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Two new inorganic–organic hybrid salts: $[NH_2Me_2]_4[NMe_4]_2$-$[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]\cdot 1.5H_2O$ and $[NMe_4]_2[NH_4]_2[Mo_8O_{26}]\cdot 2H_2O$

T. Duraisamy,[a] A. Ramanan*[a] and J. J. Vittal[b]

[a]Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India. E-mail: aramanan@chemistry.iitd.ernet.in
[b]Department of Chemistry, National University of Singapore, Singapore 119 260. E-mail: chmjjv@leonis.uus.sg

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The present paper reports the formation of two novel organic–inorganic hybrid structures from acidified, aqueous ammonium molybdate solution containing tetramethylammonium ions, $[NH_2Me_2]_4[NMe_4]_2[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]\cdot 1.5H_2O$ **1** and $[NMe_4]_2[NH_4]_2[Mo_8O_{26}]\cdot 2H_2O$ **2**. While **1** is crystallised in the presence of a reducing agent, hydrazine hydrate, **2** is formed in its absence. Crystal data: **1,** orthorhombic, space group *Pnma*, $a = 22.4037(2)$, $b = 19.5153(2)$ and $c = 12.7108(2)$ Å, $V = 5557.3(1)$ Å^3, $Z = 4$; **2**, monoclinic, space group *C2/m*, $a = 11.2641(1)$, $b = 16.3815(1)$, $c = 10.0775(1)$ Å, $\beta = 110.242(1)°$, $V = 1744.68(3)$ Å^3, $Z = 2$. Compound **1** contains layers of disordered dimethylammonium ions alternating with mixed-valent Keggin clusters which are surrounded by tetramethylammonium cations. The structure of **2** is characterised by the presence of layers containing tetramethylammonium cations alternating with layers containing β-Mo_8O_{26} anions; the cavity formed between the anionic clusters is occupied by an unusual eight-membered hydrogen bonded cluster formed between two ammonium ions and two water molecules.

In the past few decades, there has been much interest in molybdenum oxides and molybdates as they allow rich intercalation as well as polymeric oxo-anion chemistry and form structurally interesting model systems.[1–7] Recently synthesised mixed-valence polynuclear cores,[8,9] such as $\{[H_3O]^+_{12}$-$\{(H_2O)MoO_{2.5}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]O_{2.5}Mo(H_2O)\}^{12-}\}_n$, $Na_{15}\{Mo_{144}O_{409}(OH)_{28}(H_2O)_{56}\}\cdot 250H_2O$ and $(NH_4)_{25}$-$[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]\cdot 350H_2O$, suggest that the polyoxometallates may provide a unique class of clusters with unusual structural and electronic variety. Furthermore it has been noted that a few of these polyoxomolybdate clusters[10,11] possess cavities for the incorporation of several organic cations, in a manner reminiscent of the encapsulation of small guest molecules by polyoxovanadate clusters; more significantly, we have observed the role of N-containing organic molecules such as hexamethylenetetramine[12] or morpholine[13] in the formation of vanadium oxo-anion and phosphomolybdate[14] clusters with varying degree of stability for cluster architecture and reduction. In addition to functioning as structure directing cations or as counter cations, the organic templates may also serve as multifunctional ligands forming an integral part of the covalent or non-covalent scheme of the solid, or participate in the extensive network of hydrogen bonding. Although these organic cations are believed to direct the self-assembly of cluster formation, in view of the host–guest interactions present in all self-assembled systems of inorganic–organic hybrid materials, it is obviously to be noted that the fragments formed during the self-assembly process may also take part in the cluster compound as counter cations. This in effect, obviously, combines the two strategies for molecular design of solids and provides a route to prepare novel organic–inorganic hybrid materials. This expectation has been realised in the isolation and structural characterisation of two new compounds **1** and **2**. Compound **1** contains a nearly tetrahedral and pure mixed-valent β-Keggin anion, $[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]^{6-}$ encapsulating an MoO_4 tetrahedral fragment wherein the tetrahedral site is partially occupied by Mo. Compound **2** is an assembly of ordered layers containing β-$[Mo_8O_{26}]^{4-}$ and NMe_4^+ ions; the cavity formed between the anionic clusters is occupied by an unusual multi-point hydrogen bonded cluster formed between ammonium and water molecules.

Results and discussion

Deep blue crystals of **1** were isolated in 25% yield from an aqueous solution containing ammonium heptamolybdate, tetramethylammonium ions (TMA) and hydrazine hydrate, while **2** was obtained in 45% yield as colourless crystals under the same reaction conditions except that the reducing agent hydrazine hydrate was not employed. The FTIR spectra (Fig. 1) of compound **1** showed characteristic vibrational features similar to other Keggin cores reported in the literature.[15] For **1**, symmetric and asymmetric stretching of the different kinds of Mo–O bonds are observed in the following regions: the terminal Mo–O bonds are in the range 1000–960 cm^{-1}; Mo–O$_b$–Mo bridged oxygen (interbridges between corner sharing octahedra), 890–850 cm^{-1}; Mo–O$_c$–Mo bridged oxygen (intrabridges between edge sharing octahedra), 800–760 cm^{-1}. The strong band at 640 cm^{-1} and others at 550, 480 cm^{-1} are assigned to the antisymmetric stretching vibrations of Mo–O$_b$–Mo and Mo–O$_c$–Mo respectively. Bands at 3400, 3200, 2930, 1680, 1500, 1465 and 1330 cm^{-1} indicate the presence of characteristic vibrational features of dimethylammonium (DMA) and TMA cations and water molecules. The FTIR spectra of compound **2** showed characteristic vibrational features similar to other β-$[Mo_8O_{26}]^{4-}$ clusters reported in the literature.[16] The Mo–O$_t$ stretching vibrations are in the range 995–975 cm^{-1} and Mo–O stretching and bending vibrations are seen in the region 850–750 cm^{-1}. The strong bands at 700 cm^{-1} and one at 685 cm^{-1} are assigned to the Mo–O–Mo bending modes. Bands at 3390, 3150, 2830, 1600, 1580, 1500, 1465 and 1300 cm^{-1} indicate the presence of characteristic vibrational features of TMA, ammonium ions and water molecules.

Description of the structures

Crystallographic data for **1** and **2** are given in Table 1. Single crystal X-ray diffraction of **1** reveals the presence of four

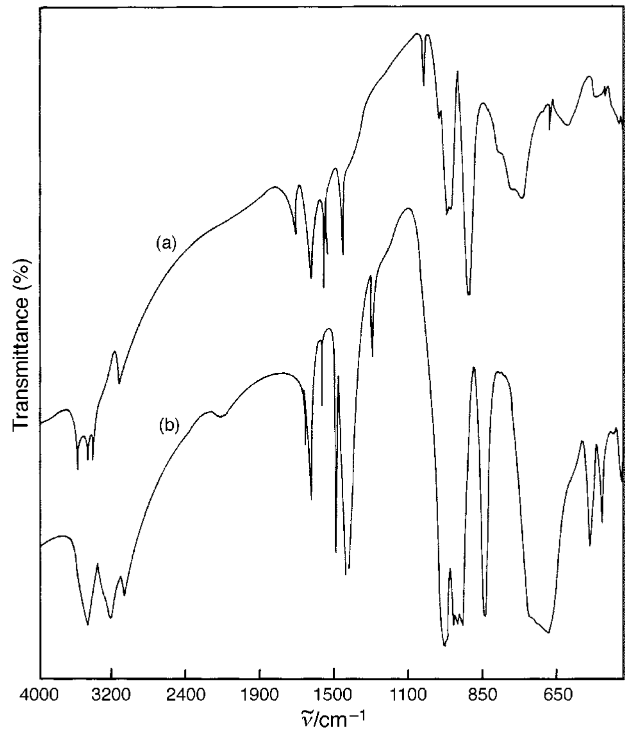

Fig. 1 FTIR spectra of **1** and **2**.

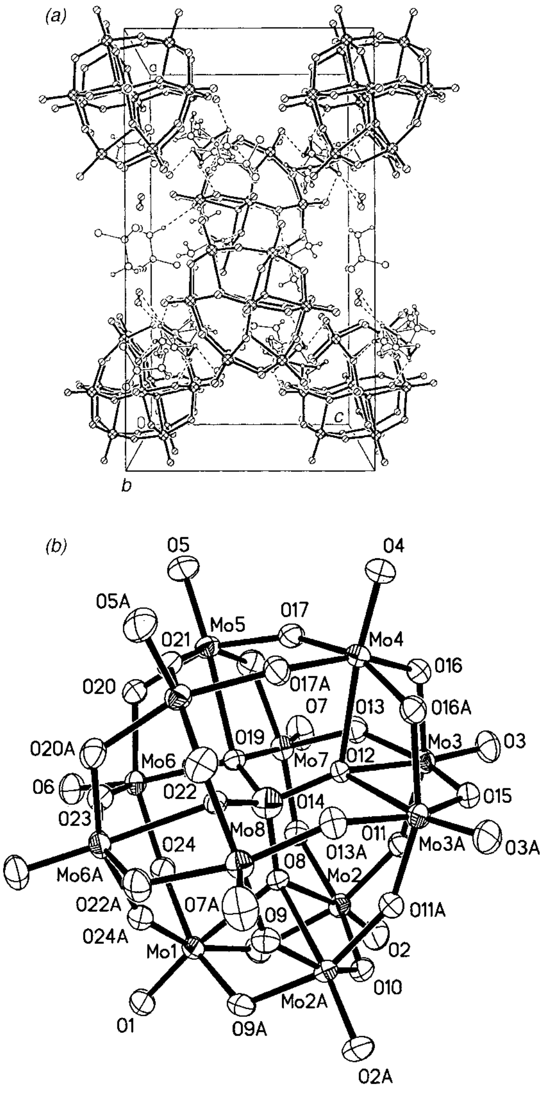

Fig. 2 (*a*) A perspective view of the unit cell packing diagram for **1** and (*b*) an ORTEP view of the β-Keggin core, $[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]^{6-}$.

DMA, two TMA and a discrete molecular anion, $[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]^{6-}$, that has a central cavity encapsulating an almost regular MoO_4 tetrahedron [Fig. 2(*a*) and (*b*)]. There is a crystallographic mirror symmetry present in the anion with the mirror plane passing through atoms Mo(1), Mo(4), Mo(8), O(1), O(4), O(8), O(10), O(12), O(15), O(21) and O(23) and N(1) of the TMA cations. Refinement of the population parameters of the sites occupied by the central encapsulated tetrahedral molybdenum unit confirms partial occupancy of nearly 0.5 and this is consistent with the formulation and charge compensation of the anion, $[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]^{6-}$. Such partial occupancy is not unusual among polyoxomolybdate clusters.[17] The Keggin anion is constructed of four Mo_3O_{13} units formed by edge sharing octahedra and connected to each other by vertices as noted in the literature.[18–23] The Mo–O_t, Mo–O(μ_2) and Mo–O(μ_6) bond distances are in the ranges 1.62–1.68, 1.70–1.94 and 2.32–2.49 Å, respectively, indicating the expected trend of increasing Mo–O bond length for one- < two- < three- < four-coordinated oxygen as reported earlier for other Keggin clusters.[18–23] Selected bond distances and angles are given in Table 2. The Mo–O bond distances [1.630(4)–1.637(6) Å] and the bond angles (108–110°) are within acceptable values for MoO_4 tetrahedra.[19] In our model, the two Mo^V centres are statistically delocalized over the twelve octahedral sites. The two-electron reduced metal–oxo framework core, $[Mo_{0.5}O_4 \subset (Mo_{12}O_{36})]^{6-}$, probably is the first example of a pure Mo/O β-Keggin cluster. Our model also showed that there is considerable disorder among both TMA and DMA ions present. The DMA ions form layers (along the *xz*-plane) alternating with mixed-valent Keggin cores which are surrounded by TMA cations. There are medium to weak non-bonding interactions between the cations and anions (Table 3).

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

	1	**2**
Chemical formula	$C_{16}H_{57.50}Mo_{12.50}N_6O_{41.50}$	$C_8H_{36}Mo_8N_4O_{28}$
Formula weight	2197.43	1399.90
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	*C*2/*m*
a/Å	22.4037(2)	11.2641(1)
b/Å	19.5153(2)	16.3815(1)
c/Å	12.7108(2)	10.0775(1)
β/°	90.00	110.242(1)
V/Å^3	5557.35(12)	1744.68(3)
T/K	293(2)	293(2)
Z	4	2
D_c/g cm^{-3}	2.626	2.665
λ/Å	0.71073	0.71073
θ Range/°	1.82–29.26	2.15–29.24
No. of reflections	33763	5644
F(000)	4210	1336
Total parameters	361	123
Extinction coefficient	0.00017(3)	0.00294(14)
μ/mm^{-1}	2.820	2.877
$R_1[I>2\sigma(I)]$	0.0472	0.0242
wR_2	0.1250	0.0633
GOF^c	1.119	1.108

$^aR_1=\sum(||F_o-F_c||)/\sum(|F_o|)$. $^bwR_2=[\sum w(F_o^2-F_c^2)/\sum wF_o^4]^{1/2}$. ^{c}GOF $=[\sum w(F_o^2-F_c^2)/(n-p)]^{1/2}$ where n is the number of reflections and p is the number of parameters refined.

In compound **2**, β-$[Mo_8O_{26}]^{4-}$ clusters and the TMA cations are ordered along the *b*-axis [Fig. 3(*a*)]. The metal–oxygen framework of the Mo_8O_{26} moieties is constructed from MoO_6 edge-sharing octahedra and the metal–oxygen distances are similar to β-$[Mo_8O_{26}]^{4-}$ clusters [Fig. 3(*b*)] found in the literature.[24–35] Crystallographic 2/*m* symmetry is present in

Table 2 Selected bond distances (Å) and angles (°) for compounds **1** and **2**[a]

Anions

β-Keggin core

Mo1–O1$_t$	1.692(6)	Mo5–O5$_t$	1.693(5)
Mo1–O24(μ_2) × 2	1.949(4)	Mo5–O20(μ_2)	1.941(4)
Mo1–O9(μ_2) × 2	1.886(4)	Mo5–O17(μ_2)	1.900(4)
Mo1–O8(μ_4)	2.345(8)	Mo5–O21(μ_2)	1.910(2)
Mo2–O2$_t$	1.690(4)	Mo5–O18(μ_2)	1.941(4)
Mo2–O14(μ_2)	1.976(4)	Mo5–O19(μ_4)	2.355(4)
Mo2–O10(μ_2)	1.901(3)	Mo6–O6$_t$	1.696(4)
Mo2–O11(μ_2)	1.897(4)	Mo6–O20(μ_2)	1.925(4)
Mo2–O9(μ_2)	1.995(4)	Mo6–O24(μ_2)	1.906(4)
Mo2–O8(μ_4)	2.345(4)	Mo6–O23(μ_2)	1.916(2)
Mo3–O3$_t$	1.687(4)	Mo6–O22(μ_2)	1.913(4)
Mo3–O11(μ_2)	1.890(4)	Mo6–O19(μ_4)	2.371(4)
Mo3–O15(μ_2)	1.913(3)	Mo7–O7$_t$	1.686(5)
Mo3–O13(μ_2)	1.983(4)	Mo7–O18(μ_2)	1.980(5)
Mo3–O16(μ_2)	1.998(4)	Mo7–O13(μ_2)	1.871(4)
Mo3–O12(μ_4)	2.339(4)	Mo7–O14(μ_2)	1.869(4)
Mo4–O4$_t$	1.693(6)	Mo7–O22(μ_2)	1.971(4)
Mo4–16(μ_2) × 2	1.889(4)	Mo7–O19(μ_4)	2.333(4)
Mo4–O17(μ_2) × 2	1.958(4)	Mo8–O19 × 2	1.630(4)
Mo4–O12(μ_4)	2.361(5)	Mo8–O12	1.635(5)
Mo8–O8	1.637(6)		

O1–Mo1–O9	99.8(2)	O19–Mo8–O8	109.6(2)
O1–Mo1–O8	172.7(3)	O19–Mo8–O12	109.9(2)
O9–Mo1–O24A	159.6(2)	O12–Mo8–O8	108.1(2)
O2–Mo2–O11	102.0(2)	Mo1–O8–Mo2	91.3(2)
O11–Mo2–O8	86.1(2)	Mo1–O9–Mo2	119.9(2)
O9–Mo2–O8	73.3(2)	Mo8–O8–Mo2	124.6(2)

β-Mo_8O_{26}

Mo1–O4$_t$	1.701(2)	Mo3–O8$_t$	1.706(3)
Mo1–O5$_t$	1.710(2)	Mo3–O9$_t$	1.708(3)
Mo1–O3(μ_2)	1.910(2)	Mo3–O3(μ_2) × 2	1.919(2)
Mo1–O2(μ_3) × 2	1.983(2)	Mo3–O7A(μ_2)	2.271(3)
Mo1–O1(μ_5)	2.376(4)	Mo3–O1(μ_5)	2.444(2)
Mo2–O6$_t$	1.694(3)		
Mo2–O7(μ_2)	1.751(2)		
Mo2–O2(μ_3) × 2	1.956(2)		
Mo2–O1(μ_5)	2.152(2)		
Mo2–O1A(μ_5)	2.404(2)		

O4–Mo1–O5	105.0(4)	Mo2–O2–Mo1	109.2(1)
O3–Mo1–O2	146.1(1)	Mo2–O1–Mo1	91.4(1)
O5–Mo1–O3	99.48(3)	Mo1–O3–Mo3	116.6(2)
O2–Mo1–O1	73.66(1)	Mo2–O1–Mo3	164.2(2)
O7–Mo2–O1	155.4(1)	Mo2–O1–O2C	104.6(2)
O7–Mo2–Mo1B	132.1(1)	O3–Mo1–Mo2	119.5(7)
O6–Mo2–Mo1C	174.6(2)		

Cations

Compound **1**

Dimethylammonium cation

N1–C2	1.476(2)
N2–C4	1.430(3)
C1A–N1–C2	109.0(1)
C4A–N2A–C3A	115.0(2)
C4–N2–C3	108.8(6)

Tetramethylammonium cation

N3–C5	1.370(1)	C5–N3–C7	111.7(4)
N3–C6A	1.469(1)	C6–N3–C7	106.8(2)
N4–C10	1.540(1)	C8–N4–C10A	108.8(2)

Compound **2**

Tetramethylammonium cation

N1–C1	1.494(6)
N1–C2	1.495(3)
C1–N1–C2	110.1(2)
C2–N1–C4D	108.7(3)

[a] Symmetry transformations: **1**, A, *x*, $-y+1/2$, *z*. **2,** A, $-x$, *y*, $-z+1$; B, *x*, $-y+1$, *z*; C, $-x$, $-y+1$, $-z+1$; D, $-x$, *y*, $-z$.

Table 3 Selected hydrogen bonding parameters [distances (Å) and angles (°)] in **1** and **2**[a]

Compound **1**

N1–H1A···O18	2.858(1)	N2–H2D···O14	3.035(1)
N1–H1B···O13	3.051(2)	N2A–H2D···O2	3.036(1)
N1–H1A···O16	3.038(1)	N2A–H2E···O22	2.990(1)
N1–H1A···O17	3.137(2)		

Compound **2**

O1S···H1D–N2D	2.231(3)	O1S···H1D–N2D	174.26(7)
O5C···H2–N2	2.416(3)	N2–H2···O4A	134.07(7)
O4A···H2–N2	2.476(3)	N2–H2···O5C	129.9(8)
O9B···H3–N2A	2.079(4)	O1S–H3···O9B	173.8(1)
N2–H2···O4A	2.961(3)	O1S–H4···O8A	165.7(1)
N2–H2···O5C	2.873(3)		
O1S···H2D–N2D	2.865(3)		
O1S–H4···O8A	2.841(4)		
O1S–H3···O9B	2.824(4)		

[a] Symmetry operators: **1**, A, *x*, $-y+1/2$, *z*. **2**, A, *x*, *y*, $z-1$; B, $-x+1$, $-y+1$, $-z+1$; C, $-x+1/2$, $-y+1/2$, $-z$; D, *x*, $-y+1$, *z*.

the anion. The atoms Mo(2), Mo(3), O(1), O(6), O(7), O(8) and O(9) lie on the crystallographic mirror plane. A two-fold symmetry axis is present perpendicular to this mirror plane and passes through the middle of the plane formed by Mo(2), Mo(2a), O(1) and O(1a). The two-fold axis also passes through the N(1) and N(2) atoms of the cations and the water molecule lies on the mirror plane. It is well known that β-$[Mo_8O_{26}]^{4-}$ is one of the most stable clusters formed in aqueous, acidic solution in the presence of several inorganic and organic cations.[24–35] A significant structural feature of **2** is that the TMA cations are ordered along the *xz*-planes around $y \approx 0.25$ and $y \approx 0.75$ forming layers. The β-$[Mo_8O_{26}]$ clusters are found in between these layers such that the C_2-axis of the molybdate cluster is parallel to the *b*-axis and the mirror planes passing through the anions occur on the *xz*-plane at $y = 0$ and 0.5. The two water molecules occur at the cavities formed between the β-$[Mo_8O_{26}]$ clusters such that the C_2-axis of the water molecule lies on the same plane that contains the mirror planes of the anions. In addition, the two water molecules are interlinked to the two ammonium molecules through hydrogen bonding as shown in Fig. 4; the hydrogen bonded cluster shows a C_{2h} symmetry. The non-bonding interactions between the ammonium ions and water molecules are listed in Table 3. Each oxygen atom of the water molecule is hydrogen bonded to two hydrogen atoms of each ammonium cation to form an eight-membered ring through N–H···O bonds. This leaves two H-atoms on each NH_4^+ and H_2O involved in hydrogen bonding to the oxygen atoms O(4), O(5), O(8) and O(9) of the anions, *i.e.*, all the hydrogen atoms of the ammonium cation and the water solvent are involved in hydrogen bonding. This type of hydrogen bonding appears to be very unusual. There is one other example reported in the literature[36] wherein a hydrogen bonded cluster cation, $Na_4(CH_4O)_8(H_2O)_2$ is located in between β-Mo_8O_{26} units.

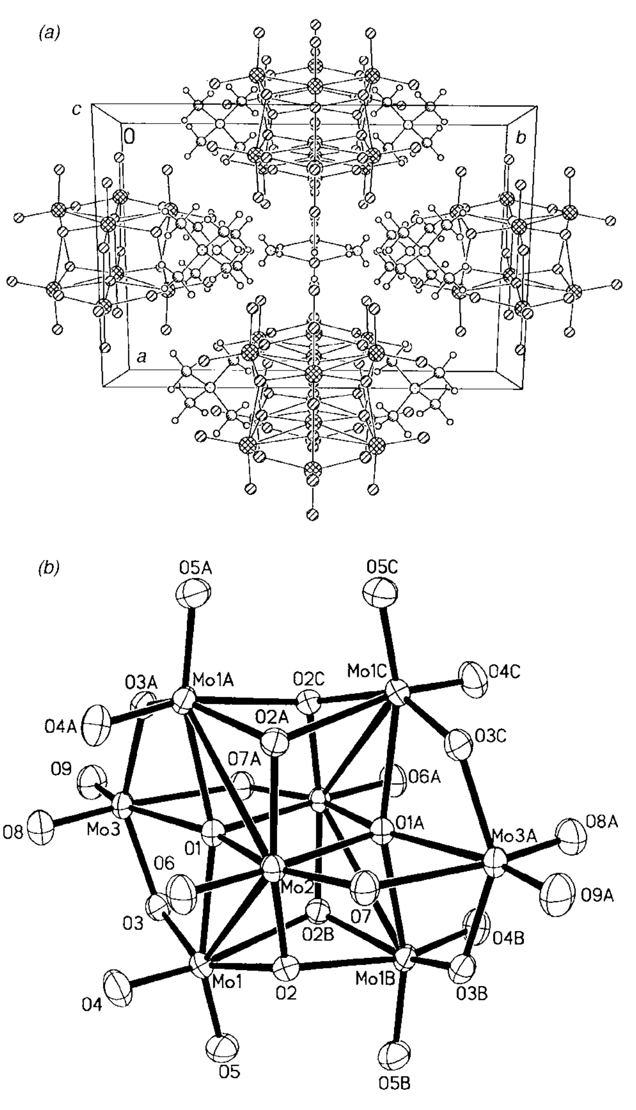

Fig. 3 (*a*) A perspective view of the unit cell packing diagram for **2** and (*b*) an ORTEP diagram of the anion β-$[Mo_8O_{26}]^{4-}$.

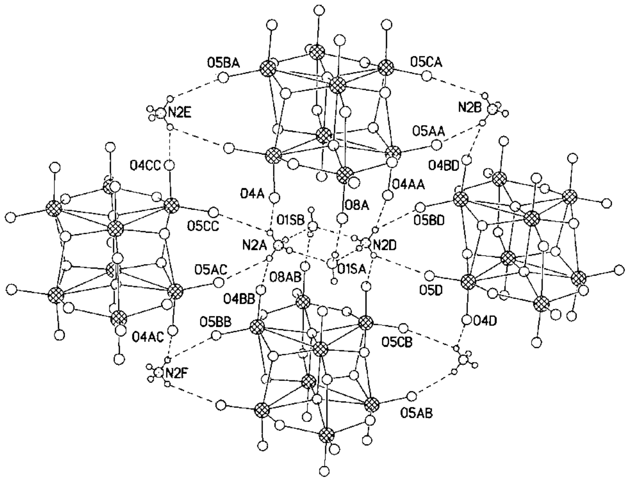

Fig. 4 A view of the hydrogen bonded cluster containing the eight-membered ring formed between two ammonium ions and two water molecules.

Formation of oxomolybdate clusters

Isolation of the polyoxomolybdates **1** and **2** in the presence of the same organic cation, TMA, is interesting, even though a number of Keggin anions in addition to several octamolybdate clusters are known to crystallize from acidified, aqueous molybdate solution. Stabilization of β-Keggin clusters under reducing conditions is not surprising in view of the recent reports by Müller *et al.*[37] and others.[18] The formation of large, reduced oxomolybdate clusters, $[NH_4]_{14}[H_{14}Mo_{37}O_{112}]\cdot 35H_2O$ under similar reaction conditions by Müller *et al.* clearly demonstrates that the nature of the cluster is strongly dependent on the experimental conditions. The presence of DMA cations in **2** in addition to TMA may not be surprising as TMA is known to undergo fragmentation.[38] The choice of the counter cations such as TMA and DMA by the oxomolybdate cluster in **1** is not obvious. In the absence of reducing agent, β-Mo_8O_{26} is the most stable species in solution. The occurrence of a solid of the type $[NMe_4]_2[NH_4]_2$-$[Mo_8O_{26}]\cdot 2H_2O$ **2**, is not unusual but the formation of a unique hydrogen bonding between ammonium and water molecules is probably responsible for the ordering of TMA and β-Mo_8O_{26} units along the *ac*-planes. In both **1** and **2** the organic cations seem to influence the packing/linking of the oxomolybdate clusters.

Experimental

Synthesis of $[NH_2Me_2]_4[NMe_4]_2[Mo_{0.5}O_4\subset(Mo_{12}O_{36})]\cdot 1.5H_2O$

Compound **1** was synthesised from an aqueous solution containing $[NH_4]_6Mo_7O_{24}\cdot 4H_2O$ (0.5 g, 0.4 mmol) and $[NMe_4]BF_4$ (0.15 g, 1.3 mmol), in a molar ratio of 1 : 3, in H_2O (200 mL; 11.0 mol)–DMF (20 mL; 0.3 mol). This was then taken in an Erlenmeyer flask and refluxed for 3 h at 90 °C. The colourless clear solution obtained was cooled to room temperature and reduced with hydrazine hydrate, N_2H_6O (0.2 mL; 3.6 mmol) and the pH of the solution was adjusted to *ca.* 1.2 with acetic acid (1.3 mL; 20.5 mmol). After 15 days dark blue crystals were filtered off and washed with water followed by acetone and dried in air. Yield: 0.12 g, 25% based on molybdenum. Elemental analysis. Found: C, 3.2; H, 1.0; N, 1.3. Calc. C, 3.3; H, 1.0; N, 1.5%; $D_m = 2.65$ g cm^{-3}, $D_c = 2.63$ g cm^{-3}. Scanning electron micrographs showed the formation of cubic block-like crystals.

Synthesis of $[NMe_4]_2[NH_4]_2[Mo_8O_{26}]\cdot 2H_2O$

Compound **2** was synthesised from an aqueous solution containing $[NH_4]_6Mo_7O_{24}\cdot 4H_2O$ (0.5 g, 0.4 mmol) and NMe_4BF_4 (0.15 g, 1.3 mmol) in the molar ratio of 1 : 3 in H_2O (200 mL; 11.0 mol)–DMF (20 mL; 0.3 mol). This was then taken in an Erlenmeyer flask and refluxed for 3 h at 90 °C. The colourless clear solution obtained was cooled to room temperature and the pH of the solution was adjusted to *ca.* 2.0 with acetic acid (1.0 mL; 15.7 mmol). After 15 days, colourless crystals were filtered off and washed with water followed by acetone. Yield: 0.15g, 45% based on molybdenum. Elemental analysis. Found: C, 2.4; H, 1.0; N, 1.3%. Calc. C, 2.6; H, 1.0; N, 1.6%. Thermogram: loss of water and ammonium ions between 200 and 450 °C (DTA shows two broad endothermic peaks centred around 270 and 400 °C) and another weight loss above 750 °C corresponding to the decomposition of organic moieties (DTA shows an endothermic peak centred around 780 °C). $D_m = 2.72$ g cm^{-3}, $D_c = 2.67$ g cm^{-3}. Scanning electron micrographs showed the formation of thick rectangular crystals.

X-Ray crystallographic studies

Single crystal diffraction studies were carried out on a Siemens SMART CCD diffractometer with a Mo-Kα sealed tube at 23 °C for both **1** and **2**. Crystals with dimensions of 0.3 × 0.23 × 0.18 mm for **1** and 0.35 × 0.30 × 0.15 mm for **2** were used for diffraction experiments. A total of 33763 reflections were collected in the range $\theta = 1.82$–29.26 ($-30 \leqslant h \leqslant 27$, $-24 \leqslant k \leqslant 26$, $-15 \leqslant l \leqslant 17$) for **1** and 5644 reflections were collected in the range $\theta = 2.15$–29.24° ($-14 \leqslant h \leqslant 14$, $-21 \leqslant k \leqslant 22$, $-6 \leqslant l \leqslant 13$) for **2**. The software SADABS was used for absorption correction and SHELXTL for space group determination, solution and refinement.[39] All the non-hydrogen atoms were refined anisotropically. Riding models were used to place the H atoms attached to carbon and nitrogen atoms. All the hydrogen atoms of the water molecules and N atoms were located in the difference Fourier map for **1** and **2**. A common O–H distance and common isotropic thermal parameters of the oxygen atoms of the water molecules were refined for **2**. The two water oxygen atoms found in **1**, were disordered over the crystal lattice. Because of this disorder, the hydrogen atoms attached to water molecules were neither located in the difference Fourier map, nor included in the model. Only isotropic thermal parameters were refined for the oxygen atoms with a site occupancy of 0.375 in **1**. Least-squares refinement cycles on F^2 were performed until the model converged. Crystallographic data and refinement details are shown in Table 1.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/35. See http://www.rsc.org/suppdata/jm/1999/763/ for crystallographic files in .cif format.

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