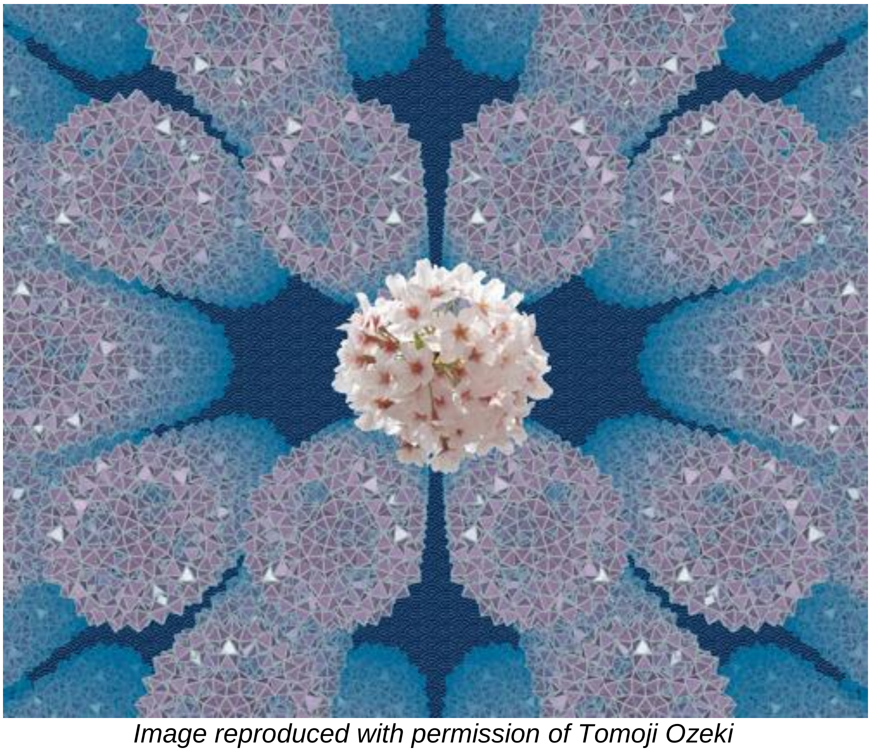
This paper is published as part of a *Dalton Transactions* themed issue entitled:

Polyoxometalates

Guest Editors: De-Liang Long and Leroy Cronin

Published in issue 33, 2012 of *Dalton Transactions*



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Cite this: *Dalton Trans.*, 2012, **41**, 9876

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COMMUNICATION

A fluorophosphate-based inverse Keggin structure†

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Received 1st March 2012, Accepted 17th July 2012
DOI: 10.1039/c2dt30501a

An unusual PFO_3^{2-}-templated "inverse Keggin" polyanion, $[Mo_{12}O_{46}(PF)_4]^{4-}$, has been isolated from the degradation reaction of an $\{Mo_{132}\}$-type Keplerate to $[PMo_{12}O_{40}]^{3-}$ by $[Cu(MeCN)_4](PF_6)$ in acetonitrile. ^{31}P-NMR studies suggest a structure-directing role for $[Cu(MeCN)_4]^+$ 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.[1] Their wide range of sizes/shapes, and possibilities for derivatization,[2,3] mean that POMs offer useful properties including magnetism,[3b,4] catalysis[1,5] and semiconductivity.[6] 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 ($n\mathrm{Bu_4N^+}$) allows their solubilization in organic media.[3,7] Organic-soluble polyoxomolybdate salts, *e.g.* $(n\mathrm{Bu_4N})_4[\alpha\text{-}Mo_8O_{26}]$ ($\{Mo_8\}$), can be reacted with other metal complexes to produce derivatized POMs, typically with nuclearities in the range $\{Mo_4\}$ to $\{Mo_6\}$.[8]

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.[9–11] For example, the reaction of $[Mo_6O_{19}]^{2-}$ with Ag(I) salts produces the β-octamolybdate-based supramolecular synthon $[Ag–Mo_8O_{26}–Ag]^{2-}$, which can be trapped as $[Ag_2Mo_8O_{26}(dmso)_4]^{2-}$ or allowed to form network structures.[10] The related β-octamolybdate $[Mo_8O_{26}Cu_2(CH_3CN)_4]^{4-}$ self-assembles through the reaction of $(n\mathrm{Bu_4N})_2[Mo_2O_7]$ with $[Cu(MeCN)_4](PF_6)$,[11] indicating that the $[Cu(MeCN)_4]^+$ 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 $[Cu(MeCN)_4](PF_6)$ with larger polyoxomolybdates such as Keplerates of the $\{Mo_{132}\}$ type in non-aqueous media. Surprisingly, in acetonitrile solutions, $\{Mo_{132}\}$ hydrolyses PF_6^- to PO_4^{3-} (*via* $PF_2O_2^-$ and PFO_3^{2-}) to form the well-known phosphomolybdate $[\alpha\text{-}PMo_{12}O_{40}]^{3-}$ (**3a**) and the inverse Keggin-type fluorophosphomolybdate $[Mo_{12}O_{46}(PF)_4]^{4-}$ (**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 M_3O_{13} triads are turned inside-out. Apart from a single tetraarsenate-based species,[12a] all known examples are based on organoarsonates or organophosphonates,[12b–d] 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 $n\mathrm{Bu_4N^+}$ salt of a $\{Mo_{132}\}$ Keplerate species (**1**, see ESI†), which is soluble in acetonitrile, with a large excess of $[Cu(MeCN)_4](PF_6)$ at room temperature results in a mixture of $(n\mathrm{Bu_4N})_2[Mo_6O_{19}]$ and unreacted $\{Mo_{132}\}$. Reflux induces the complete break-up of $\{Mo_{132}\}$ and simultaneous step-wise hydrolysis of PF_6^- to PO_4^{3-}, leading to the isolation of $(n\mathrm{Bu_4N})_3[\alpha\text{-}PMo_{12}O_{40}]$ (**3**) in up to 50% yield. Interestingly, a small quantity of dark-green crystals of the fluorophosphate-based inverse Keggin compound $H_3[Cu(MeCN)_4][Mo_{12}O_{46}(PF)_4]\cdot 4CH_3CN\cdot 32H_2O$ (**2**)[13] was serendipitously obtained as a by-product of this reaction.

Compound **2** crystallizes in the space group *Cmcm*. The $[Mo_{12}O_{46}(PF)_4]^{4-}$ cluster anion (Fig. 1) has idealized T_d symmetry and is templated by four 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 MoO_6 octahedra are linked by the PFO_3 moieties, and by corner-sharing interactions with each other. As a result, the fluorophosphate units occupy the center of planar $Mo_6O_{21}PF$ faces with *cis*-dioxo-terminated Mo centers. Bond valence sum calculations[14] support the assignment of the $[Mo^{VI}{}_{12}O_{46}(P^{V}F)_4]^{4-}$

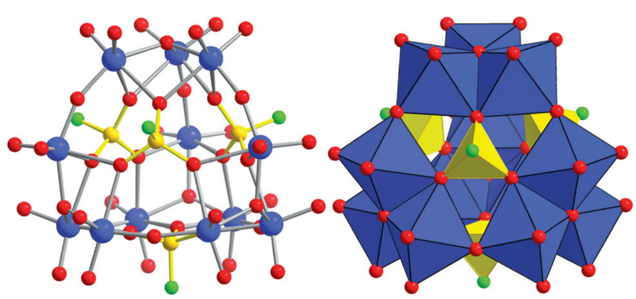

Fig. 1 Structure of the inverse Keggin fluorophosphomolybdate $[Mo_{12}O_{46}(PF)_4]^{4-}$ (**2a**). P: yellow; F: green; Mo: blue; O: red.

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† Electronic supplementary information (ESI) available: Experimental and crystallographic details. CCDC 869892. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30501a

anion as a fully oxidized species; reduced inverse Keggin species are unstable.[12] Mo–O bond lengths (Table S2, ESI†) are consistent with the observed terminal, μ-, and μ_3-oxo coordination modes. P–O and P–F bond lengths are comparable to those observed in existing PFO_3 structures,[15] 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_3 groups is also evident from IR spectra with bands at 1213, 1145, 1017 and 940 cm^{-1} associated with PO_3 stretching, and two bands at 840 and 682 cm^{-1} which can be assigned to P–F stretching modes.[15c]

In the crystal lattice of **2**, $[Mo_{12}O_{46}(PF)_4]^{4-}$ anions, $[Cu(MeCN)_4]^+$ cations and disordered acetonitrile pack in layers coplanar to the crystallographic *bc* plane (Fig. 2). Within the layers, the $[Cu(MeCN)_4]^+$ 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[16] 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.[16] Although the elusive nature of **2** has prevented full characterization, IR spectra (see ESI†) suggest that this void space is filled by water.

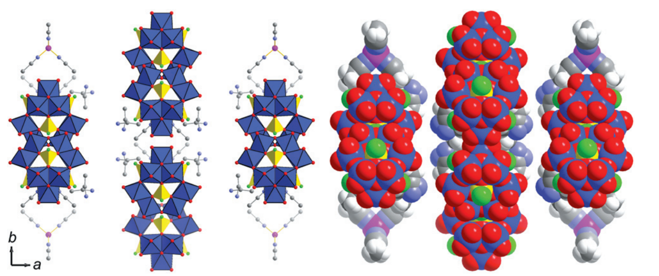

Fig. 2 Crystal packing in **2** viewed along the *c* axis, showing layers of **2a** cluster anions and $[Cu(CH_3CN)_4]^+$ cations. Left: polyhedral (anion)/ball-and-stick (cation) representation. Right: space-filling representation revealing the substantial void space in the structure of **2**. Color scheme as for Fig. 1, with H: white.

Despite the difficulty in repeatedly isolating solid **2**, ^{31}P-NMR investigations provide strong evidence for the formation of $[Mo_{12}O_{46}(PF)_4]^{4-}$ (**2a**) in solutions at high yields, and suggest that this is contingent upon the presence of $[Cu(MeCN)_4]^+$. $(nBu_4N)_2[Mo_2O_7]$, $\{Mo_8\}$ or **1** were reacted with H_2PFO_3 in dry MeCN at room temperature, with or without $[Cu(MeCN)_4](PF_6)$, and with the addition of nBu$_4$NF (F^- is required to prevent breaking of the P–F bond). ^{31}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 $[Cu(MeCN)_4](PF_6)$ (Fig. 3 and Table 1). These signals are all strongly split ($^1J_{PF}$ = 860–905 Hz) sharp doublets covering a chemical shift range of *ca.* −2 to −12 ppm.

Previous ^{31}P-NMR studies on phenylphosphomolybdates (with stoichiometries $\{Mo_5P_2\}$, $\{Mo_6P\}$ and $\{Mo_7P\}$) indicate a trend for δ to shift upfield with increasing aggregate size, as larger and more negatively charged anions are better able to shield the ^{31}P nucleus.[17] 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 $[Cu(MeCN)_4]^+$, are

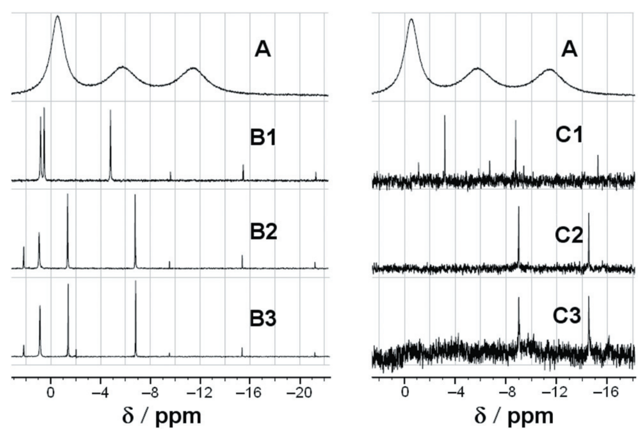

Fig. 3 ^{31}P NMR spectra of reactions of H_2PFO_3 and molybdates in the presence of nBu$_4$NF. **A**: H_2PFO_3 (showing substantial amounts of H_3PO_4). **B**: *without* $[Cu(CH_3CN)_4](PF_6)$; **B1** = $\{Mo_2\}$, **B2** = $\{Mo_8\}$, **B3** = $\{Mo_{132}\}$. **C**: *with* $[Cu(CH_3CN)_4](PF_6)$; **C1** = $\{Mo_2\}$, **C2** = $\{Mo_8\}$, **C3** = $\{Mo_{132}\}$.

Table 1 ^{31}P NMR shifts of known phenylphosphomolybdates in water, and assignment for fluorophosphomolybdates in acetonitrile

Phenylphosphomolybdates[17]		Fluorophosphomolybdates		
δ/ppm	Assignment	δ/ppm ($^1J_{PF}$/Hz)	Starting materials[a]	Assignment[b]
12.1	$C_6H_5PO_3^{2-}$	−8.5 (900)	H_2PFO_3	$[H_xPFO_3]^{x-2}$
14.0	$C_6H_5PO_3H^-$	−2.1 (860)	$\{Mo_2\}$	$[H_x(PF)_2Mo_5O_{21}]^{x-4}$
17.7	$C_6H_5PO_3H_2$	−4.1 (880)	$\{Mo_8\}$ or $\{Mo_{132}\}$	$[H_x(PF)Mo_7O_{26}]^{x-6}$
22.0	$[(C_6H_5P)_2Mo_5O_{20}(OH)]^{3-}$	−6.0 (905)	$\{Mo_2\}$ + $[Cu(CH_3CN)_4](PF_6)$	$[H_{x-1}(PF)Mo_7O_{26}]^{x-7}$
21.3	$[(C_6H_5P)_2Mo_5O_{21}]^{4-}$	−11.8 (895)	$\{Mo_8\}/\{Mo_{132}\}$ + $[Cu(CH_3CN)_4](PF_6)$	$[H_x(PF)_4Mo_{12}O_{46}]^{x-4}$
20.2	$[(C_6H_5P)Mo_6O_{21}(H_2O)_6]^{2-}$			
19.2	$[(C_6H_5P)Mo_7O_{25}(H_2O)]^{4-}$			
17.1	$[(C_6H_5P)Mo_7O_{25}(OH)]^{5-}$			

[a] All molybdate reactions contain 1 eq Mo atoms and 1.03 eq each of H_2PFO_3 and nBu$_4$NF; where stated 1.03 eq $[Cu(CH_3CN)_4](PF_6)$ was also added.
[b] Tentative assignment of cluster nuclearity based on chemical shift patterns in phenylphosphomolybdates and (where possible) integrals relative to a PF_6^- reference; undetermined protonation states.

assigned as {Mo_5P_2} and {Mo_7P} aggregates. The 2 ppm difference in δ between these signals is similar to that observed between {Mo_5P_2} and {Mo_7P} phenylphosphomolybdates, and {Mo_7P} clusters seem very likely to form in the {Mo_8} based system (Fig. 3 B2) as they require displacement of only one Mo from $[Mo_8O_{26}]^{4-}$. The −2.1 ppm signal is assigned to {Mo_5P_2}, as formation of the hexahydrated {Mo_6P} anion seems unlikely in non-aqueous conditions. Considerable speciation of PFO_3^{2-} also appears to occur, due to the presence of other peaks resulting from PO_4^{3-} and $PF_2O_2^-$ based aggregates.

In all cases, the addition of (diamagnetic) $[Cu(MeCN)_4](PF_6)$ results in an upfield shift in the observed PFO_3 signals, suggesting the formation of larger clusters. For the {Mo_2} based system, the signal at −6 ppm is likely to come from an {Mo_7P} aggregate, as $[Cu(MeCN)_4]^+$ induces condensation of {Mo_2} to the related {Mo_8} in these conditions.[11] For {Mo_8} and {Mo_{132}}, only one signal is observed, with a more dramatic upfield shift to −11.8 ppm ($^1J_{PF}$ = 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 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}P resonance *vs.* H_2PFO_3 is comparable to the *ca.* 4 ppm upfield shift in the similar sized $[PMo_{12}O_{40}]^{3-}$ relative to H_3PO_4.[18]

(*iv*) Comparison of the integral for this product with that of the known quantity of 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 {Mo_6P} and {Mo_7P} 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 $[Cu(MeCN)_4]^+$ cation. However, the only crystalline product recovered from these NMR reactions was $(nBu_4N)_3[PMo_{12}O_{40}]$ (**3**). ^{31}P-NMR of recovered bulk solid material showed no PFO_3 signals, instead showing a singlet at $\delta \approx -4.6$ ppm, consistent with $[PMo_{12}O_{40}]^{3-}$. 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 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, $[Mo_{12}O_{46}(PF)_4]^{4-}$, 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 $[PMo_{12}O_{40}]^{3-}$, perhaps providing an insight into the mechanisms of POM formation. As $[Mo_{12}O_{46}(PF)_4]^{4-}$ appears only to form in the presence of $[Cu(CH_3CN)_4]^+$, this result is in line with our previous observation that the $[Cu(CH_3CN)_4]^+$ cation can induce condensation of smaller molybdate species and that bulky, flexible cations can trap or template unusual POM species.

Acknowledgements

We thank Claire Besson, Arkady Ellern and De-Liang Long for helpful discussions. Work at the Ames Laboratory (initial synthesis and structural characterization) was supported by the Department of Energy-Basic Energy Sciences under Contract No. DE-AC02-07CH11358.

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