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Polyoxometalates

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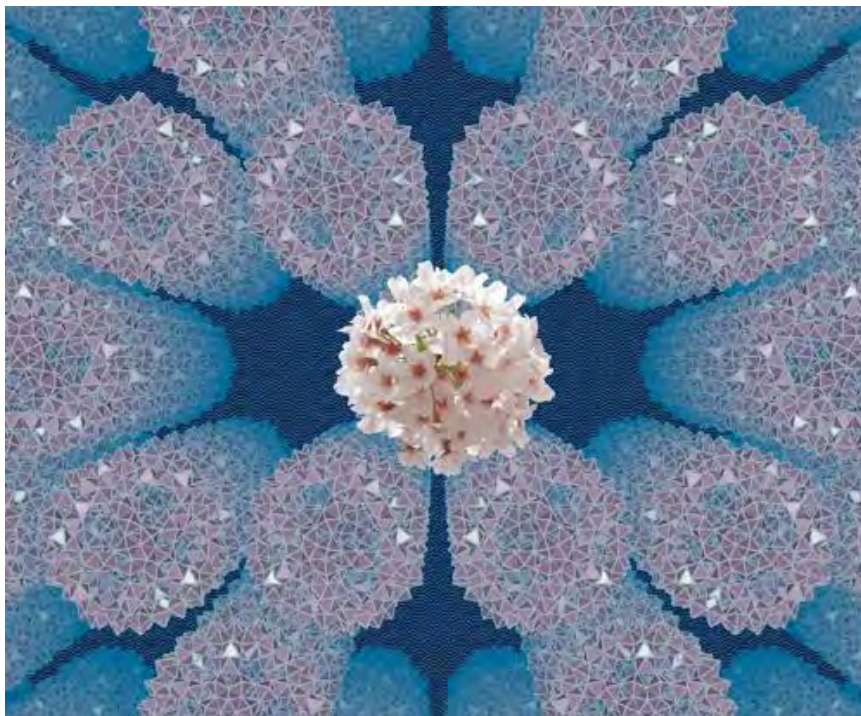


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COMMUNICATION

A fluorophosphate-based inverse Keggin structure†

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An unusual 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}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.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 ($n\text{Bu}_4\text{N}^+$) allows their solubilization in organic media.^{3,7} 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 $\{\text{Mo}_6\}$.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 $[\text{Mo}_6\text{O}_{19}]^{2-}$ with $\text{Ag}(\text{I})$ salts produces the β -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.¹⁰ The related β -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 $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$,¹¹ indicating that the $[\text{Cu}(\text{MeCN})_4]^+$ cation can trap new POM anions, provide $\text{Cu}(\text{I})$ 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 Keplerates of the $\{\text{Mo}_{132}\}$ type in non-aqueous media. Surprisingly, in acetonitrile solutions, $\{\text{Mo}_{132}\}$ hydrolyses PF_6^- to PO_4^{3-} (*via* PF_2O_2^- and PFO_3^{2-}) to form the well-known phosphomolybdate

$[\alpha\text{-PMo}_{12}\text{O}_{40}]^{3-}$ (**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 M_3O_{13} triads are turned inside-out. Apart from a single tetraarsenate-based species,^{12a} all known examples are based on organoarsenates 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 $n\text{Bu}_4\text{N}^+$ 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 PF_6^- to 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**)¹³ 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 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 $\text{Mo}_6\text{O}_{21}\text{PF}$ faces with *cis*-dioxo-terminated Mo centers. Bond valence sum calculations¹⁴ support the assignment of the $[\text{Mo}^{\text{VI}}_{12}\text{O}_{46}(\text{P}^{\text{V}}\text{F})_4]^{4-}$

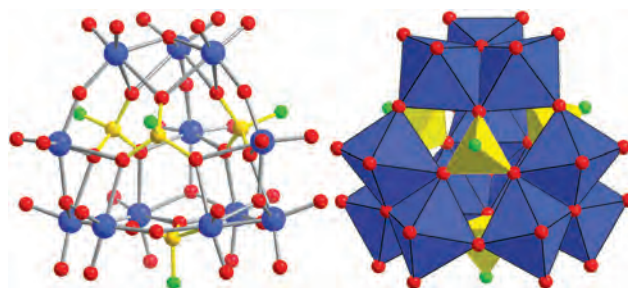


Fig. 1 Structure of the inverse Keggin fluorophosphomolybdate $[\text{Mo}_{12}\text{O}_{46}(\text{PF})_4]^{4-}$ (**2a**). P: yellow; F: green; Mo: blue; O: red.

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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 PFO₃ 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 PFO₃ groups is also evident from IR spectra with bands at 1213, 1145, 1017 and 940 cm⁻¹ associated with PO₃ 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**, [Mo₁₂O₄₆(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 calculations¹⁶ 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.

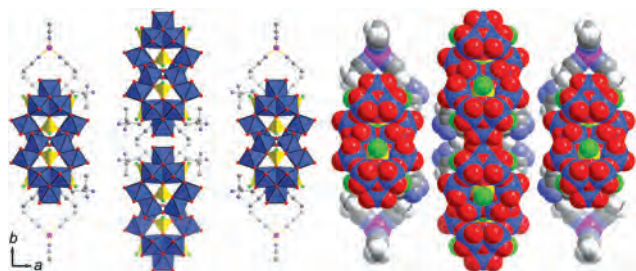


Fig. 2 Crystal packing in **2** viewed along the *c* axis, showing layers of **2a** cluster anions and [Cu(CH₃CN)₄]⁺ cations. Left: polyhedral (anion)/ball-and-stick (cation) representation. Right: space-filling representation revealing the substantial void space in the structure of **2**. Color scheme as for Fig. 1, with H: white.

Despite the difficulty in repeatedly isolating solid **2**, ³¹P-NMR investigations provide strong evidence for the formation of [Mo₁₂O₄₆(PF)₄]⁴⁻ (**2a**) in solutions at high yields, and suggest that this is contingent upon the presence of [Cu(MeCN)₄]⁺. (*n*Bu₄N)₂[Mo₂O₇], {Mo₈} or **1** were reacted with H₂PFO₃ in dry MeCN at room temperature, with or without [Cu(MeCN)₄](PF₆), and with the addition of *n*Bu₄NF (F⁻ is required to prevent breaking of the P–F bond). ³¹P-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](PF₆) (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 ³¹P-NMR studies on phenylphosphomolybdates (with stoichiometries {Mo₅P₂}, {Mo₆P} and {Mo₇P}) 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 ³¹P 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

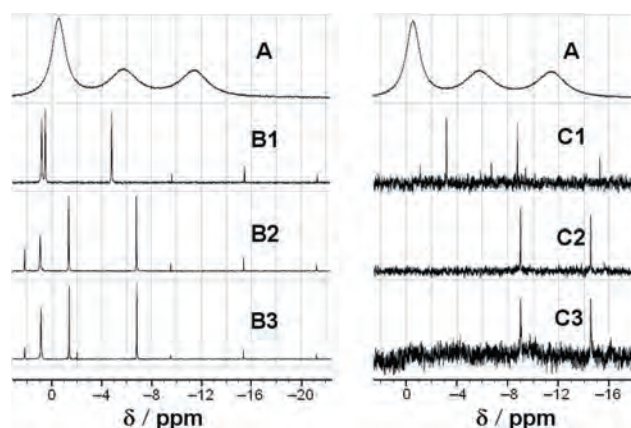


Fig. 3 ³¹P NMR spectra of reactions of H₂PFO₃ and molybdates in the presence of *n*Bu₄NF. **A**: H₂PFO₃ (showing substantial amounts of H₃PO₄). **B**: without [Cu(CH₃CN)₄](PF₆); **B1** = {Mo₂}, **B2** = {Mo₈}, **B3** = {Mo₁₃₂}. **C**: with [Cu(CH₃CN)₄](PF₆); **C1** = {Mo₂}, **C2** = {Mo₈}, **C3** = {Mo₁₃₂}.

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

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

^a All molybdate reactions contain 1 eq Mo atoms and 1.03 eq each of H₂PFO₃ and *n*Bu₄NF; where stated 1.03 eq [Cu(CH₃CN)₄](PF₆) was also added.

^b Tentative assignment of cluster nuclearity based on chemical shift patterns in phenylphosphomolybdates and (where possible) integrals relative to a PF₆⁻ reference; undetermined protonation states.

assigned as $\{\text{Mo}_5\text{P}_2\}$ and $\{\text{Mo}_7\text{P}\}$ aggregates. The 2 ppm difference in δ 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 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) $[\text{Cu}(\text{MeCN})_4](\text{PF}_6)$ results in an upfield shift in the observed 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.¹¹ 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 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 $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ 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 $\{\text{Mo}_6\text{P}\}$ 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}P -NMR of recovered bulk solid material showed no 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 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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Notes and references

- D.-L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105.
- (a) H. Liu, C. J. Gómez-García, J. Peng, J. Sha, Y. Li and Y. Yan, *Dalton Trans.*, 2008, 6211; (b) M. D. Ritorto, T. M. Anderson, W. A. Neiwert and C. L. Hill, *Inorg. Chem.*, 2004, **43**, 44.
- (a) A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, 1837; (b) P. Mialane, A. Dolbecq and F. Sécheresse, *Chem. Commun.*, 2006, 3477.
- A. Müller, E. Krickemeyer, S. K. Das, P. Kögerler, S. Sarkar, H. Bögge, K. Schmidtman and S. Sarkar, *Angew. Chem., Int. Ed.*, 2000, **39**, 1612.
- C. L. Hill, *Angew. Chem., Int. Ed.*, 2004, **43**, 402.
- E. Coronado, C. Giménez-Saiz and C. J. Gómez-García, *Coord. Chem. Rev.*, 2005, **249**, 1776.
- (a) W. G. Klemperer, *Inorg. Synth.*, 1990, **27**, 74; (b) J. Fuchs, S. Mahjour and R. Palm, *Z. Naturforsch. B*, 1976, **31**, 544; (c) J. Fuchs and I. Brudgam, *Z. Naturforsch. B*, 1977, **32**, 403.
- (a) S. Takara, S. Ogo, Y. Watanabe, K. Nishikawa, I. Kinoshita and K. Isobe, *Angew. Chem., Int. Ed.*, 1999, **38**, 3051; (b) T. M. Che, V. W. Day, L. C. Francesconi, M. F. Fredrich, W. G. Klemperer and W. Shum, *Inorg. Chem.*, 1985, **24**, 4055; (c) R. Villanneau, R. Delmont, A. Proust and P. Gouzerh, *Chem.–Eur. J.*, 2000, **6**, 1184; (d) A. Proust, R. Thouvenot, S.-G. Roh, J.-K. Yoo and P. Gouzerh, *Inorg. Chem.*, 1995, **34**, 4106; (e) B. Hasenknopf, R. Delmont, P. Herson and P. Gouzerh, *Eur. J. Inorg. Chem.*, 2002, 1081; (f) H. Kang and J. Zubietta, *J. Chem. Soc., Chem. Commun.*, 1988, 1192.
- (a) D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180; (b) D.-L. Long, P. Kögerler, A. D. C. Parenty, J. Fielden and L. Cronin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4798.
- (a) H. Abbas, A. L. Pickering, D.-L. Long, P. Kögerler and L. Cronin, *Chem.–Eur. J.*, 2005, **11**, 1071; (b) H. Abbas, C. Streb, A. L. Pickering, A. R. Neil, D.-L. Long and L. Cronin, *Cryst. Growth Des.*, 2008, **8**, 635.
- J. Fielden, D.-L. Long, L. Cronin and P. Kögerler, *Polyhedron*, 2009, **28**, 2803.
- (a) T. Nishikawa and Y. Sasaki, *Chem. Lett.*, 1975, 1185; (b) K. M. Barkigia, L. M. Rajković-Blazer, M. T. Pope and C. O. Quicksall, *Inorg. Chem.*, 1981, **20**, 3318; (c) B. J. S. Johnson, R. C. Schroden, C. Zhu and A. Stein, *Inorg. Chem.*, 2001, **40**, 5972; (d) T. Ueda, T. Yonemura, M. Shiro, M. Fukudome and M. Hojo, *Inorg. Chem. Commun.*, 2007, **10**, 1301.
- 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).
- BVS calculations were performed using VaList, release 2008, A. S. Wills, program available from www.ccp14.ac.uk.
- (a) T. Kuroda-Sowa, M. Munakata, H. Matsuda, S. Akiyama and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1995, 2201; (b) P. S. Halasyamani, M. J. Drevitt and D. O'Hare, *Chem. Commun.*, 1997, 867; (c) M. Zeibig, B. Wallis, F. Mówius and M. Meisel, *Z. Anorg. Allg. Chem.*, 1991, **600**, 231.
- A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- A. Yagasaki, I. Andersson and L. Pettersson, *Inorg. Chem.*, 1987, **26**, 3926.
- M. Pourayoubi and A. R. Mahjoub, *J. Iran. Chem. Soc.*, 2008, **5**, 430.