

## Synthesis of Cu(I) octamolybdates using *tetrakis*-acetonitrilecopper(I) hexafluorophosphate

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### ABSTRACT

Reaction of  $(\text{NBu}_4)_2[\text{Mo}_2\text{O}_7]$  with  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  in acetonitrile results in isolation of the orange  $\beta$ -octamolybdate  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]$  (**1**) along with the colourless  $\alpha$ -octamolybdate  $[\text{Cu}(\text{CH}_3\text{CN})_4]_4[\text{Mo}_8\text{O}_{26}] \cdot 2\text{CH}_3\text{CN}$  (**2**). Both products decompose rapidly upon removal from their mother liquors, forming an insoluble, dark brown coloured phase with the composition  $\text{Cu}_4[\text{Mo}_8\text{O}_{26}] \cdot 0.6\text{CH}_3\text{CN} \cdot 16\text{H}_2\text{O}$  (**3**). The copper(I) acetonitrile derivatised isopolyanion in **1** thus represents an intermediate structure between the simple, underderivatised octamolybdate **2** and fully condensed, polymeric phase **3**.

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### 1. Introduction

Polyoxometalates (POMs) are a large, incredibly varied family of metal oxide clusters based on the early transition metals V, Mo and W in high oxidation states [1]. Their wide range of sizes and shapes, and possibility for derivatisation with transition metal heteroatoms [2,3] and organic ligands [3,4], mean that POMs can display many useful properties including magnetism [4,5], catalysis [1,6] and semiconductivity [7]. POMs are usually synthesised by condensation of metalate anions in acidic aqueous conditions, with subsequent exchange of inorganic cations for bulky organic cations such as tetrabutylammonium ( $\text{NBu}_4^+$ ) allowing their solubilisation in organic media [3,8]. Organic soluble polyoxometalate anions of this type, such as  $(\text{NBu}_4)_2[\text{Mo}_2\text{O}_7]$  ( $\{\text{Mo}_2\}$ ) and  $(\text{NBu}_4)_4[\text{Mo}_8\text{O}_{26}]$  ( $\{\text{Mo}_8\}$ ), can be reacted with other metal complexes to produce derivatised POMs, typically with nuclearities in the range  $\{\text{Mo}_4\}$  to  $\{\text{Mo}_6\}$  [9–14].

Recently, we have developed an approach to the synthesis of POM clusters which uses high concentrations of bulky organic cations to “direct” the formation of novel polyoxoanions in solution. For example, use of protonated hexamethylenetetramine cations has enabled isolation of the highly charged polyoxomolybdate  $[\text{H}_2\text{Mo}_4\text{Mo}_{16}\text{O}_{52}]^{10-}$  [15], while triethanolammonium cations have been used to generate the isopolyoxotungstate  $[\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}$  [16]. In particular, investigating the reaction of alkylammonium salts of the Lindqvist hexamolybdate,  $[\text{Mo}_6\text{O}_{19}]^{2-}$ , with Ag(I) salts found that the Lindqvist anion rearranges to form the silver derivatised  $\beta$ -octa-

molybdate supramolecular synthon  $[\text{Ag}-\text{Mo}_8\text{O}_{26}-\text{Ag}]^{2-}$ , which in turn forms network structures [17–19]. These networks, often linked via  $\text{Ag}\cdots\text{Ag}$  interactions, are directed by the bulky organic cations. The reactive synthon itself can be isolated with terminal dmsol ligands as  $[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{dmsol})_4]^{2-}$  by using the rigid  $\text{Ph}_4\text{P}^+$  to block network formation.

Herein, we extend this work by exploring the reaction of molybdates with the first row  $d^{10}$  transition metal cation Cu(I), using the well known  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  complex as the Cu(I) source.  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  was selected because the Lewis acidity of the  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cation provides a means to induce aggregation of small molybdate anions into larger polyoxoanions, its acetonitrile ligands can be displaced to yield Cu(I) derivatised molybdates, and its steric bulk may allow it to play a structure directing role. In this study, the first two roles are observed in the assembly of octamolybdates  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]$  (**1**) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]_4[\text{Mo}_8\text{O}_{26}] \cdot 2\text{CH}_3\text{CN}$  (**2**) from  $\{\text{Mo}_2\}$  in acetonitrile. Compounds **1** and **2** are among the largest clusters formed by self-assembly of  $\{\text{Mo}_2\}$  in organic media [15], and both rapidly form the insoluble, polymeric phase  $\text{Cu}_4[\text{Mo}_8\text{O}_{26}] \cdot 0.6\text{CH}_3\text{CN} \cdot 16\text{H}_2\text{O}$  (**3**) upon exposure to air. To our knowledge, these are the first studies of the reaction of POMs with Cu(I) salts in organic media, and demonstrate the ability of  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  to induce assembly of novel derivatised POM clusters.

### 2. Experimental

#### 2.1. Materials, methods and instrumentation

All reactions were carried under argon or nitrogen. Tetrabutylammonium dimolybdate and octamolybdate [8], and

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tetrakis-acetonitrilecopper(I) hexafluorophosphate [20] were synthesised according to established procedures. Dry KBr for FTIR was supplied in small sachets by Thermo Fisher. All other reagents were obtained commercially as ACS grade and used without further purification. IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Single crystal X-ray diffraction data were collected on a Bruker CCD-1000 diffractometer with Mo K $\alpha$  radiation. Thermal data (TGA) were measured on a Perkin Elmer TGA 7, CHN analyses were performed using a Perkin Elmer 2400 CHNS Analyzer, and analyses for Mo and Cu were obtained using ICP-OES at the Forschungszentrum Jülich (Jülich, Germany) ZCH elemental analysis service.

## 2.2. Preparation of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>Cu<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>] (**1**) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·2CH<sub>3</sub>CN (**2**) and their decomposition to Cu<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·0.6CH<sub>3</sub>CN·16H<sub>2</sub>O (**3**)

tetrakis-Acetonitrilecopper(I) hexafluorophosphate (0.428 g, 1.14 mmol) was added to a solution of tetrabutylammonium dimolybdate (0.40 g, 0.51 mmol) in acetonitrile (20 mL), resulting in instantaneous production of a yellow–brown precipitate. After reflux for 3 days under an inert atmosphere the resulting suspension was hot filtered to give a pale green solution. Crystallisation by diffusion of diethyl ether into the acetonitrile solution produced red–orange crystals of  $\beta$ -octamolybdate **1**, and colourless crystals of **2**. Note: higher rates of ether diffusion favour crystallisation of **1**. Both **1** and **2** decompose upon exposure to air, rapidly forming a hygroscopic brown material with the stoichiometry Cu<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·0.6CH<sub>3</sub>CN·16H<sub>2</sub>O (**3**) (0.024 g, 0.014 mmol, 11%). While **1** and **2** could not be recovered quickly enough to record individual yields, FTIR spectra were obtained by very rapidly transferring crystals to KBr. FTIR of **1** (KBr disc): cm<sup>-1</sup> 3500 (s), 2976 (w), 2927 (w), 2363 (vw), 2254 (vw), 1616 (m), 1404 (w), 1365 (w), 1046 (w), 950 (vs), 915 (vs), 848 (s), 715 (s), 666 (s), 560 (w). FTIR of **2** (KBr disc): cm<sup>-1</sup> 3474 (m), 2967 (w), 2926 (w), 2363 (vw), 2254 (vw), 2135 (w), 2099 (vw), 1655 (m), 1613 (m), 1405 (w), 1365 (w), 950 (vs), 910 (vs), 846 (s), 712 (s), 672 (s), 560 (w). FTIR of **3** (KBr disc): cm<sup>-1</sup> 3442 (s), 2926 (w), 1619 (m), 10 310 (w), 942 (s), 907 (s), 707 (s). Elemental Anal. Calc. for C<sub>1.2</sub>CuH<sub>33.8</sub>Mo<sub>8</sub>N<sub>0.6</sub>O<sub>42</sub> (**3**): C, 0.82; H, 1.94; N, 0.48; Cu, 14.52; Mo, 43.84. Found: C, 0.83; H, 1.75; N, 0.42; Cu, 14.70; Mo, 43.60%. Thermogravimetric analysis of **3** is consistent with this formula, indicating a mass loss of ca. 18% by 250 °C.

## 2.3. Synthesis of Cu<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·0.6CH<sub>3</sub>CN·16H<sub>2</sub>O (**3**) via [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·2CH<sub>3</sub>CN (**2**)

tetrakis-Acetonitrilecopper(I) hexafluorophosphate (0.070 g, 0.19 mmol) was added to a solution of tetrabutylammonium octamolybdate (0.050 g, 0.023 mmol) in acetonitrile (5 mL), producing a yellow solution. After stirring for 7 h, the now slightly cloudy solution was filtered before vapour diffusion of diethyl ether produced colourless crystals of **2**. These rapidly decomposed upon removal from the mother liquor, producing **3** (0.031 g, 95%).

## 2.4. Single crystal structure determination

Suitable single crystals of **1** and **2** were mounted on the end of a thin glass fibre under ambient conditions using Fomblin oil, and X-ray diffraction intensity data were measured at 193 K on a Bruker CCD-1000 diffractometer [ $\lambda$ (Mo K $\alpha$ ) = 0.7107 Å, graphite monochromator]. For each compound, initial cell constants were obtained from three 30 frame series of  $\omega$  scans at different starting angles, while final cell constants were calculated from a set of strong reflections from the actual data collection. These datasets were corrected for Lorentz and polarization effects and the absorp-

**Table 1**  
Crystallographic data for compounds **1** and **2**.

	<b>1</b>	<b>2</b>
Chemical formula	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ] <sub>2</sub> [Mo <sub>8</sub> O <sub>26</sub> Cu <sub>2</sub> (CH <sub>3</sub> CN) <sub>4</sub> ]	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ] <sub>4</sub> [Mo <sub>8</sub> O <sub>26</sub> ] <sub>2</sub> ·2CH <sub>3</sub> CN
Formula weight	1930.33	2176.65
Crystal system	triclinic	monoclinic
Space group	P $\bar{1}$	P2(1)/n
a (Å)	11.158(2)	12.387(3)
b (Å)	11.699(2)	13.064(3)
c (Å)	12.173(2)	22.378(6)
$\alpha$ (°)	62.991(2)	90
$\beta$ (°)	74.332(2)	103.044(5)
$\gamma$ (°)	80.637(3)	90
V (Å <sup>3</sup> )	1361.6(3)	3527.7(16)
Z	1	2
T (K)	193(2)	193(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.354	2.049
$\mu$ (mm <sup>-1</sup> )	3.386	2.629
Reflections collected	12 427	31 082
Unique reflections ( $R_{\text{int}}$ )	6299(0.0311)	8448(0.1068)
Completeness to $\theta = 25.00^\circ$	99.6%	100%
Data/restraints/parameters	6299/0/340	8448/0/424
Goodness-of-fit (GOF) on $F^2$	1.031	0.998
Residuals <sup>a</sup> : $R_1$ ; $wR_2$	0.0316; 0.0785	0.0464; 0.1257

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

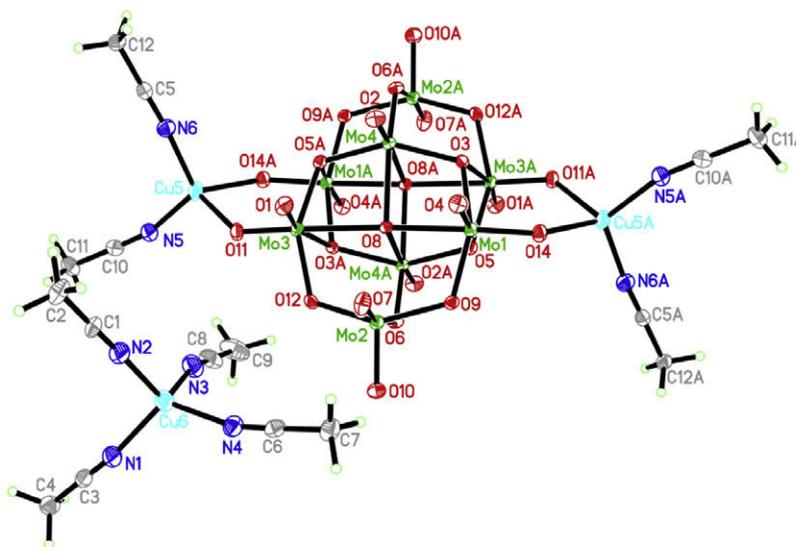
tion correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [21] using SADABS software [22]. Structure solution and refinement was carried out using the SHELXTL program suite [22]. Compound **1** crystallized in the space group P $\bar{1}$  and **2** in P2(1)/n. Both structures were solved by a combination of direct methods and difference Fourier syntheses and refined against  $F^2$  by the full-matrix least-squares technique. Hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Crystal data, data collection parameters and refinement statistics for **1** and **2** are listed in Table 1.

## 3. Results and discussion

### 3.1. Synthesis of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>Cu<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>] (**1**) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·2CH<sub>3</sub>CN (**2**); decomposition to Cu<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·0.6CH<sub>3</sub>CN·16H<sub>2</sub>O (**3**)

The red  $\beta$ -octamolybdate [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>Cu<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>] (**1**, Fig. 1) and colourless  $\alpha$ -octamolybdate [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·2CH<sub>3</sub>CN (**2**, Fig. 3), have both been characterized by high quality crystal structures, and are formed in the same reaction between tetrabutylammonium dimolybdate and tetrakis-acetonitrile copper(I) hexafluorophosphate in refluxing acetonitrile. Upon removal from the mother liquor, both materials rapidly decompose (e.g. within seconds) forming insoluble, hygroscopic dark brown materials with identical FTIR spectra – thus preventing their characterization by elemental analysis or thermal techniques. FTIR spectra of **1** and **2** (see Supplementary data), which appear very similar, were obtained before complete decomposition by pipetting crystals on to a filter paper and rapidly transferring them to dry KBr. In addition to FTIR, the dark brown material has been characterized by full elemental analysis (Mo, Cu, C, H and N) and TGA to reveal the composition Cu<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>]<sub>2</sub>·0.6CH<sub>3</sub>CN·16 H<sub>2</sub>O (**3**). This indicates that **3** is formed by rapid expulsion of acetonitrile from the structure with an accompanying uptake of atmospheric water, while its insolubility suggests formation of a Cu(I) linked {Mo<sub>8</sub>} coordination polymer.

Octamolybdates such as **1** and **2** are typically synthesized by acidifying aqueous solutions of sodium molybdate [8], and



**Fig. 1.** ORTEP representation of the  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cation and  $[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]^{2-}$  cluster anion in **1**. Thermal ellipsoids are drawn at the 30% probability level. C atoms are grey; N, blue; O, red; Mo, green; Cu, cyan; H atoms are white spheres of arbitrary radius. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

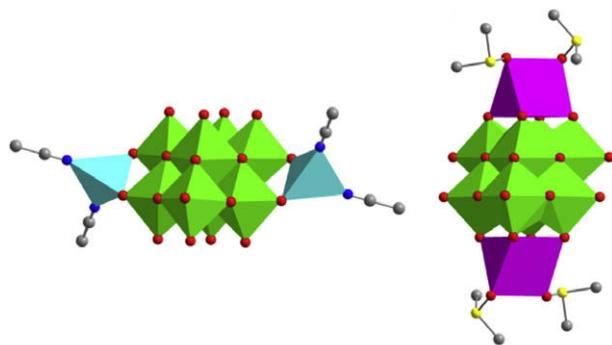
although we have previously observed rearrangement of hexamolybdate anions to such species upon treatment with  $\text{Ag}(\text{I})$  [17–19], to our knowledge they have not previously been synthesized by self-assembly of small molybdate building blocks in organic media. One unusual alkoxy-substituted  $\{\text{Mo}_8\}$  cluster, constructed from two weakly bridged, readily dissociated corner sharing  $\{\text{Mo}_4\}$  units has previously been assembled from  $(\text{NBu}_4)_2[\text{Mo}_8\text{O}_7]$  in methanol [23]. However, this is a fundamentally different type of isopolyanion to the more highly condensed  $\alpha$ - and  $\beta$ -octamolybdates reported here.

The ability of our conditions to induce condensation of molybdate polyhedra may be a consequence of the Lewis acidity of  $\text{Cu}(\text{I})$ , with coordination of terminal  $\text{Mo}=\text{O}$  groups to  $\text{Cu}(\text{I})$  activating them as leaving groups in an analogous fashion to protonation in aqueous systems. It is also worth noting that interconversion of  $\alpha$ - and  $\beta$ -octamolybdates has previously been observed [24], suggesting that **1** and **2** form via a common reaction pathway. Mixtures of **1** and **2** are also obtained by refluxing  $\alpha$ - $\{\text{Mo}_8\}$  (as  $(\text{NBu}_4)_4[\text{Mo}_8\text{O}_{26}]$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  in acetonitrile, while compound **2** could be prepared exclusively by simple, room temperature cation metathesis of  $(\text{NBu}_4)_4[\text{Mo}_8\text{O}_{26}]$  with  $[\text{Cu}(\text{CH}_3\text{CN})_4]$

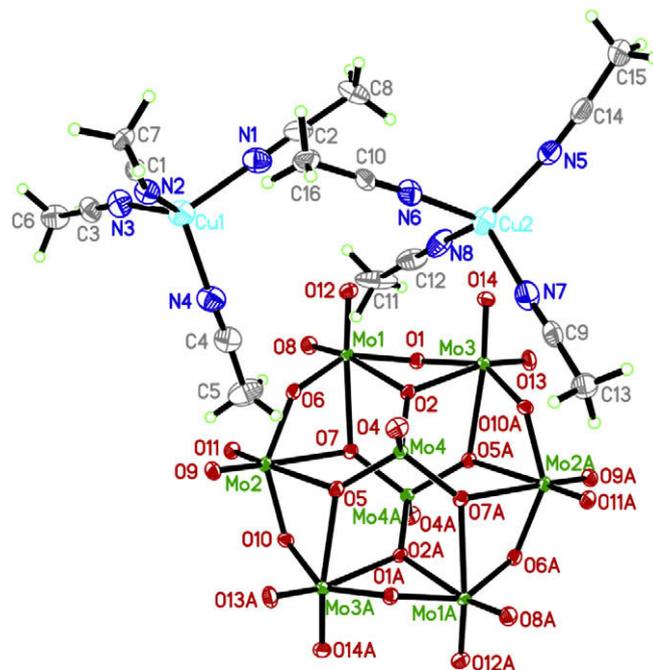
$(\text{PF}_6)$ , leading to a high yield (95%) of isolated **3**. This implies that the uncoordinated octamolybdate cluster **2** forms first and then, given sufficient thermal energy, displaces acetonitrile ligands from  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  to form **1**. As such, **1** can be seen as an intermediate step in the conversion of **2** to the almost acetonitrile free  $\text{Cu}(\text{I})$  octamolybdate **3**.

### 3.2. X-ray structural characterization

Good quality X-ray structural data were obtained for both **1** and **2**. The cluster anion in compound **1**, which crystallises in the space group  $P\bar{1}$ , is a  $\beta$ -octamolybdate cluster composed of two oxygen



**Fig. 2.** Polyhedral representation comparing the derivatised  $\beta$ -octamolybdate anions  $[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]^{2-}$  (**1**, this work) and  $[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{dmsO})_4]^{2-}$  (Ref. [17]). Colour scheme is as Fig. 1, with  $\text{Ag}$  purple,  $\text{S}$  yellow and  $\text{H}$  omitted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** ORTEP representation of the  $[\text{Mo}_8\text{O}_{26}]^{4-}$  cluster anion and two crystallographically independent  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cations in **2**. The acetonitrile solvent molecule has been omitted for clarity. Colour scheme as for Fig. 1.

centred  $\{\text{Mo}_4\text{O}_{13}\}$  units (Fig. 1) with  $\{\text{Cu}(\text{CH}_3\text{CN})_2\}$  units bound to terminal oxo positions on opposite sides of the cluster.

The cluster anion in **1** is comparable to our previously isolated  $[\text{Ag}-\text{Mo}_8\text{O}_{26}-\text{Ag}]^{2-}$  synthon,  $[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{dmsO})_4]^{2-}$  [17], with terminal ligation provided by  $\text{CH}_3\text{CN}$  rather than DMSO. However, the geometries and locations of the transition metal heteroatoms in these structures are different (Fig. 2). Each Ag(I) in  $[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{dmsO})_4]^{2-}$  has a trigonal prismatic geometry and binds to four terminal Mo=O groups on the “top” or “bottom” of the cluster, while the preference of Cu(I) for tetrahedral coordination means that in **1** the two Cu(I) atoms each coordinate to two terminal oxo positions on the “sides” of the cluster. In this way, the  $\beta$ -octamolybdate cluster in **1** is comparable to a number of transition metal derivatised  $\beta$ -octamolybdates. However, these clusters typically feature completely oxidized transition metals with terminal coordination sites occupied by more strongly binding amine ligands such as example di-2-picolyamine [25] or 1,10-phenanthroline [26]. As such, **1** can be seen as an isolated, reactive intermediate cluster or “synthon” – with its propensity to form networks indicated by the rapid formation of the presumed coordination polymer  $\text{Cu}_4[\text{Mo}_8\text{O}_{26}]\cdot 0.6\text{CH}_3\text{CN}\cdot 16\text{H}_2\text{O}$  (**3**) upon removal from acetonitrile saturated environments.

In **1**, the  $\beta$ - $\{\text{Mo}_8\}$  cluster is formed by two  $\{\text{Mo}_4\text{O}_{13}\}$  units which are connected off centre to each other with the central  $\mu_5$ -oxo position (O8) of each  $\{\text{Mo}_4\text{O}_{13}\}$  unit positioned directly above/below one of the surrounding Mo atoms (Mo4) of the other tetramolybdate subunit, Mo–O distances are displayed in Table 2. A further six bridging oxo ligands complete the link between the equatorial coordination sites of each  $\{\text{Mo}_4\text{O}_{13}\}$  unit and the axial coordination sites of its partner. The two symmetry related Cu(I) atoms each coordinate to two terminal oxo sites, with a slight lengthening of the Mo–O distances indicating a corresponding weakening of the Mo–O double bond character (Table 2). While bond valence sum calculations [27] suggest roughly equal probabilities for a fully oxidized molybdate cluster coordinated to Cu(I), or a mixed valence cluster coordinated to Cu(II), the *pseudo*-tetrahedral Cu coordination environment provides a clear indicator that copper is in the +1 oxidation state. Slight distortion from idealized tetrahedral geometry is indicated by the tight O–Cu–O angle ( $87.9(2)^\circ$ ) result-

**Table 3**

Coordination bond lengths (Å) and selected angles ( $^\circ$ ) in  $[\text{Cu}(\text{CH}_3\text{CN})_4]_4[\text{Mo}_8\text{O}_{26}]\cdot 2\text{CH}_3\text{CN}$  (**2**).

	Mo centres		Cu centres		
Mo=O	Mo1–O8	1.704(5)	Cu1–N1	2.002(9)	
	Mo1–O8	1.699(5)	Cu1–N2	1.985(8)	
	Mo2–O9	1.704(5)	Cu1–N3	2.012(9)	
	Mo2–O11	1.701(5)	Cu1–N4	2.021(9)	
	Mo3–O13	1.701(5)	Cu2–N5	1.974(8)	
	Mo3–O14	1.706(5)	Cu2–N6	2.006(8)	
	Mo4–O4	1.707(5)	Cu2–N7	1.979(9)	
	$\mu_2$ Mo–O	Mo1–O1	1.908(5)	Cu2–N8	1.988(9)
		Mo1–O6	1.916(5)	N2–Cu1–N1	103.9(3)
		Mo2–O6	1.915(5)	N2–Cu1–N3	113.2(3)
Mo2–O10		1.906(5)	N1–Cu1–N3	116.0(3)	
Mo3–O1		1.912(5)	N2–Cu1–N4	120.2(3)	
Mo3–O10a		1.920(5)	N1–Cu1–N4	104.4(3)	
			N3–Cu1–N4	99.5(3)	
$\mu_3$ Mo–O	Mo1–O2	2.400(4)	N5–Cu2–N7	104.5(3)	
	Mo1–O7	2.411(5)	N5–Cu2–N8	120.4(3)	
	Mo2–O5	2.394(5)	N7–Cu2–N8	113.6(3)	
			N5–Cu2–N6	108.9(3)	
	Mo2–O7	2.412(5)	N7–Cu2–N6	108.4(3)	
	Mo3–O2	2.419(5)	N8–Cu2–N6	100.6(3)	
	Mo3–O5a	2.421(5)			
	Mo4–O2	1.782(5)			
	Mo4–O5	1.784(5)			
	Mo4–O7a	1.782(5)			

ing from coordination to the molybdate oxygen sites, while the terminal acetonitrile ligands coordinate with Cu–N distances that are slightly shorter than those observed in the accompanying  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cation (Table 1). Nonetheless, these ligands appear to be highly labile, as indicated by expulsion of acetonitrile in the ambient atmosphere leading to formation of **3**. The extended structure of **1** is constructed from layers of molybdate clusters running parallel to the crystallographic *ab* plane, separated by layers of  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cations; note that the numerous short contacts between the acetonitrile ligands and molybdate oxygens ( $\text{C}\cdots\text{O}$  distances ranging from *ca.* 2.94 to 3.18 Å) may be responsible for the distortion observed in the  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cation (two large N–Cu–N angles of  $119.9(2)$  and  $117.4(2)^\circ$ ).

**Table 2**

Coordination bond lengths (Å) and selected angles ( $^\circ$ ) in  $[\text{Cu}(\text{CH}_3\text{CN})_4]_2[\text{Mo}_8\text{O}_{26}\text{Cu}_2(\text{CH}_3\text{CN})_4]$  (**1**).

Mo centres				Cu centres	
Mo=O	Mo1–O4	1.696(3)	Cluster anion	Cu5–N5	1.944(4)
	Mo2–O7	1.702(3)		Cu5–N6	1.947(4)
	Mo2–O10	1.695(3)		Cu5–O11	2.086(3)
	Mo3–O1	1.700(3)		Cu5–O14a	2.065(3)
	Mo4–O2	1.685(3)		N5–Cu5–N6	114.67(17)
Mo=O–Cu	Mo1–O14	1.726(3)		N5–Cu5–O14a	114.68(15)
	Mo3–O11	1.726(3)		N6–Cu5–O14a	112.83(15)
	$\mu_2$ Mo–O	Mo1–O9	1.884(3)		N5–Cu5–O11
Mo2–O9		1.923(3)		N6–Cu5–O11	110.22(15)
Mo2–O12		1.996(3)		O14a–Cu5–O11	87.84(11)
Mo2–O6		2.273(3)			
Mo3–O12		1.888(3)			
Mo4–O6a		1.748(3)			
$\mu_3$ Mo–O		Mo1–O3	1.996(3)	Cation	Cu6–N1
	Mo1–O5	2.375(3)	Cu6–N2		1.987(4)
	Mo3–O3a	2.364(3)	Cu6–N3		1.993(5)
	Mo3–O5a	1.994(3)	Cu6–N4		1.994(4)
	Mo4–O3	1.931(3)	N1–Cu6–N3		102.30(19)
	Mo4–O5a	1.942(3)	N1–Cu6–N4		119.86(18)
$\mu_5$ Mo–O	Mo1–O8	2.252(3)		N2–Cu6–N1	106.00(17)
	Mo2–O8	2.564(3)		N2–Cu6–N3	117.4(2)
	Mo3–O8	2.267(2)		N2–Cu6–N4	106.80(17)
	Mo4–O8	2.161(3)		N3–Cu6–N4	105.14(18)
		2.430(2)			

Compound **2** crystallises in  $P2(1)/n$  and is simply an  $\alpha$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster anion accompanied by [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup> cations. The  $\alpha$ -octamolybdate cluster anion in **2** can be viewed as an {Mo<sub>6</sub>O<sub>18</sub>} belt capped by two {MoO<sub>4</sub>} tetrahedra (Fig. 3); selected bond lengths and angles are shown in Table 3. There are two crystallographically independent [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup> positions present with Cu–N distances ranging from 1.975(9) to 2.021(9) Å. More significant distortion is observed in the N–Cu–N bond angles of these *pseudo*-tetrahedral cations, which range from ca. 100 to 120°. Such distortion is to be expected from the combination of such coordinatively flexible *d*<sup>10</sup> metal cations with large molybdate anions capable of exerting substantial crystal packing forces. In the extended structure, alternating layers of octamolybdate clusters and cations/solvent propagate parallel to a plane described by the crystallographic *b* axis and a line intersecting *c* at 31.68°.

#### 4. Conclusions

[Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) is capable of inducing aggregation of [Mo<sub>2</sub>O<sub>7</sub>]<sup>2-</sup> to form larger molybdate species, presumably as a consequence of the Lewis acidity of Cu(I), and also provides a source of Cu(I) that can coordinate to the resulting polyoxoanions. This is shown by the isolation of a novel {Cu(CH<sub>3</sub>CN)<sub>2</sub>} derivatised  $\beta$ -octamolybdate cluster anion, in which the preference of Cu(I) for tetrahedral coordination results in it occupying a different coordination site on the cluster anion to the previously described {Ag(DMSO)<sub>2</sub>} analogue. As such, [Cu(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>) is an interesting reagent for use in non-aqueous POM chemistry. In this study, the isolation of cluster anions belonging to known structural types suggests the absence of templation effects from the [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup> cation, in contrast to our previous work with several organic cations. This may be because the high lability of the Cu(I)–N coordination bond compared to covalent bonds, coupled with the absence of hydrogen bonding groups that can interact strongly with molybdate anions, limits the ability of this [Cu(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup> to template molybdates. In future studies, we aim to use organic co-cations to help stabilise compound **1**, and exploit its reactivity as a building block for reaction with organic ligands and coordination clusters.

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#### Appendix A. Supplementary data

CCDC 726620 and 726621 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.058.

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