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## Polyoxometalates

Guest Editors: De-Liang Long and Leroy Cronin

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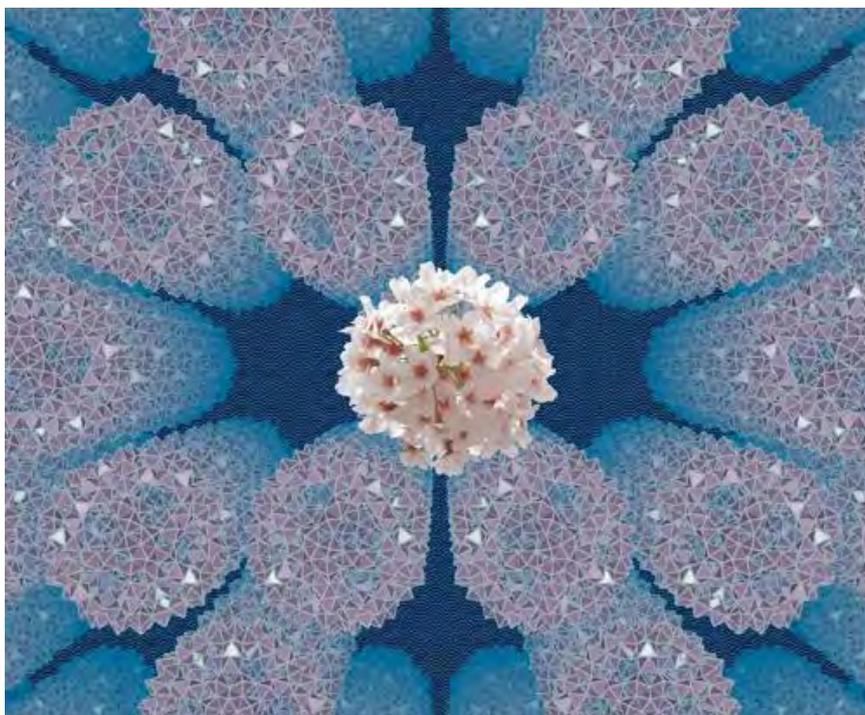


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## COMMUNICATION

## A fluorophosphate-based inverse Keggin structure†

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An unusual  $\text{PFO}_3^{2-}$ -templated “inverse Keggin” polyanion,  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$ , has been isolated from the degradation reaction of an  $\{\text{Mo}_{132}\}$ -type Keplerate to  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  by  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$  in acetonitrile.  $^{31}\text{P}$ -NMR studies suggest a structure-directing role for  $[\text{Cu}(\text{MeCN})_4]^+$  in the formation of the highly unusual all-inorganic inverse Keggin structure.

Polyoxometalates (POMs) are a large family of metal oxide clusters based on V, Mo and W in high oxidation states.<sup>1</sup> Their wide range of sizes/shapes, and possibilities for derivatization,<sup>2,3</sup> mean that POMs offer useful properties including magnetism,<sup>3b,4</sup> catalysis<sup>1,5</sup> and semiconductivity.<sup>6</sup> Synthesis is usually achieved by condensation of metalate anions in acidic aqueous conditions; however exchange of inorganic cations for large organic cations such as tetra-*n*-butylammonium ( $n\text{Bu}_4\text{N}^+$ ) allows their solubilization in organic media.<sup>3,7</sup> Organic-soluble polyoxomolybdate salts, *e.g.*  $(n\text{Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$  ( $\{\text{Mo}_8\}$ ), can be reacted with other metal complexes to produce derivatized POMs, typically with nuclearities in the range  $\{\text{Mo}_4\}$  to  $\{\text{Mo}_6\}$ .<sup>8</sup>

Recently, we have developed an approach for the synthesis of POM clusters which uses high concentrations of bulky organic cations to direct the formation of novel polyoxoanions in solution, and trap (“shrink-wrap”) these otherwise transient species.<sup>9–11</sup> For example, the reaction of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  with Ag(I) salts produces the  $\beta$ -octamolybdate-based supramolecular synthon  $[\text{Ag}-\text{Mo}_8\text{O}_{26}-\text{Ag}]^{2-}$ , which can be trapped as  $[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{dmso})_4]^{2-}$  or allowed to form network structures.<sup>10</sup> The related  $\beta$ -octamolybdate  $[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]^{4-}$  self-assembles through the reaction of  $(n\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  with  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$ ,<sup>11</sup> indicating that the  $[\text{Cu}(\text{MeCN})_4]^+$  cation can trap new POM anions, provide Cu(I) for coordination to POMs, and induce the condensation of small molybdates into larger species.

Consequently, we probed the reaction of  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$  with larger polyoxomolybdates such as Keplirates of the  $\{\text{Mo}_{132}\}$  type in non-aqueous media. Surprisingly, in acetonitrile solutions,  $\{\text{Mo}_{132}\}$  hydrolyses  $\text{PF}_6^-$  to  $\text{PO}_4^{3-}$  (via  $\text{PF}_2\text{O}_2^-$  and  $\text{PFO}_3^{2-}$ ) to form the well-known phosphomolybdate

$[\alpha\text{-PMo}_{12}\text{O}_{40}]^{3-}$  (**3a**) and the inverse Keggin-type fluorophosphomolybdate  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$  (**2a**). Inverse Keggin clusters are so called because four heteroatoms are located on the *outside* of the cluster, in place of one at the center, resulting in a tetrahedral cluster in which the four  $\text{M}_3\text{O}_{13}$  triads are turned inside-out. Apart from a single tetraarsenate-based species,<sup>12a</sup> all known examples are based on organoarsenates or organophosphonates,<sup>12b–d</sup> where the organic group prevents the heteroatom from coordinating at the center of the cluster. The cluster anion **2a** thus represents the second known all-inorganic inverse Keggin species, and its metastability is evident from rearrangement reactions to **3a**.

Reaction of the  $n\text{Bu}_4\text{N}^+$  salt of a  $\{\text{Mo}_{132}\}$  Keplerate species (**1**, see ESI†), which is soluble in acetonitrile, with a large excess of  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$  at room temperature results in a mixture of  $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$  and unreacted  $\{\text{Mo}_{132}\}$ . Reflux induces the complete break-up of  $\{\text{Mo}_{132}\}$  and simultaneous step-wise hydrolysis of  $\text{PF}_6^-$  to  $\text{PO}_4^{3-}$ , leading to the isolation of  $(n\text{Bu}_4\text{N})_3[\alpha\text{-PMo}_{12}\text{O}_{40}]$  (**3**) in up to 50% yield. Interestingly, a small quantity of dark-green crystals of the fluorophosphate-based inverse Keggin compound  $\text{H}_3[\text{Cu}(\text{MeCN})_4][\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]\cdot 4\text{CH}_3\text{CN}\cdot 32\text{H}_2\text{O}$  (**2**)<sup>13</sup> was serendipitously obtained as a by-product of this reaction.

Compound **2** crystallizes in the space group *Cmcm*. The  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$  cluster anion (Fig. 1) has idealized  $T_d$  symmetry and is templated by four  $\text{PFO}_3^{2-}$  anions which describe a tetrahedron, with each P atom between 2.712 and 2.729 Å from the center of the cluster. Four groups of three edge-sharing  $\text{MoO}_6$  octahedra are linked by the  $\text{PFO}_3$  moieties, and by corner-sharing interactions with each other. As a result, the fluorophosphate units occupy the center of planar  $\text{Mo}_6\text{O}_{21}\text{PF}$  faces with *cis*-dioxo-terminated Mo centers. Bond valence sum calculations<sup>14</sup> support the assignment of the  $[\text{Mo}^{\text{VI}}_{12}\text{O}_{46}(\text{P}^{\text{V}}\text{F})_4]^{4-}$

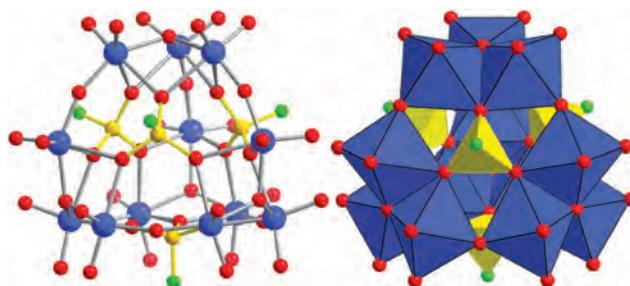


Fig. 1 Structure of the inverse Keggin fluorophosphomolybdate  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$  (**2a**). P: yellow; F: green; Mo: blue; O: red.

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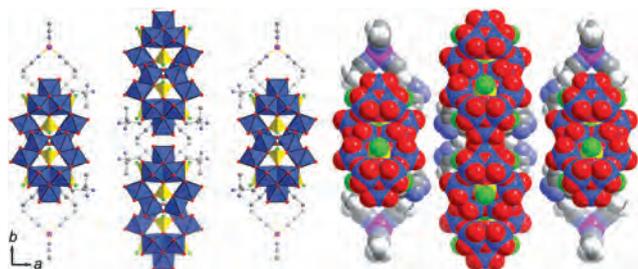
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anion as a fully oxidized species; reduced inverse Keggin species are unstable.<sup>12</sup> Mo–O bond lengths (Table S2, ESI†) are consistent with the observed terminal,  $\mu$ -, and  $\mu_3$ -oxo coordination modes. P–O and P–F bond lengths are comparable to those observed in existing PFO<sub>3</sub> structures,<sup>15</sup> with the P–F bond significantly longer than the three P–O distances and the O–P–F angles tighter than the O–P–O angles. The inclusion of PFO<sub>3</sub> groups is also evident from IR spectra with bands at 1213, 1145, 1017 and 940 cm<sup>-1</sup> associated with PO<sub>3</sub> stretching, and two bands at 840 and 682 cm<sup>-1</sup> which can be assigned to P–F stretching modes.<sup>15c</sup>

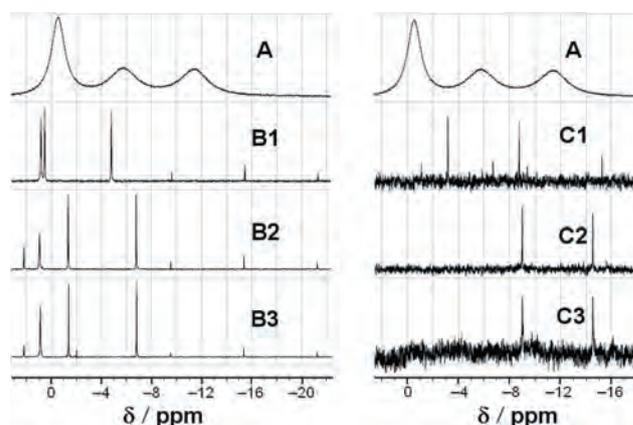
In the crystal lattice of **2**, [Mo<sub>12</sub>O<sub>46</sub>(PF)<sub>4</sub>]<sup>4-</sup> anions, [Cu(MeCN)<sub>4</sub>]<sup>+</sup> cations and disordered acetonitrile pack in layers coplanar to the crystallographic *bc* plane (Fig. 2). Within the layers, the [Cu(MeCN)<sub>4</sub>]<sup>+</sup> cations and POM anions pack closely, with short contacts between the cation methyl groups and terminal O and F positions (C...X distances of *ca.* 3.301 and 3.398 Å, respectively) suggesting the presence of non-classical hydrogen bonds. There are large voids between the layers, with calculations<sup>16</sup> indicating around 36% solvent accessible void space. This is occupied by disordered solvent which would not refine successfully, and was removed using the PLATON SQUEEZE routine.<sup>16</sup> Although the elusive nature of **2** has prevented full characterization, IR spectra (see ESI†) suggest that this void space is filled by water.



**Fig. 2** Crystal packing in **2** viewed along the *c* axis, showing layers of **2a** cluster anions and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup> cations. Left: polyhedral (anion)/ball-and-stick (cation) representation. Right: space-filling representation revealing the substantial void space in the structure of **2**. Color scheme as for Fig. 1, with H: white.

Despite the difficulty in repeatedly isolating solid **2**, <sup>31</sup>P-NMR investigations provide strong evidence for the formation of [Mo<sub>12</sub>O<sub>46</sub>(PF)<sub>4</sub>]<sup>4-</sup> (**2a**) in solutions at high yields, and suggest that this is contingent upon the presence of [Cu(MeCN)<sub>4</sub>]<sup>+</sup>. (*n*Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>], {Mo<sub>8</sub>} or **1** were reacted with H<sub>2</sub>PFO<sub>3</sub> in dry MeCN at room temperature, with or without [Cu(MeCN)<sub>4</sub>](PF<sub>6</sub>), and with the addition of *n*Bu<sub>4</sub>NF (F<sup>-</sup> is required to prevent breaking of the P–F bond). <sup>31</sup>P-NMR spectra were acquired after 24 hours, and signals indicating the presence of four different fluorophosphomolybdate species were observed – depending on the molybdate starting material, and on the addition of [Cu(MeCN)<sub>4</sub>](PF<sub>6</sub>) (Fig. 3 and Table 1). These signals are all strongly split (<sup>1</sup>J<sub>PF</sub> = 860–905 Hz) sharp doublets covering a chemical shift range of *ca.* –2 to –12 ppm.

Previous <sup>31</sup>P-NMR studies on phenylphosphomolybdates (with stoichiometries {Mo<sub>5</sub>P<sub>2</sub>}, {Mo<sub>6</sub>P} and {Mo<sub>7</sub>P}) indicate a trend for  $\delta$  to shift upfield with increasing aggregate size, as larger and more negatively charged anions are better able to shield the <sup>31</sup>P nucleus.<sup>17</sup> Using this trend, the products with the most downfield signals (–2.1 ppm and –4.1 ppm, Fig. 3 B1 to B3), resulting from the reaction without [Cu(MeCN)<sub>4</sub>]<sup>+</sup>, are



**Fig. 3** <sup>31</sup>P NMR spectra of reactions of H<sub>2</sub>PFO<sub>3</sub> and molybdates in the presence of *n*Bu<sub>4</sub>NF. **A**: H<sub>2</sub>PFO<sub>3</sub> (showing substantial amounts of H<sub>3</sub>PO<sub>4</sub>). **B**: without [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>); **B1** = {Mo<sub>2</sub>}, **B2** = {Mo<sub>8</sub>}, **B3** = {Mo<sub>132</sub>}. **C**: with [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>); **C1** = {Mo<sub>2</sub>}, **C2** = {Mo<sub>8</sub>}, **C3** = {Mo<sub>132</sub>}.

**Table 1** <sup>31</sup>P NMR shifts of known phenylphosphomolybdates in water, and assignment for fluorophosphomolybdates in acetonitrile

Phenylphosphomolybdates <sup>17</sup>		Fluorophosphomolybdates		
$\delta$ /ppm	Assignment	$\delta$ /ppm ( <sup>1</sup> J <sub>PF</sub> /Hz)	Starting materials <sup>a</sup>	Assignment <sup>b</sup>
12.1	C <sub>6</sub> H <sub>5</sub> PO <sub>3</sub> <sup>2-</sup>	–8.5 (900)	H <sub>2</sub> PFO <sub>3</sub>	[H <sub>x</sub> PFO <sub>3</sub> ] <sup>x-2</sup>
14.0	C <sub>6</sub> H <sub>5</sub> PO <sub>3</sub> H <sup>-</sup>	–2.1 (860)	{Mo <sub>2</sub> }	[H <sub>x</sub> (PF) <sub>2</sub> Mo <sub>5</sub> O <sub>21</sub> ] <sup>x-4</sup>
17.7	C <sub>6</sub> H <sub>5</sub> PO <sub>3</sub> H <sub>2</sub>	–4.1 (880)	{Mo <sub>8</sub> } or {Mo <sub>132</sub> }	[H <sub>x</sub> (PF)Mo <sub>7</sub> O <sub>26</sub> ] <sup>x-6</sup>
22.0	[(C <sub>6</sub> H <sub>5</sub> P) <sub>2</sub> Mo <sub>5</sub> O <sub>20</sub> (OH)] <sup>3-</sup>	–6.0 (905)	{Mo <sub>2</sub> } + [Cu(CH <sub>3</sub> CN) <sub>4</sub> ](PF <sub>6</sub> )	[H <sub>x-1</sub> (PF)Mo <sub>7</sub> O <sub>26</sub> ] <sup>x-7</sup>
21.3	[(C <sub>6</sub> H <sub>5</sub> P) <sub>2</sub> Mo <sub>5</sub> O <sub>21</sub> ] <sup>4-</sup>	–11.8 (895)	{Mo <sub>8</sub> }/ {Mo <sub>132</sub> } + [Cu(CH <sub>3</sub> CN) <sub>4</sub> ](PF <sub>6</sub> )	[H <sub>x</sub> (PF) <sub>4</sub> Mo <sub>12</sub> O <sub>46</sub> ] <sup>x-4</sup>
20.2	[(C <sub>6</sub> H <sub>5</sub> P)Mo <sub>6</sub> O <sub>21</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sup>2-</sup>			
19.2	[(C <sub>6</sub> H <sub>5</sub> P)Mo <sub>7</sub> O <sub>25</sub> (H <sub>2</sub> O)] <sup>1-</sup>			
17.1	[(C <sub>6</sub> H <sub>5</sub> P)Mo <sub>7</sub> O <sub>25</sub> (OH)] <sup>5-</sup>			

<sup>a</sup> All molybdate reactions contain 1 eq Mo atoms and 1.03 eq each of H<sub>2</sub>PFO<sub>3</sub> and *n*Bu<sub>4</sub>NF; where stated 1.03 eq [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) was also added.

<sup>b</sup> Tentative assignment of cluster nuclearity based on chemical shift patterns in phenylphosphomolybdates and (where possible) integrals relative to a PF<sub>6</sub><sup>-</sup> reference; undetermined protonation states.

assigned as  $\{\text{Mo}_5\text{P}_2\}$  and  $\{\text{Mo}_7\text{P}\}$  aggregates. The 2 ppm difference in  $\delta$  between these signals is similar to that observed between  $\{\text{Mo}_5\text{P}_2\}$  and  $\{\text{Mo}_7\text{P}\}$  phenylphosphomolybdates, and  $\{\text{Mo}_7\text{P}\}$  clusters seem very likely to form in the  $\{\text{Mo}_8\}$  based system (Fig. 3 B2) as they require displacement of only one Mo from  $[\text{Mo}_8\text{O}_{26}]^{4-}$ . The  $-2.1$  ppm signal is assigned to  $\{\text{Mo}_5\text{P}_2\}$ , as formation of the hexahydrated  $\{\text{Mo}_6\text{P}\}$  anion seems unlikely in non-aqueous conditions. Considerable speciation of  $\text{PFO}_3^{2-}$  also appears to occur, due to the presence of other peaks resulting from  $\text{PO}_4^{3-}$  and  $\text{PF}_2\text{O}_2^-$  based aggregates.

In all cases, the addition of (diamagnetic)  $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$  results in an upfield shift in the observed  $\text{PFO}_3$  signals, suggesting the formation of larger clusters. For the  $\{\text{Mo}_2\}$  based system, the signal at  $-6$  ppm is likely to come from an  $\{\text{Mo}_7\text{P}\}$  aggregate, as  $[\text{Cu}(\text{MeCN})_4]^+$  induces condensation of  $\{\text{Mo}_2\}$  to the related  $\{\text{Mo}_8\}$  in these conditions.<sup>11</sup> For  $\{\text{Mo}_8\}$  and  $\{\text{Mo}_{132}\}$ , only one signal is observed, with a more dramatic upfield shift to  $-11.8$  ppm ( $^1J_{\text{PF}} = 895$  Hz, Fig. 3 C2 and C3). This is assigned to the inverse Keggin cluster anion **2a** on the basis of the following lines of evidence:

(i) The 5.8 ppm upfield shift from the range of the other fluorophosphomolybdates should indicate the formation of a larger  $\text{PFO}_3$ -based structure. This shift is much larger than any other, suggesting a substantially different structural type.

(ii) Solid **2** was isolated from a similar reaction mixture.

(iii) The 3.3 ppm upfield shift in the  $^{31}\text{P}$  resonance vs.  $\text{H}_2\text{PFO}_3$  is comparable to the ca. 4 ppm upfield shift in the similar sized  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  relative to  $\text{H}_3\text{PO}_4$ .<sup>18</sup>

(iv) Comparison of the integral for this product with that of the known quantity of  $\text{PF}_6^-$  in the system indicates that as **2a** (Mo–P ratio 3 : 1) it would account for ca. 60% of the Mo in the system. Therefore, clusters such as  $\{\text{Mo}_6\text{P}\}$  and  $\{\text{Mo}_7\text{P}\}$  with much higher Mo–P ratios are highly unlikely.

Therefore, it appears that the formation of **2a** can occur in high yields in solution, and is dependent on the influence of the  $[\text{Cu}(\text{MeCN})_4]^+$  cation. However, the only crystalline product recovered from these NMR reactions was  $(n\text{Bu}_4\text{N})_3[\text{PMo}_{12}\text{O}_{40}]$  (**3**).  $^{31}\text{P}$ -NMR of recovered bulk solid material showed no  $\text{PFO}_3$  signals, instead showing a singlet at  $\delta \approx -4.6$  ppm, consistent with  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ . This indicates that during the crystallization process hydrolysis and rearrangement occurs to produce **3**. Therefore, it seems that cluster anion **2a** is an intermediate that, while able to form in high yields in solution in the presence of a sufficient  $\text{F}^-$  concentration, does not crystallize reproducibly as it tends to readily rearrange to form normal Keggin products.

## Conclusions

We have isolated a novel fluorophosphate polyoxomolybdate anion,  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$ , in the solid state, and seen strong evidence for its formation in solution. The observed “inverse Keggin” is a rare example of a fully inorganic structure of its kind, and we postulate it as one intermediate enroute to the formation of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ , perhaps providing an insight into the mechanisms of POM formation. As  $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$  appears only to form in the presence of  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$ , this result is in line with our previous observation that the  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cation can induce condensation of smaller molybdate species

and that bulky, flexible cations can trap or template unusual POM species.

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- The formula  $\text{H}_3[\text{Cu}(\text{CH}_3\text{CN})_4][\text{Mo}_{12}\text{O}_{46}(\text{PF})_4] \cdot 4\text{CH}_3\text{CN} \cdot 32\text{H}_2\text{O}$  used for **2** is based on crystallography and IR spectroscopic measurements only. Sufficient material could not be isolated for elemental analysis or TGA. The quantity of crystal water is based on a PLATON SQUEEZE estimate of the electron density in the substantial void spaces (see ESI† for further details).
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