond to the design of bi-functional systems of which elaboration could pass by the incorporation of further heterometallic cations in these organic/inorganic POM hybrids. These cations, when suitably chosen, are able to provide new catalytic, luminescent or magnetic properties to the target systems. However, the nucleophilicity of all oxygen atoms dramatically lowered after the grafting of the organic functions, so that their coordination chemistry is then in general very poor. Yet, a few examples of class II organically-derivatized POMs allow the complexation of transition-metal cations either *via* oxygen atoms (including those of RP=O groups)<sup>[10]</sup> or through the covalent

linkage of organometallic catalysts to POMs scaffolds. Wilkinson-type complexes, metallo-salen or N-Heterocyclic carbenes Pd complexes have been successively described by using the latter path,<sup>[11-13]</sup> while photosensitization of POMs by covalent anchorage of chromophores is under active investigation.<sup>[14]</sup> We have recently studied the coordination chemistry of vacant organophosphonate derivatives of POMs towards Zr<sup>4+</sup> or Ln<sup>3+</sup> (Ln = La, Ce, Nd...). Indeed, we have shown that the anions A- $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>{P(O)R}<sub>2</sub>]<sup>5-</sup> (R = *t*Bu, Ph) are able to form discrete monomeric (with Ln<sup>3+</sup>) or dimeric (with Zr<sup>4+</sup>) complexes in which the cations are bound to oxygen atoms of the {PW<sub>9</sub>O<sub>34</sub>} units and/or of the {RP=O} groups.<sup>[15]</sup> In this work, we have extended these preliminary studies to the reactivity of various cations from s group (Ca<sup>2+</sup>) or early-transition metals (Ti<sup>4+</sup> and V<sup>5+</sup>). We have also checked the comparative behaviour of La<sup>3+</sup> ions towards organo-arsonyle and -phosphonyle derivatives of A- $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> in the one hand, and of organo-phosphonyle derivatives of A- $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> and B- $\alpha$ -[AsW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> anions in the other hand.

### Results and Discussion

#### Comparative coordination of La<sup>3+</sup> ions with bis-organophosphonyle and bis-organoarsonyle derivatives of A- $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> or B- $\alpha$ -[AsW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup>

In a previous work, we have explored the coordination properties of the vacant bis-phosphonyle derivatives of the phosphotungstates A- $\alpha$ -[PW<sub>9</sub>O<sub>34</sub>{P(O)R}<sub>2</sub>]<sup>5-</sup> (R = Ph, *t*Bu) anions. The preparation and crystallographic structure of their Zr<sup>4+</sup> (anion **1**, figure 1) and La<sup>3+</sup> (anion **2**, figure 2) complexes have been described in a preliminary communication.<sup>[15]</sup> We have thus shown that four oxygen atoms of these anions still have nucleophilic properties despite the grafting of two {RP=O} functions: two from these {RP=O} groups and the two free O atoms of the lacuna in the case

of the coordination of the  $Zr^{4+}$  ions. Monomeric complex was also obtained by reacting  $A-\alpha-[PW_9O_{34}\{P(O)R\}_2]^{5-}$  with an excess of  $Ln^{3+}$  ions.

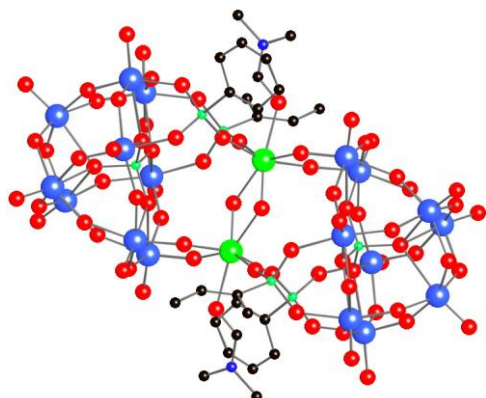


Figure 1. Structure of the anion  $[PW_9O_{34}\{P(O)tBu\}_2]^{2-}\{Zr(dmf)(\mu-OH)\}_2^+$  (**1**) W atoms in blue, O atoms in red, C atoms in black, N atoms in deep blue, P atoms are small green balls, Zr atoms are big green balls

We observed in this case that the POMs act as bidentate ligands, only the oxygen atoms of the two  $\{RP=O\}$  groups being coordinated to the lanthanides (see figure 2a). This particular coordination mode being *a priori* unexpected, we tried to modulate the coordination site of the organophosphonyl POM by varying:

i) the nature of the polyoxoanionic platform ( $B-\alpha-[AsW_9O_{33}]^{9-}$  and  $A-\alpha-[PW_9O_{34}]^{9-}$ ). The synthesis of the organophosphonyl derivatives of  $B-\alpha-[AsW_9O_{33}]^{9-}$  has been performed, leading to the preparation of  $(nBu_4N)_3NaH[AsW_9O_{33}\{P(O)tBu\}_2]$  and  $(nBu_4N)_3NaH[AsW_9O_{33}\{P(O)(CH_2CH_2CO_2H)\}_2]$ .<sup>[6]</sup>

ii) the type of the grafted function (phosphonyl vs arsonyl). The compounds  $(nBu_4N)_3NaH[PW_9O_{34}\{As(O)C_6H_5\}_2]$  and  $(nBu_4N)_3NaH[PW_9O_{34}\{As(O)C_6H_4-p-NH_2\}_2]$  have been thus obtained by reacting  $Na_8H[A,\beta-PW_9O_{34}]\cdot 24H_2O$  with the corresponding organoarsonic acid (see supplementary informations for the details of the syntheses).

iii) the function linked to the organic fragment. As mentioned above, several organophosphonic and organoarsonic acids were used in these syntheses.

All these POM hybrids were obtained by extrapolation of the method used for the synthesis of the  $A-\alpha-[PW_9O_{34}\{P(O)R\}_2]^{5-}$  anions.<sup>[16]</sup> The reaction of these POMs hybrids with 1.5 equivalents of  $La(NO_3)_3\cdot 6H_2O$  or  $LaCl_3\cdot 7H_2O$  at room temperature in acetonitrile led systematically to the formation of complexes of lanthanum ions with a 1:1 POM: $La^{3+}$  stoichiometry. Their recrystallization in dimethylformamide (dmf) allowed us to obtain single-crystals that were suitable for an X-ray diffraction analysis. The details of the coordination of the  $La^{3+}$  ions in the different complexes are shown in figure 2. In these compounds,  $La^{3+}$  ions display all a coordination number equal to 8 with various solvents molecules. Furthermore, in these particular cases, the modifications of the nature of the POM subunits or of the  $\{As/P=O\}$  do not modify dramatically the La-O distances: the average values in the three compounds are equivalent (2.49(12) Å for anion **2**, 2.52(15) Å for **3** and 2.55(9) Å for **4**). It is also noteworthy that the La-O distances involving the oxygen atoms of the  $\{As/P=O\}$  functions do not depend on the As/P atom ( $d(O_{As}-La) = 2.373(3)$  Å and 2.438(3) Å for **3**;  $d(O_p-La) = 2.367(8)$  Å and 2.404(7) Å for **2**). Nevertheless, they all remain significantly shorter than those involving the solvents molecules (in the range 2.481(9) to 2.66(4) Å, within the error limits). However, the coordination of the  $La^{3+}$  to the anions  $[PW_9O_{34}\{As(O)C_6H_4-p-NH_2\}_2]^{5-}$  and  $[AsW_9O_{33}\{P(O)CH_2CH_2CO_2H\}_2]^{5-}$  in complexes **3** and **4** are significantly different from that observed in anion **2**. Indeed the POMs subunits in **3** and **4** play the role of tetradentate ligands owing to the direct linking of the two oxygen atoms which delimit the lacuna of  $\{XW_9\}$  subunits and which are not involved in the grafting of the  $\{RP=O\}$  or  $\{RAS=O\}$  functions. These interactions are thus probably weak and energy differences between the bidentate and tetradentate states of the POMs ligands may be low in this family of complexes.

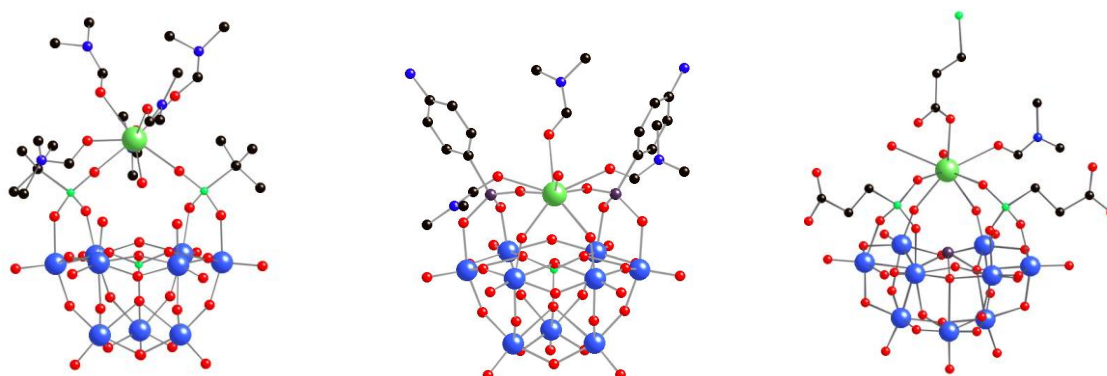


Figure 2. Structures of the anions  $[PW_9O_{34}\{P(O)tBu\}_2\{La(dmf)_5(H_2O)\}]^{2-}$  (**2**) (left),  $[PW_9O_{34}\{As(O)C_6H_4-p-NH_2\}_2\{La(dmf)_3(H_2O)_2\}]^{2-}$  (**3**) (middle) and details of the coordination of the  $La^{3+}$  ions in polymeric  $[AsW_9O_{33}\{P(O)CH_2CH_2CO_2H\}_2\{La(dmf)(H_2O)_2\}]_x$  compound (**4**) (right).

More interestingly, in the case of the  $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2]^{5-}$  POM hybrid, we did not isolate a discrete complex in the solid state, but a polymeric assembly of  $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}$  moieties. Indeed, we observed the coordination of each lanthanum ion by one carboxylate function of a second  $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}$  subunit, leading to the formation of wriggled chains (figure 3), the second carboxylic acid function remaining free. The organization of the subunits into chains may hardly be conserved in solution. This has been also confirmed experimentally by the presence of a single set of data for the  $\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}$  functions in NMR spectroscopy ( $^{31}\text{P}$  and  $^{13}\text{C}$ ), proving thus the equivalence of all carboxylic chains in solution.

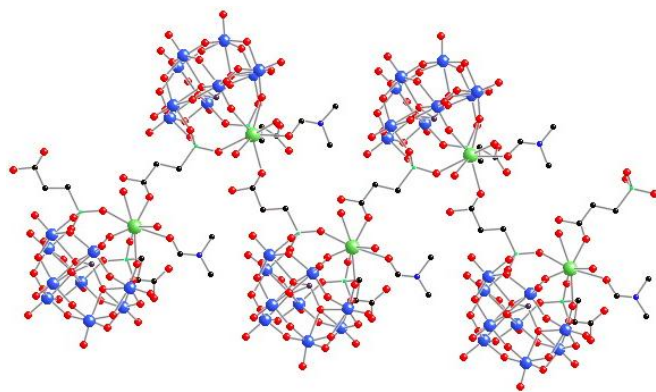


Figure 3. Structure of the polymeric  $[\{\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}_x$  compound (4).

Lastly, it is noteworthy that the formation of only monomeric moieties with Ln:POMs stoichiometry of 1:1 has been observed, whatever the nature of the polyoxoanionic platforms or the organic functions we used. As previously underlined by Francesconi *et al.* the dimerization of lanthanides-containing heteropolyanions may indeed be hardly obtained in organic media, because of a higher electrostatic repulsion between the highly charged POMs in such less polar solvents.<sup>[17]</sup>

### Coordination Properties of Bis-organophosphonyle Derivatives of POMs toward other metallic cations.

In order to have an overlook on the coordination properties of the bis-organophosphonyle derivatives of the trivalent POMs, we have studied their reactivity toward alkaline earth-metal and d transition metal cations. Interestingly, we were not able to isolate or identify complexes with divalent cations from the first row transition metals. In most cases, despite variation of the experimental conditions, we observed the appearance of several peaks by  $^{31}\text{P}$  NMR spectroscopy directly on the mother liquor, this attesting the apparent formation of a mixture of species, depending on the cation. However, despite all our efforts, only the initial POMs were systematically recovered by crystallization or precipitation from the mother liquor. Similar results were obtained with other soft cations such as  $\text{Pd}^{2+}$  or  $\text{Ru}^{2+}$ . On the other hand, the behaviour of these POM hybrids toward harder cations (other than  $\text{Ln}^{3+}$  or  $\text{Zr}^{4+}$ ) is obviously different as presented below.

**Alkaline earth-metal complexes of  $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2]^{5-}$  anion: formation of  $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2\{\text{Ca}(\text{H}_2\text{O})(\text{dmf})_2\}]^{3-}$  (anion 5).** The reaction of  $(n\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2]$  with an excess (1.5 equivalents) of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{BaCl}_2$  leads to the formation of two similar 1:1 complexes between the POM and the alkaline earth-metal ions at room temperature, as attested by their

IR spectra. The structure of the  $\text{Ca}^{2+}$  complex  $(n\text{Bu}_4\text{N})_3[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2\{\text{Ca}(\text{H}_2\text{O})(\text{dmf})_2\}]^{3-}$  (**5**) - is shown figure 3. In this structure, the  $\text{Ca}^{2+}$  ion is in six coordination, the POM playing the role of bidentate ligands just as observed in anion 2. Its coordination is achieved through the coordination of 4 molecules of solvent (two water and 2 dmf). The Ca-O distances involving the oxygen of the phosphonate groups are respectively equal to 2.278(7) Å and 2.300(8) Å.

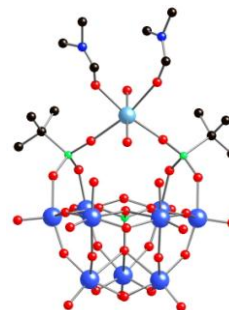


Figure 4. Structure of the anion  $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2\{\text{Ca}(\text{H}_2\text{O})(\text{dmf})_2\}]^{3-}$  (5)

**Titanium complex of  $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2]^{5-}$  anion : formation of  $[\{\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2\}_2\{(\text{CH}_3\text{COCH}_3)\text{Ti}\}_2(\mu\text{-O})]^{4-}$  (anion 6).** The formation of tetravalent titanium complexes of POMs has been largely studied in the literature, in particular in the groups of Nomiyama,<sup>[18]</sup> Kortz<sup>[19]</sup> and/or Kholdeeva.<sup>[20]</sup> Indeed, many complexes have found applications in the field of oxidation catalysis (including epoxidation of various alkanes with  $\text{H}_2\text{O}_2$ ). Regarding their synthesis, few complexes have been prepared in organic solvents despite the important number of complexes described. However, the classical precursors used for their preparation ( $\text{TiO}(\text{SO}_4)$  being probably the most used in the literature) did not react properly in acetonitrile with our POM hybrids. We thus turned ourselves to the unusual  $[\text{TiCl}_4(\text{thf})_2]$  ( $\text{thf}$  = tetrahydrofuran) which is soluble in polar organic media. This reaction was driven in refluxing acetonitrile for 12 hours, leading to the precipitation of fairly pure crude materials (as attested by subsequent controls by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy). Its recrystallization in propanone allowed us to obtain crystals suitable for a single-crystal X-ray analysis. This structure is presented in figure 5. The complete formula of the anion is  $[\{\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2\}_2\{(\text{CH}_3\text{COCH}_3)\text{Ti}\}_2(\mu\text{-O})]^{4-}$  (anion 6), and the crystal lattice contains four tetrabutylammonium cations and three further molecules of propanone. The structure of the anion is really close to that observed in anion 1, the  $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})t\text{Bu}\}_2]^{5-}$  subunits acting as bisbidentate ligands toward a classical  $\{\text{Ti}-\text{O}_b-\text{Ti}\}^{4+}$  linear bridge. The coordination sphere of each  $\text{Ti}^{4+}$  ion is completed by a solvent molecule (propanone) for a distorted octahedral environment. In this structure  $\text{O}_b$  is located on an inversion center, the  $\text{Ti}-\text{O}_b$  distance being equal to 1.8104(7) Å. The  $\text{O}_b-\text{Ti}-\text{O}_{\text{prop}}$  segment ( $\text{O}_{\text{prop}}$  being the oxygen atom of the propanone) is nearly linear (178.64(10) Å), so that the distance  $\text{Ti}-\text{O}_{\text{prop}}$  is quite longer (2.248(4) Å). The Ti-O distances involving the oxygen atoms of the POMs (either linked to W or P atoms) are all equivalent and in the range 1.925(3) Å – 1.960(3) Å.

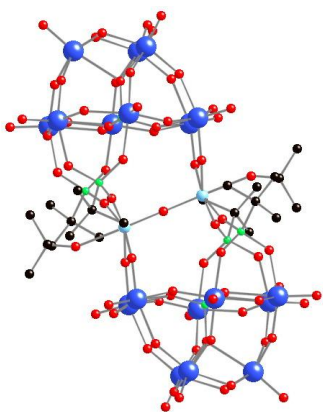


Figure 5. Structure of the anion  $[\{PW_9O_{34}\{P(O)(tBu)_2\}_2\}(\mu-O)]^{4-}$  (6)

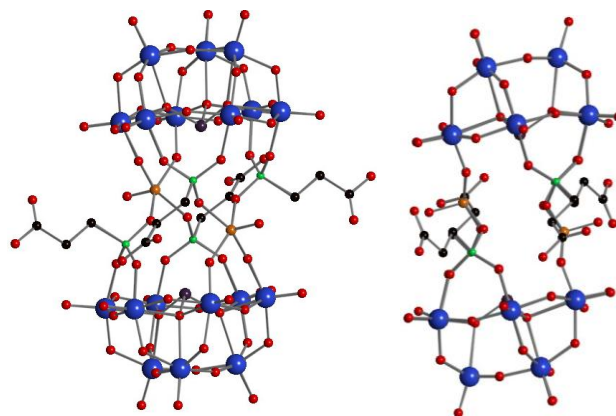


Figure 6. Two different views showing the structure of the anion 7 in  $(nBu_4N)_4[AsW_9O_{33}\{P(O)CH_2CH_2CO_2H\}_2\{VO\}]_2(nBu_4N)_4$  7

**Vanadium (V<sup>V</sup>) complex of [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>]<sup>5-</sup> anion: formation of [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>{VO}]<sub>2</sub><sup>4-</sup> (anion 7).** In relation with our work on the heterogenization of the POM hybrid [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>]<sup>5-</sup>[6] we also focused on the coordination properties of this particular anion. As mentioned above, the presence of the propanoic acid functions led, in the case of the coordination of La<sup>3+</sup> to the formation of wriggled chains in the solid-state. We were wondering if such behaviour (*i.e.* the utilization of these side-functions for further complexation) would be observed with other cations. Reaction with an excess (1.5 equivalents) of V<sup>V</sup> precursor [VOCl<sub>3</sub>] in acetonitrile at room temperature led to the formation of a yellow precipitate, which can be filtered after one night. Its study by solid-state IR and by <sup>51</sup>V and <sup>31</sup>P NMR spectroscopy in solution revealed the presence of a major species. This powder was recrystallized in propanone by slow diffusion of diethylether, leading to the formation of single-crystals suitable for XRD analysis. The crystal structure consists of a discrete dimeric [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>{VO}]<sub>2</sub><sup>4-</sup> anion (7), four tetrabutylammonium ions and five molecules of solvent (one water and four propanone molecules). The structure of the anion (figure 6) may be described as the association of two [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>{VO}]<sup>2-</sup> subunits in which the V<sup>V</sup> ions are in square pyramidal environment. The basis of the square pyramid is constituted by the oxygen atoms of the phosphonate groups of one [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>]<sup>5-</sup> subunits (d(V-O) in the range 1.916(9) to 1.940(10) Å) and by the two unsaturated oxygen atoms of the lacuna of the second sub-unit (d(V-O) in the range 1.836(9) to 1.848(10) Å). The coordination sphere of the vanadium ion is completed by a terminal oxo ligand, with a short (V=O) distance equal to 1.56(1) Å.

While we did not observe any modification of the <sup>31</sup>P NMR signal in propanone after a few days, NMR spectra in more coordinating solvents (dmf or dimethylsulfoxide) were strongly evolving in a few hours. Indeed, after 12 hours, we observed a modification of the colour of the solution (from yellow to deep green) and the presence of a new resonance (29 ppm in dmf) assigned to the free [AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>]<sup>5-</sup> anion. This attribution in dmf was done after addition of a small amount of the precursor (nBu<sub>4</sub>N)<sub>3</sub>NaH[AsW<sub>9</sub>O<sub>33</sub>{P(O)CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H}<sub>2</sub>] directly in the NMR tube. After a few weeks, we observed the precipitation of a yellow/green solid of which IR spectrum is significantly different from that of compound (nBu<sub>4</sub>N)<sub>4</sub>7. However, efforts for elucidating the structure of this new compound remain currently unsuccessful.

Lastly, it is noteworthy that we were not able to coordinate {V<sup>IV</sup>O}<sup>2+</sup> fragments whatever the conditions and/or the vanadyle precursors used.

## Concluding Remarks.

In this work, we elicited the coordination properties of class II POM hybrids incorporating various organo-phosphonyl or -arsonyl functions toward cations from different families of the periodic table, *i. e.* lanthanides (La<sup>3+</sup>), alkaline earth-metals (Ca<sup>2+</sup>) or d-transition metals ions (V<sup>V</sup>, Ti<sup>IV</sup>). These complexes were characterized by various techniques, including X-ray diffraction, IR and <sup>31</sup>P NMR spectroscopies. In the different complexes described in this manuscript, we showed that the POM hybrids may play the role of bidentate, bisbidentate or tetradentate ligands, all coordination modes involving systematically both {P=O} or {As=O} groups of the POMs. However, in the case of the La<sup>3+</sup> complexes, we observed that the coordination of the cations did not necessarily involve the {W=O<sub>t</sub>} oxygen atoms bordering the lacuna. We then concluded that the interaction between the lanthanide and these oxygen atoms is probably weak.

Finally, we have shown that “soft” cations (regarding the HSAB classification by Pearson) are hardly bound to the coordination sites of this particular family of POMs. Indeed, only highly charged cations with small ionic radii were able to be coordinated by the POM hybrids. In order to modulate the properties of the POMs hybrids, it would be interesting to modify the intrinsic nature of these coordination sites by introducing further nucleophilic atoms *via* the side chains or by replacing the {P=O}/{As=O} functions by their {P=S}/{As=S} softer equivalents. These studies are currently in progress and results will be reported in due time.

## Experimental Section

**Materials and methods.** Solvents and other reagents were obtained from commercial sources and used without purification. As(O)(OH)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>-*p*-NH<sub>2</sub>) (TCI), As(O)(OH)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>) (TCI), P(O)(OH)<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H) (Acros Organics) and P(O)(OH)<sub>2</sub>(*t*Bu) (Acros Organics) were used as received. (nBu<sub>4</sub>N)<sub>3</sub>NaH[As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>{P(O)(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>]<sup>[6]</sup> was prepared following a modification of the protocole of synthesis of the bisphosphonyle derivatives of the A-α-[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> anion,<sup>[16]</sup> by using Na<sub>8</sub>H[B,α-As<sup>III</sup>W<sub>9</sub>O<sub>33</sub>]·24H<sub>2</sub>O<sup>[21]</sup> instead of β-A-Na<sub>8</sub>H[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup>·24H<sub>2</sub>O. IR spectra were recorded from KBr pellets on a Biorad FT 165 spectrometer. The <sup>1</sup>H and {<sup>1</sup>H} <sup>31</sup>P NMR solution spectra were recorded in 5 mm o.d. tubes on a Bruker Avance II 300 spectrometer equipped with a QNP probehead. The <sup>51</sup>V NMR spectra were recorded on a Bruker Avance III 400. Chemical shifts are referenced with respect to external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and 90% VOCl<sub>3</sub> (<sup>51</sup>V) with 10 % of C<sub>6</sub>D<sub>6</sub>. Elemental analyses were

performed by the Service Central d'Analyse of the CNRS (Vernaison, France) or by the service de microanalyse (ICSN, Gif sur Yvette, France).

#### Synthesis and characterization of $(n\text{Bu}_4\text{N})_2[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-}\text{NH}_2\}_2\{\text{La}(\text{dmf})_3(\text{H}_2\text{O})_2\}]\cdot 3\text{dmf}$ , compound $(n\text{Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$ .

$(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-}\text{NH}_2\}_2]$  (1.00g, 0.29 mmol) and  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (0.19g, 0.45 mmol, 1.5 eqv) were dissolved in 30 ml of acetonitrile. The solution was then refluxed overnight and allowed to stand at room temperature for a few days, during which a yellow microcrystalline precipitate formed. This precipitate was filtered then recrystallized in the minimum of dmf. After a few weeks, yellow single crystals of  $(n\text{Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$  formed (0.41 g, 0.11 mmol, yielding 38.5 %), were collected and analysed by X-ray diffraction.

Anal. Calcd for  $\text{C}_{62}\text{H}_{129}\text{As}_2\text{La}_1\text{N}_{10}\text{O}_{43}\text{P}_1\text{W}_9$ : C, 20.25; H, 3.54; N, 3.81. Found: C, 20.07; H, 3.39; N, 3.51. NMR  $^1\text{H}$  (121.5 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) 11.93. IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3456 (s), 3363 (s), 3234 (w), 2962 (s), 2934 (m), 2874 (s), 1649 (vs), 1594 (s), 1504 (w), 1486 (w), 1385 (m), 1088 (s), 1031 (m), 962 (s), 940 (m), 914 (w), 850 (vs), 775 (s), 740 (s), 675 (sh), 522 (m).

#### Synthesis and characterization of $(n\text{Bu}_4\text{N})_2[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]\cdot \text{dmf}$ , compound $(n\text{Bu}_4\text{N})_2(\mathbf{4})$ .

$(n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$  (1.00g, 0.31 mmol) and  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (0.20g, 0.46 mmol, 1.5 eqv) were dissolved in 10 ml of acetonitrile. The mixture was allowed to stand at room temperature for a few days, leading to the formation of a white precipitate. Since the IR spectrum of this solid shows that the expected compound  $(n\text{Bu}_4\text{N})_2(\mathbf{4})$  contains significant amounts of nitrates, it has been recrystallized in dmf at room temperature, leading to the formation of uncoloured crystals, suitable for an X-ray diffraction analysis ( $m = 0.65$  g, yielding 65%).

Anal. Calcd for  $\text{C}_{41}\text{H}_{93}\text{As}_1\text{La}_1\text{N}_3\text{O}_{42}\text{P}_2\text{W}_9$ : C, 15.24; H, 2.90; N, 1.30. Found: C, 15.57; H, 3.00; N, 1.31. NMR  $^1\text{H}$  (121.5 MHz, dmf):  $\delta$  (ppm) 19.07.  $^{13}\text{C}\{^1\text{H}\}$  (75.6 MHz, dmf/ $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) 175.2 (d,  $^3J_{\text{PC}} = 143$  Hz, 2 C,  $\{-\text{COOH}\}$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 674 (m), 747 (s), 784 (s), 823 (s), 887 (s), 968 (s), 1024 (s), 1111 (m), 1168 (s), 1253 (m), 1384 (m), 1437 (w), 1419 (w), 1484 (m), 1649 (s), 1718 (m), 2874 (m), 2935 (m), 2962 (s).

#### Synthesis and characterization of $(n\text{Bu}_4\text{N})_3[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{tBu}\}_2\{\text{Ca}(\text{H}_2\text{O})_2(\text{dmf})_2\}]$ , compound $(n\text{Bu}_4\text{N})_3(\mathbf{5})$ .

$(n\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{tBu}\}_2]$  (1 g, 0.31 mmol) and  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (0.100 mg, 0.46 mmol, 1.5 eqv) were dissolved in 10 mL of acetonitrile. The resulting uncoloured solution was stirred overnight, at room temperature. Slow evaporation of this solution led to the formation of a polycrystalline material, identified as  $(n\text{Bu}_4\text{N})_3[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{tBu}\}_2\{\text{Ca}(\text{H}_2\text{O})_2\}] \cdot 0.33(n\text{Bu}_4\text{N})\text{NO}_3$  (0.67g, yielding 64 %) owing to the chemical analysis and IR spectroscopy. The solid was recrystallized in a minimum of dmf. Crystals suitable for an X-ray diffraction analysis of  $(n\text{Bu}_4\text{N})_3(\mathbf{5})$  were obtained after several weeks.

Anal. Calcd  $\text{C}_{61.28}\text{H}_{145.88}\text{CaN}_{3.66}\text{O}_{41}\text{P}_3\text{W}_9$ : C, 21.79; H, 4.35; N, 1.52. Found: C, 21.96; H, 4.39; N, 1.47. NMR  $\{^1\text{H}\}^1\text{H}$  (121.5 MHz,  $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$ , 300 K):  $\delta$  (ppm) 33.65 (2 P,  $\text{P}(\text{O})\text{tBu}$ ); -11.92 (1 P,  $\text{PW}_9\text{O}_{34}$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2962 (s), 2935 (m), 2874 (m), 1480 (m), 1384 (m),<sup>\*</sup> 1177 (w), 1091 (s), 1004(m), 960 (s), 876 (s), 841(s), 747 (s), 598 (m).

#### Synthesis and characterization of $(n\text{Bu}_4\text{N})_4[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{tBu}\}_2\{(\text{CH}_3\text{COCH}_3)\text{Ti}(\mu\text{-O})\}]$ , compound $(n\text{Bu}_4\text{N})_4(\mathbf{6})$ .

\* The shape of this peak (very sharp) and its unusual intensity in this family of POMs hybrids tends to confirm the presence of  $\text{NO}_3^-$  ions (under the form of a  $(n\text{Bu}_4\text{N})^+$  salt) in the sample at this step of the reaction.

$(n\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{tBu}\}_2]$  (0.5 g, 0.16 mmol) and  $[\text{TiCl}_4(\text{thf})_2]$  (0.078 mg, 0.23 mmol, 1.5 eqv) were dissolved in 10 mL of acetonitrile. The resulting solution was refluxed overnight, leading to the formation of 0.15 g of a pale yellow precipitate. The mother solution was discarded after analysis by  $^{31}\text{P}$  NMR spectroscopy since the corresponding spectrum displayed several peaks, which may be attributed to different POMs, among which only  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  was recognized. The yellow solid was recrystallized in propanone by slow diffusion of diethylether. Light yellow crystals (0.020 g, yielding 4%) of  $(n\text{Bu}_4\text{N})_4(\mathbf{6})\cdot 3\text{CH}_3\text{COCH}_3$  suitable for an X-ray diffraction analysis were thus obtained. NMR  $\{^1\text{H}\}^1\text{H}$  (121.5 MHz,  $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$ , 300 K):  $\delta$  (ppm) 30.36 (2 P,  $\text{P}(\text{O})\text{tBu}$ ); -15.86 (1 P,  $\text{PW}_9\text{O}_{34}$ ). IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2962 (s), 2935 (m), 2874 (m), 1484 (m), 1382 (m), 1114 (m), 1024 (s), 972 (s), 945 (s), 863 (vs), 785 (vs), 668 (m).

#### Synthesis and characterization of $(n\text{Bu}_4\text{N})_4[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{VO}\}]_2$ , compound $(n\text{Bu}_4\text{N})_4(\mathbf{7})$ .

$(\text{TBA})_3\text{H}_2[\text{AsW}_9\text{O}_{33}(\text{HOOCCH}_2\text{CH}_2\text{PO}_2)]_2$  (2.00 g ; 0.65 mmol) was dissolved in acetonitrile (10 mL). A solution of  $\text{VOCl}_3$  was prepared (0.17 mg; 0.98 mmol ; 1.5 eqv) in 10 mL of acetonitrile separately. The dropwise addition of the latter solution in the former led to the progressive precipitation of the expected complex  $(n\text{Bu}_4\text{N})_4(\mathbf{7})$  as a yellow powder ( $m = 1.50$ g, yielding 76 %). This precipitate was filtered, washed with acetonitrile and diethylether and can be recrystallized in propanone by slow diffusion of diethylether. After 3 days yellow crystals of  $(n\text{Bu}_4\text{N})_4(\mathbf{7})\cdot \text{H}_2\text{O}\cdot 4\text{CH}_3\text{COCH}_3$  suitable for X-ray diffraction study were obtained. Anal. Calcd  $\text{C}_{76}\text{H}_{164}\text{N}_4\text{As}_2\text{P}_4\text{W}_{18}\text{O}_{80}\text{V}_2$ : C, 14.97; H, 2.71; N, 0.92. Found: C, 14.58; H, 2.39; N, 0.75 (the chemical analysis was performed on a previously dried sample. It is compatible with the loss of 3 propanone). NMR  $^{51}\text{V}$  (105.2 MHz, dmf/ $\text{CD}_3\text{CN}$ , 300K):  $\delta$  (ppm) -336. NMR  $\{^1\text{H}\}^1\text{H}$  (121.5 MHz, dmf/ $\text{CD}_3\text{CN}$ , 300 K):  $\delta$  (ppm) 31.56. IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3440 (s), 3205 (sh), 2962 (s), 2935 (m), 2874 (m), 1715 (m), 1654 (m), 1484 (m), 1382 (m), 1251 (m), 1181 (m), 1034 (s), 973 (s), 908 (s), 815 (vs), 780 (vs), 747 (s).

**Supporting Information:** Detailed syntheses of the bisorganoarsonyle precursors of POMs. IR spectra of compounds  $(n\text{Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$ ,  $(n\text{Bu}_4\text{N})_2(\mathbf{4})$ ,  $(n\text{Bu}_4\text{N})_3(\mathbf{5})$ ,  $(n\text{Bu}_4\text{N})_4(\mathbf{6})\cdot 3\text{CH}_3\text{COCH}_3$  and  $(n\text{Bu}_4\text{N})_4(\mathbf{7})\cdot \text{H}_2\text{O}\cdot 4\text{CH}_3\text{COCH}_3$ . Table of crystallographic data and Cif files for compounds  $(n\text{Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$  to  $(n\text{Bu}_4\text{N})_4(\mathbf{7})\cdot \text{H}_2\text{O}\cdot 4\text{CH}_3\text{COCH}_3$  (respectively CCDC numbers 905231 to 905235).

## Acknowledgments

This work was supported by the Centre National de la Recherche Scientifique (CNRS) and the Université Pierre et Marie Curie – Paris 6. The authors thank Mme Séverine Renaudineau for the synthesis of alkaline salts of the POMs precursors, and Mlle Albena Petkova for achieving the crystallization of compound  $(n\text{Bu}_4\text{N})_3(\mathbf{5})$ .

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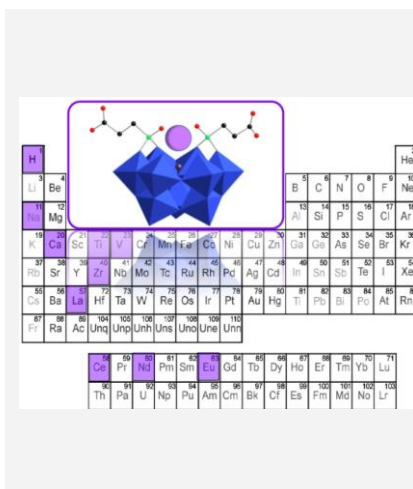
Received: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

## Layout 1:

((Key Topic))

**Rock in a hard place:** Coordination properties of class II POM hybrids incorporating organo-phosphonyl or -arsonyl functions were studied toward cations from different families of the periodic table ( $\text{La}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{V}^{5+}$ ,  $\text{Ti}^{4+}$ ). The structure of all complexes was determined by single-crystal X-ray diffraction, showing evidences for the particular hardness of the coordination sites in these POM hybrids.



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Bis-organophosphonyl and -organoarsonyl derivatives of heteropolytungstates as hard ligands for early-transition metal cations and lanthanides

**Keywords:** polyoxometalates hybrids / phosphonate / coordination chemistry / lanthanum / early-transition cations



## Supporting Information

**Synthesis of  $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]$ :**  $(n\text{Bu}_4\text{N})\text{Br}$  (0.42 g, 1.31 mmol),  $\text{As}(\text{O})(\text{OH})_2(\text{C}_6\text{H}_4\text{-}p\text{-NH}_2)$  (0.15 g, 7.2 mmol) and  $\beta\text{-A-Na}_8\text{H}[\text{PW}_9\text{O}_{34}]\approx 24\text{H}_2\text{O}^{[\text{S}1]}$  (1 g, 0.35 mmol) were introduced in a 100 mL flash with a rod neck. Acetonitrile (20 mL) and concentrated chlorhydric acid (0.12 mL) were successively added at room temperature. The suspension was then heated overnight and filtered in order to remove a white precipitate, which contained a mixture of sodium chloride and bromide but also an appreciable amount of the expected  $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]$  as attested by IR spectrum. The light yellow filtrate (characterized in  $^{31}\text{P}$  NMR spectroscopy by a single resonance at -10.97 ppm) was evaporated leading to the formation of a yellow precipitate of  $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]\cdot 0.2(n\text{Bu}_4\text{N})\text{Br}$ , which was washed with ethanol (20 mL). This precipitate can be recrystallized in DMF. Crystals of  $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]\cdot x\text{DMF}$  were obtained by slow evaporation of this solution ( $m = 0.77\text{g}$ , yielding 66 %). An X-ray diffraction study was performed, but due to the poor quality of the crystals, the resolution of the structure did not allow us to obtain a sufficient model to be published. However, the crystallographic data obtained confirmed the presence of a  $[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]^{5-}$  anion and of three tetrabutylammonium cations in the structure (quadratic system; space group:  $I4_1md$ ;  $a = 37.975(3)\text{\AA}$ ,  $c = 14.450(1)\text{\AA}$ ,  $V = 20838(3)\text{\AA}^3$ ).

Anal. Calc. for  $\text{C}_{63.2}\text{H}_{128.8}\text{As}_2\text{Br}_{0.2}\text{N}_{5.2}\text{Na}_1\text{O}_{36}\text{P}_1\text{W}_9$ : C, 22.25; H, 3.79; N, 2.14. Found: C, 22.14; H, 3.89; N, 2.36. IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 749 (s), 788 (s), 841 (s), 867 (m), 903 (sh), 940 (s), 958 (s), 1033 (m), 1083 (s), 1484 (m), 1597 (s), 1631 (s), 2874 (m), 2933 (m), 2962 (s), 3067 (s).  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CD}_3\text{CN}$ , 300 K)  $\delta$  (ppm): 10.71.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CD}_3\text{CN}$ , 300 K)  $\delta$  (ppm): 0.97 (t, 37H,  $(\text{CH}_3(\text{CH}_2)_3)_4\text{N}^+$ ), 1.38 (h, 25H,  $(\text{CH}_3\text{CH}_2(\text{CH}_2)_2)_4\text{N}^+$ ), 1.67 (m, 25H,  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$ ), 3.17 (m, 25H,  $(\text{CH}_3(\text{CH}_2)_2\text{CH}_2)_4\text{N}^+$ ), 6.77 (d,  $J = 8.0$  Hz, 4H,  $p\text{-C}_6\text{H}_4\text{-NH}_2$ ), 7.48 (d,  $J = 8$  Hz, 4H,  $p\text{-C}_6\text{H}_4\text{-NH}_2$ ).

### Synthesis of $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_5\}_2]$ :

The synthesis of this compound is similar to that of  $(n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]$ , using  $\text{As}(\text{O})(\text{OH})_2(\text{C}_6\text{H}_5)$  instead of  $\text{As}(\text{O})(\text{OH})_2(\text{C}_6\text{H}_4\text{-}p\text{-NH}_2)$ .

Anal. Calc. for  $\text{C}_{60}\text{H}_{119}\text{As}_2\text{N}_3\text{Na}_1\text{P}_1\text{O}_{36}\text{W}_9$ : C, 21.73; H, 3.62; N, 1.27. Found: C, 21.31; H, 3.61; N, 1.27. IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 735 (s), 805 (s), 850 (s), 871 (sh), 911 (m), 940 (s), 960 (s), 1030 (m), 1087 (s), 1484 (m), 2874 (m), 2935 (m), 2962 (s), 3050 (s).  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CD}_3\text{CN}$ , 300 K)  $\delta$  (ppm): 10.88.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CD}_3\text{CN}$ , 300 K)  $\delta$  (ppm): 0.97 (t, 37H,  $(\text{CH}_3(\text{CH}_2)_3)_4\text{N}^+$ ), 1.38 (h, 25H,  $(\text{CH}_3\text{CH}_2(\text{CH}_2)_2)_4\text{N}^+$ ), 1.67 (m, 25H,  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$ ), 3.17 (m, 25H,  $(\text{CH}_3(\text{CH}_2)_2\text{CH}_2)_4\text{N}^+$ ), 7.65 (m, 6H,  $\text{C}_6\text{H}_5$ ), 7.86 (d,  $J = 7$  Hz, 4H,  $\text{C}_6\text{H}_5$ ).

### IR Spectra of all compounds:

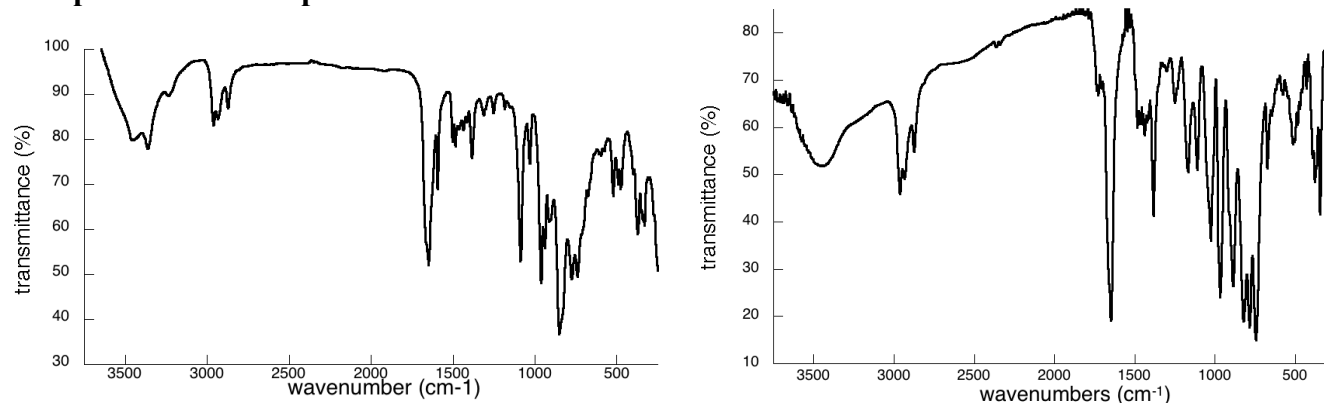


Figure S1: IR Spectra of  $(n\text{Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$  (left) and of  $(n\text{Bu}_4\text{N})_2(\mathbf{4})$  (right)

<sup>S1</sup> R. Massart, R. Contant, J.-M. Fruchart, J.-P. Ciabrini, M. Fournier, *Inorg. Chem.* **1984**, *16*, 2916.

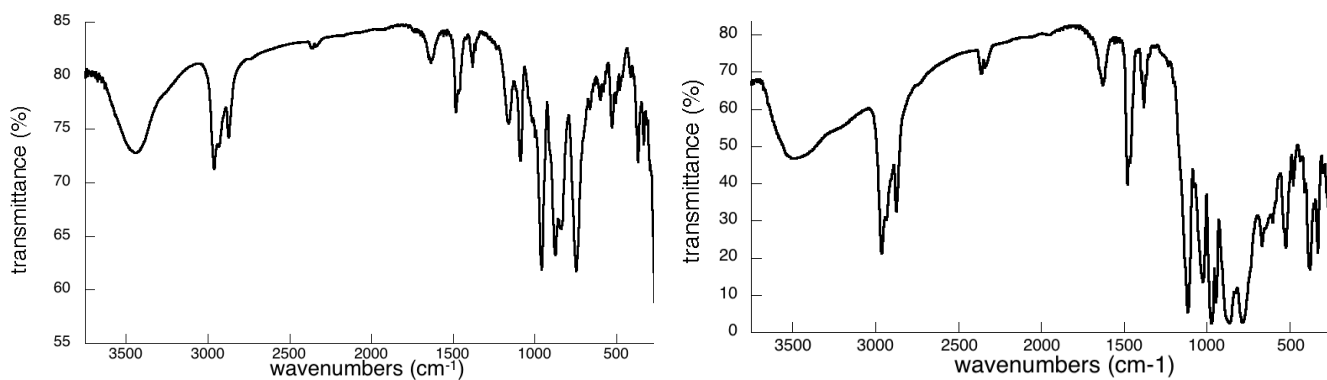


Figure S2: IR Spectra of  $(n\text{Bu}_4\text{N})_3$ (5) (left) and of  $(n\text{Bu}_4\text{N})_4$ (6)·3CH<sub>3</sub>COCH<sub>3</sub> (right)

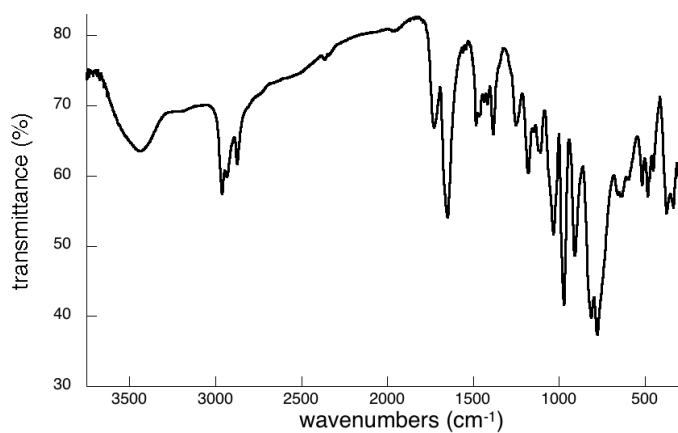


Figure S3: IR Spectrum of  $(n\text{Bu}_4\text{N})_4$ (7)·H<sub>2</sub>O·4CH<sub>3</sub>COCH<sub>3</sub>

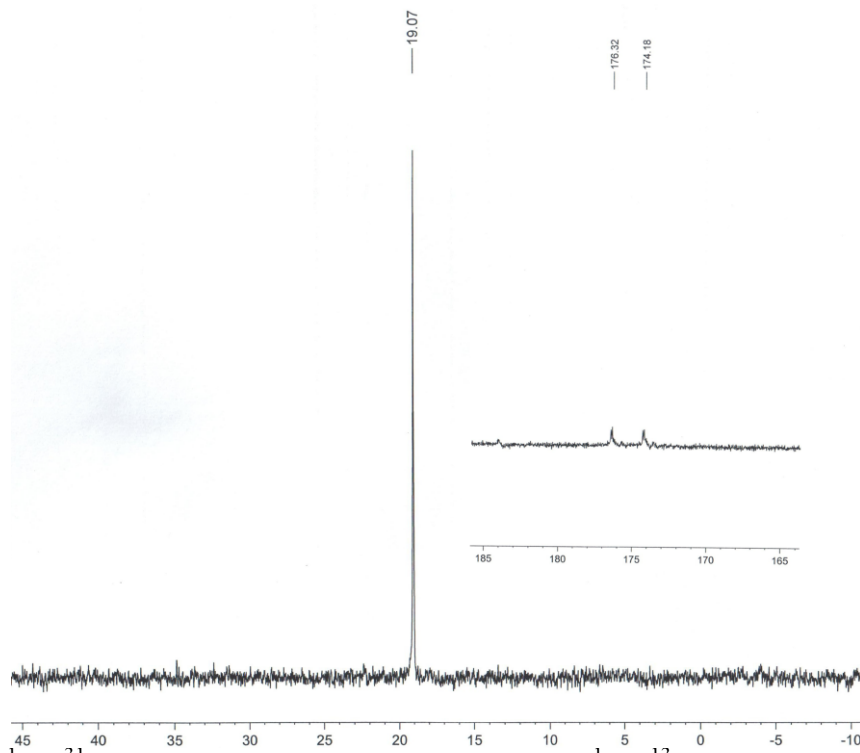


Figure S4:  $\{^1\text{H}\} \text{}^{31}\text{P}$  NMR spectrum (insert: detail of the  $\{^1\text{H}\} \text{}^{13}\text{C}$  spectrum) of  $(n\text{Bu}_4\text{N})_2$ (4)

Table S5: Crystallographic data for compounds  $(n\text{Bu}_4\text{N})_2$ (3)·3dmf to  $(n\text{Bu}_4\text{N})_4$ (7)·H<sub>2</sub>O·4CH<sub>3</sub>COCH<sub>3</sub>.

	( <i>n</i> Bu <sub>4</sub> N) <sub>2</sub> (3)3dmf	( <i>n</i> Bu <sub>4</sub> N) <sub>2</sub> (4)	( <i>n</i> Bu <sub>4</sub> N) <sub>3</sub> (5)	( <i>n</i> Bu <sub>4</sub> N) <sub>4</sub> (6)3CH <sub>3</sub> COCH <sub>3</sub>	( <i>n</i> Bu <sub>4</sub> N) <sub>4</sub> (7)H <sub>2</sub> O·4CH <sub>3</sub> COCH <sub>3</sub>
Empirical formula	C <sub>62</sub> H <sub>128</sub> As <sub>2</sub> LaN <sub>10</sub> O <sub>43</sub> PW <sub>9</sub>	C <sub>39</sub> H <sub>17</sub> AsLaN <sub>5</sub> O <sub>42</sub> P <sub>2</sub> W <sub>9</sub>	C <sub>63.5</sub> H <sub>150.5</sub> CaN <sub>5.5</sub> O <sub>41.5</sub> P <sub>3</sub> W <sub>9</sub>	C <sub>95</sub> H <sub>210</sub> N <sub>4</sub> O <sub>78</sub> P <sub>6</sub> Ti <sub>2</sub> W <sub>18</sub>	C <sub>88</sub> H <sub>184</sub> As <sub>2</sub> N <sub>4</sub> O <sub>85</sub> P <sub>4</sub> V <sub>2</sub> W <sub>18</sub>
Formula weight	3676.11	3129.98	3443.03	6247.35	6343.11
Crystal system	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> <sub>1</sub>	<i>P b c a</i>	<i>P n a 2</i> <sub>1</sub>	<i>P 2</i> <sub>1/m</sub>	<i>P 2</i> <sub>1/c</sub>
<i>a</i> [Å]	14.2067(5)	14.1979(7)	18.7583(5)	14.4031(3)	30.5149(6)
<i>b</i> [Å]	14.6927(5)	27.0930(13)	21.7707(5)	28.1920(7)	18.9784(4)
<i>c</i> [Å]	26.0606(9)	51.430(3)	25.8187(6)	20.4657(5)	28.8526(6)
$\alpha$ [°]	90.289(2)	90	90	90	90
$\beta$ [°]	103.714(2)	90	90	93.629(1)	105.291(1)
$\gamma$ [°]	111.2530(10)	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	4900.3(3)	19783.1(17)	10543.9(4)	8293.5(3)	16117.7(6)
<i>Z</i>	2	8	4	2	4
<i>D</i> <sub>calculated</sub> [Mg/m <sup>3</sup> ]	2.491	2.102	2.169	2.495	2.556
$\mu$ [mm <sup>-1</sup> ]	11.715	11.271	9.947	12.656	13.429
<i>F</i> (000)	3436	11152	6532	5760	11328
Crystal size [mm <sup>3</sup> ]	0.33x0.27x0.09	0.30x0.30x0.10	0.17x0.11x0.08	0.20x0.10x0.10	0.15x0.15x0.15
$\theta$ range [°]	1.59–32.63	1.55–30.51	1.87–30.03	1.44–30.63	1.28–28.07
Index ranges	-13 < <i>h</i> < 21 -22 < <i>k</i> < 21 -39 < <i>l</i> < 36	-20 < <i>h</i> < 18 -23 < <i>k</i> < 38 -73 < <i>l</i> < 67	-13 < <i>h</i> < 21 -22 < <i>k</i> < 21 -39 < <i>l</i> < 36	-20 < <i>h</i> < 20 -40 < <i>k</i> < 39 -29 < <i>l</i> < 28	-40 < <i>h</i> < 39 -25 < <i>k</i> < 24 -38 < <i>l</i> < 38
Refl. collected/unique	131543/35605	152795/30184	65081/23553	150718/25514	246849/39027
Data/restraints/parameters	35605/0/1232	30184/0/779	23553/9/1101	25514/0/930	39027/0/1670
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.197	1.286	1.051	1.095	1.141
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0262 <i>wR</i> <sub>2</sub> = 0.0525	<i>R</i> <sub>1</sub> = 0.1274 <i>wR</i> <sub>2</sub> = 0.2779	<i>R</i> <sub>1</sub> = 0.0349 <i>wR</i> <sub>2</sub> = 0.0734	<i>R</i> <sub>1</sub> = 0.047 <i>wR</i> <sub>2</sub> = 0.0525	<i>R</i> <sub>1</sub> = 0.0580 <i>wR</i> <sub>2</sub> = 0.0525
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0369 <i>wR</i> <sub>2</sub> = 0.0576	<i>R</i> <sub>1</sub> = 0.1448 <i>wR</i> <sub>2</sub> = 0.2708	<i>R</i> <sub>1</sub> = 0.0535 <i>wR</i> <sub>2</sub> = 0.0811	<i>R</i> <sub>1</sub> = 0.0572 <i>wR</i> <sub>2</sub> = 0.0675	<i>R</i> <sub>1</sub> = 0.1174 <i>wR</i> <sub>2</sub> = 0.1410
Largest difference peak and hole [e.Å <sup>-3</sup> ]	1.638 and -3.006	4.228 and -5.784	2.780 and -1.934	2.275 and -1.326	3.557 and -2.457
CCDC deposition numbers	905231	905232	905233	905234	905235