

Short communication

Synthesis and characterization of two benzylarsonate functionalized polyoxomolybdates with catalytic activity for oxidation of benzyl alcohol to benzaldehyde

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ABSTRACT

Two polyoxomolybdates $(\text{DMAH})_{2.75}\text{Na}_{1.25}[\text{H}_2\text{Mo}_6\text{O}_{19}(\text{C}_7\text{H}_7\text{AsO}_3)_2] \cdot 6\text{H}_2\text{O}$ (1) and $\text{In}_{0.5}\text{Na}_{3.5}[\text{Mo}_{12}\text{O}_{34}(\text{C}_7\text{H}_7\text{AsO}_3)_2] \cdot 16\text{H}_2\text{O}$ (2) have been synthesized by the reactions of benzyl arsonate with molybdate in aqueous solution with the existence of In^{3+} ions and characterized. The $[\text{H}_2\text{Mo}_6\text{O}_{19}(\text{C}_7\text{H}_7\text{AsO}_3)_2]^{4-}$ in 1 is a new derivative of Strandberg-Type cluster and compound 2 is 3D network which is constructed by “inverse-Keggin” cluster and In^{3+} and Na^+ cations. Both of the compounds show efficient catalytic activity on selective oxidation of benzyl alcohol to benzaldehyde.

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Polyoxometalates (POMs) are a unique class of metal oxygen clusters with matchless diversity of structural architectures and many properties that are of interest in different fields including catalysis, medicine, optics, and materials science [1–3]. Recently, targeting improves relatively poor processability of these inorganic clusters, functionalization of POMs with organic group or organometallic compounds have attracted considerable attention [4]. A lot of efforts have been done in synthesis and characterization of POM based on hybrid clusters and a large number of species have been produced. The covalently bound organic groups majorly include imido, alkoxy, carboxylic acid, organosilicon, organophosphonates, organotin and organoruthenium *etc.* [5–11]. Among these clusters, organophosphonates has been demonstrated as good modification reagents and have received considerable attention. Pope [9a,b] and Kortz [9c,d] synthesized the penta- and hexanuclear Mo^{VI} core with monophosphonate and bisphosphonates respectively. And then Zubieta [9e,f] and Sevov [9g] et al. isolated a series of organophosphonates functionalized POMs with a diversity of sizes, nuclearities and multi-dimensional frameworks.

Alternatively, the POM hybrid chemistry containing other organic group with similar structures such as organoarsenate was far less investigated and most of the studies focus on the structural characterization,

while the organoarsenate has shown good reactivity with POMs fragment and the resulting hybrid molecules have revealed interesting assembly behaviors from the point view of structural tuning and control [12]. The major cluster type includes $[\text{Mo}_5\text{O}_{15}(\text{O}_3\text{AsR})_2]^{4-}$ ($\{\text{Mo}_5\}$) with R = Alkyl chain [13], and $[\text{Mo}_{12}\text{O}_{34}(\text{O}_3\text{AsR})_4]^{4-}$ ($\{\text{Mo}_{12}\}$) with R = phenyl derivatives [14]. In view of the noticeable work of the above mentioned, recently we have thus initiated a study on the reaction of organoarsenate with Mo, and W trying to construct novel organic derivatives of POMs, which are expected to possess unique self-assembly behavior and good catalytic activities [1c,15]. Among the various organoarsenate, benzylarsonate detained our attention because it is a commercially used efficient collector agent in flotation process but little chemistry between this organic collector and oxometallate has been reported. Also, the methyl linker between phenyl and arsonate group could tune the flexibility of the whole ligand, and the preliminary self-assembly studies of benzylarsonate based POM hybrid cluster has shown both of the $\{\text{Mo}_5\}$ and $\{\text{Mo}_{12}\}$ type clusters could be isolated by the synthetic pH control. Herein, as a continuation of this research, we report the discovery of another two polyoxomolybdates: $[\text{H}_2\text{Mo}_6\text{O}_{19}(\text{C}_7\text{H}_7\text{AsO}_3)_2]^{4-}$ (1a) and $[\text{Mo}_{12}\text{O}_{34}(\text{C}_7\text{H}_7\text{AsO}_3)_4]^{4-}$ (2a); which are isolation and characterization as $(\text{DMA})_{2.75}\text{Na}_{1.25}[\text{H}_2\text{Mo}_6\text{O}_{19}(\text{C}_7\text{H}_7\text{AsO}_3)_2] \cdot 6\text{H}_2\text{O}$ (1) and $\text{Na}_{3.5}\text{In}_{0.5}[\text{Mo}_{12}\text{O}_{34}(\text{C}_7\text{H}_7\text{AsO}_3)_4]\text{NO}_3 \cdot 16\text{H}_2\text{O}$ (2) respectively. Both compounds show an efficient catalytic activity for oxidation of benzyl alcohol to benzaldehyde with H_2O_2 .

All the compounds were all synthesized in conventional conditions. The synthetic parameters including Mo source, pH of the solution, and existence of “Innocent” ions were scanned during the synthesis (See

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supporting information). The Mo source type is crucial in forming new clusters. Due to the difference of condensation and hydrolysis process between MoO_4^{2-} and $[\text{Mo}_7\text{O}_{24}]^{6-}$ during the solution acidification process, new building units such as $\{\text{Mo}_2\text{O}_9\}$ was made from the condensation of MoO_4^{2-} built self-assembly process. Therefore, a new type polyanion **1a** was isolated using mixture Mo sources of MoO_4^{2-} and $[\text{Mo}_7\text{O}_{24}]^{6-}$. Although the cluster **1a** cannot be isolated without “Innocent” In^{3+} in solution yet, the role of In^{3+} are still unclear in this system. Further, the isolation of **2a** at lower pH demonstrates that the “inverse-Keggin” cluster is the most stable hybrid anion in this system under strong acidic aqueous condition. Only trace amount of In^{3+} was detected in the solid crystal of **2a**. In view of the other work about In^{3+} containing POM, we find the pH value of the reaction system is crucial in embedding In^{3+} ions into POM based frameworks [16], and increasing In^{3+} concentration does not obviously influence the content of metal ions in the solid structure in this system.

Single crystal X-ray analysis revealed that **1a** can be described as a derivative of Strandberg-Type molybdate hybrid (Table S1) [13]. The inorganic polyanion $\{\text{Mo}_6\text{O}_{19}\}$ part is located in the middle of two organic benzylarsonate ligands. All six Mo centres are six coordinated with two terminal O ligands, and the average $\text{Mo}=\text{O}$ bond length is 1.71(1)Å. One $\{\text{Mo}_6\}$ in the Strandberg cluster is replaced by a $\{\text{Mo}_2\text{O}_9\}$ unit. Remarkably, the $\{\text{Mo}_2\text{O}_9\}$ is built by two $\{\text{MoO}_6\}$ octahedral with O ligand arranging in rare face sharing mode, as shown in Fig. 1. The organic benzylarsonate group bonds to the inorganic part by forming $\text{As}-\text{O}-\text{Mo}$ bonds. One of the AsO_3 group bond four of the six $\{\text{MoO}_6\}$, but the other AsO_3 group linked all the $\{\text{MoO}_6\}$ in a corner sharing mode. Therefore the whole cluster becomes asymmetric. Both of the AsO_3 groups are slightly compressed with the $\text{O}-\text{As}-\text{O}$ bond angle in the range of $112.8(2)^\circ$ and $106.7(2)^\circ$. The phenyl rings are located at the side of the metal oxide units with dihedral angle of $88.5(2)^\circ$.

Further, four **1a** anions linked five Na^+ cations and formed a tetramer aggregate. As shown in Fig. 2, all Na^+ ions well arranged in the central of the cluster with a few coordination waters on them, and all phenyl rings located on the surface of the tetramer. The forming of $\{\text{Na}_5\}$ core in the center indicates that **1a** is promising hybrid ligand in building nano-sized high nuclear coordination clusters. This tetramer hybrid cluster further enclosed by ten DMAH^+ cations to balance the charges. Chemical analysis shows that the cluster is double protonated, and the BVS results shows one of the bridge O ligand in $\{\text{Mo}_2\text{O}_9\}$ unit is mono-protonated. The other proton could disorder on all terminal O

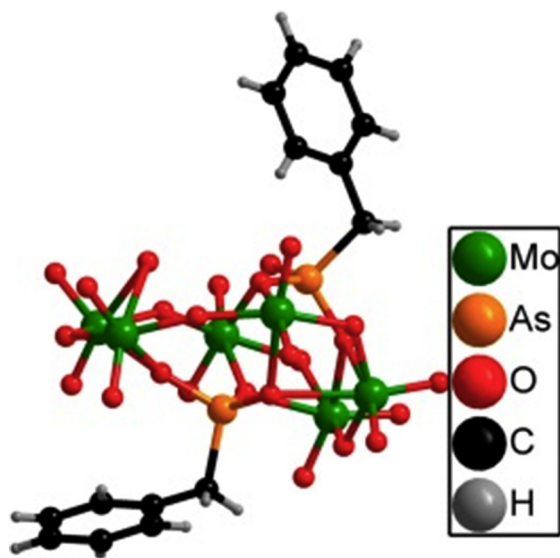


Fig. 1. Ball-and-stick representations of the hybrid cluster **1a**. (O, red; Mo, Green; As, Orange; C, black; Na, cyan; H, gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

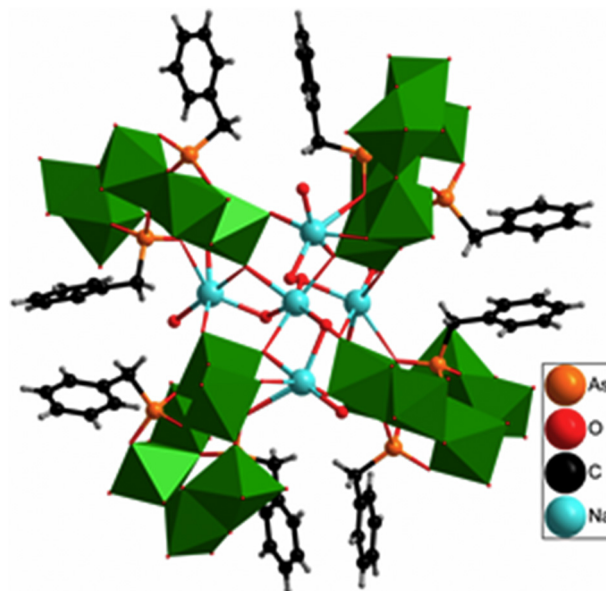


Fig. 2. Mixed Polyhedron and Ball-and-stick representations of Tetramer cluster in compound **1**. ($\{\text{MoO}_6\}$, Green octahedral; As, Orange; C, black; Na, cyan; H, gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ligands. Although compound **1** was isolated from the solution containing In^{3+} , the ICP-MS result clearly shown no In^{3+} exists in the solid crystals (mole ration Mo: As: In = 6.1(0.2):2.0(0.1): 0.03(10)).

The polyanion $[\text{Mo}_{12}\text{O}_{34}(\text{C}_7\text{H}_7\text{AsO}_3)_4]^{4-}$ in **2** is a classic “inverse-Keggin” cluster, where the tetrahedral $\{\text{R}-\text{AsO}_3\}$ ($\text{R} = \text{C}_7\text{H}_7$) units are located on the surface of the cluster. As shown in Fig. S1, the rotation of phenyl groups was majorly fixed by the coordinated Na^+ on **2a** surface. Eight Na^+ cations attach the cluster on the terminal O ligand, and link the near hybrid cluster in *cis* mode. Therefore, the cluster formed 3D coordination polymer, which crystallized from aqueous solution in the space group of $I4_1/a$. Some zigzag channel was observed in the crystals, which were occupied by disordered solvent waters. Remarkably, different from the previous report, the rotation of phenyl groups in **2a** is well ordered and the hybrid polyanion is achiral (Fig. 3). The unique isomerization process of the hybrid cluster shows that the chirality regulation could potentially accessible by chemical controlling. The ICP-MS

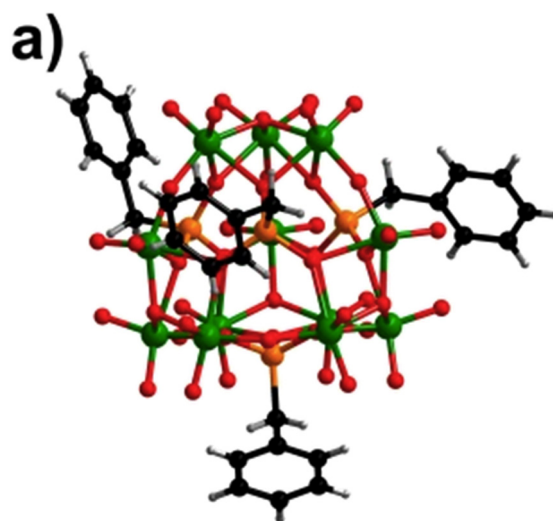


Fig. 3. Ball-and-stick representations of the hybrid cluster **2a**. (O, red; Mo, Green; As, Orange; C, black; Na, cyan; H, gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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