Three New Organically Templated Polyoxomolybdates with Capping Selenite Anions

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Three new organically templated polyoxomolybdates with selenite anions as capping groups have been synthesized by hydrothermal reactions and structurally characterized. The structure of {Hbipy}$_3${KMo$_4$O$_{13}$(SeO$_3$)} (**1**; bipy = 4,4′-bipyridine) features a 1D anionic double chain of {KMo$_4$O$_{13}$(SeO$_3$)}$^{3-}$ units. Four Mo^{VI}O$_6$ octahedra in compound **1** form a planar Mo$_4$O$_{13}$ cluster unit through corner-, edge- and face-sharing. The Mo$_4$O$_{13}$ cluster unit is further capped by an Se^{IV}O$_3$ group in a bidentate fashion. These monocapped cluster units are further interconnected by bridging K$^+$ cations into a 1D double chain. Both {H$_2$bipy}$_2${Mo$_5$O$_{15}$(SeO$_3$)$_2$}·H$_2$O (**2**) and {H$_2$pip}$_2${Mo$_5$O$_{15}$(SeO$_3$)$_2$}·3H$_2$O (**3**; pip = piperazine) contain a bicapped Mo$_5$O$_{15}$ cluster unit in which five Mo^{VI}O$_6$ octahedra form a planar Mo$_5$O$_{15}$ cluster unit through edge- and corner-sharing, with the two Se^{IV}O$_3$ anions as tridentate capping groups on the two open sides of the cluster unit to form an {Mo$_5$O$_{15}$(SeO$_3$)$_2$}$^{4-}$ anion. The {Mo$_5$O$_{15}$(SeO$_3$)$_2$}$^{4-}$ cluster anions in compounds **2** and **3** are further inter-linked by the organic templates through hydrogen bonds to form a 2D layer.

Introduction

Polyoxometalates (POMs) are one of the most widely used inorganic components due to the extreme variability of their compositions, molecular characteristics, properties and applications.[1] Recently, a lot of research efforts have been focused on the functionalization of POMs with transition metal complex or lanthanide complex moieties — the coordinated transition metal or lanthanide metal complex cation serves to provide charge-compensation, space-filling, and structure-directing roles. In most cases, the transitional-metal and the rare-earth ions are found to be either sandwiched between two polymolybdate anions or as a capping atom on the cluster unit.[2−5] For polyoxomolybdates with a small cluster unit, such as Mo$_4$O$_{13}$, Mo$_5$O$_{15}$ and Mo$_6$O$_{18}$, the cluster unit can be further capped by one or two tetrahedral groups such as PO$_4$, RPO$_3$, SO$_4$, AsO$_4$, RAsO$_3$, etc.[6−8] However, studies on polymolybdates with capping XO$_3$ groups (X = Se^{IV}, Te^{IV}, As^{III}, Sb^{III}, Bi^{III}) are rare.[9]

We are particularly interested in metal selenites. A few examples of open frameworks of metal selenites have been reported.[10−13] An organically templated 2D zinc selenite was first reported by Harrison et al.[10] Organically templated 3D iron(II), cobalt(II), nickel(II) and zinc(II) selenites have also been reported by Rao and co-workers.[11] Both organically templated and organically linked vanadium selenites have also been reported.[12,13] So far only polyoxomolybdates with an Mo$_6$O$_{18}$ cluster unit capped by a selenite group have been reported.[9] We therefore decided to study systematically the syntheses and crystal structures of organically templated polyoxomolybdates containing capping selenite groups. Our research efforts led to three new organically templated polyoxomolybates with selenite anions as capping groups, namely {Hbipy}$_3${KMo$_4$O$_{13}$(SeO$_3$)} (**1**), with an {Mo$_4$O$_{13}$}$^{2-}$ cluster unit, and {H$_2$bipy}$_2${Mo$_5$O$_{15}$(SeO$_3$)$_2$}·H$_2$O (**2**) and {H$_2$pip}$_2${Mo$_5$O$_{15}$(SeO$_3$)$_2$}·3H$_2$O (**3**) containing an Mo$_5$O$_{15}$ cluster unit capped by two Se^{IV}O$_3$ anions. We report here their syntheses, characterizations and crystal structures.

Results and Discussion

The synthetic procedures for the formation of compounds **1**−**3** are interesting. Both compounds **1** and **2** were obtained from the same starting materials but in a different molar ratio: a higher Mo/Se ratio leads to compound **2** with an MO$_5$O$_{15}$ cluster unit but without K$^+$ as an inter-cluster linker. For the synthesis of compound **3**, it is necessary to use (NH$_4$)$_6$Mo$_7$O$_{24}$ as the source of the Mo^{VI} ions as the use of K$_2$MoO$_4$ led to {H$_2$bipy}$_3${Mo$_8$O$_{27}$} with a known {Mo$_8$O$_{27}$}$^{6-}$ cluster unit.[14] Thus, the source of molybdenum, the Mo/Se ratio, the cation used and the pH value of the reaction have a strong effect on the compound formed.

The structure of compound **1** (Figure 1) features a 1D anionic double chain composed of {KMo$_4$O$_{13}$(SeO$_3$)}$^{3-}$ units in which the monocapped Mo$_4$O$_{13}$(SeO$_3$) cluster units are interconnected by bridging K$^+$ cations. As shown in

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Figure 1, there are four Mo and one Se atoms in an asymmetric unit. All four Mo atoms are octahedrally coordinated. The Mo−O bonds are in the range 1.689(4)−2.416(4) Å. The MoO_6 octahedra are severely distorted, two Mo−O bonds are significantly elongated and two Mo−O(terminal) bonds are much shorter than the remaining ones. The Se atom is three-coordinate, with Se−O distances ranging from 1.644(5) to 1.738(4) Å. These Mo−O and Se−O distances are similar to those reported in the literature.[6,9] Based on the results of bond-valence calculations, all Mo atoms are in the +6 oxidation state, and the Se atom has a +4 oxidation state: the calculated total bond valences for the Mo atoms are in the range of 5.945 to 6.062, and that for the Se atom is 4.03.[15] Thus, the polyhedron of Se^{IV} can be described as a ψ-SeO_3 tetrahedron with one corner of the tetrahedron occupied by the lone pair of electrons.

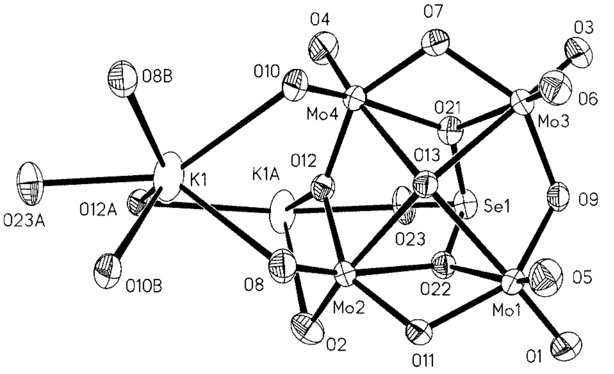

Figure 1. ORTEP representation of the asymmetric unit of compound **1**; thermal ellipsoids are drawn at 50% probability; the organic templates have been omitted for clarity; symmetry codes for the generated atoms: a: $-x + 1/2$, $-y + 1/2$, $-z + 1/2$; b: $-x + 1/2$, $-y + 1/2$, $-z + 2$

The four $Mo^{VI}O_6$ octahedra are interconnected by edge- and face-sharing to form a planar $Mo_4O_{13}(SeO_3)$ cluster unit. The mean deviation from the plane defined by Mo(1), Mo(2), Mo(3), and Mo(4) is 0.0104 Å. O(13) is a μ_4 metal linker, bridging all four Mo^{VI} centers and lies 0.734 Å out of the Mo_4 plane. The selenite group is capping on the opposite site of O(13) in a bidentate fashion. O(21) and O(22) each bridge two Mo^{VI} centers, whereas O(23) is not bonded to the Mo^{VI} center. Two $Mo^{VI}O_6$ octahedra [Mo(1) and Mo(2) or Mo(3) and Mo(4)] form a dimer by face-sharing, resulting in two relatively short Mo···Mo separations [3.1428(8) and 3.1543(8) Å]. These dimers are further interconnected by edge-sharing, although with larger Mo···Mo separations [3.304(1) and 3.329(1) Å]. The Mo−O(SeO_3) bond lengths are in the range 2.258(4)−2.289(4) Å (Table 1), and are similar to those reported in heteropolymolybdates of Se^{IV} functionalized by amino acids containing an $Mo_6O_{18}(SeO_3)$ cluster core.[9] To some extent, such a $Mo_4O_{13}(SeO_3)$ cluster unit resembles those reported in tetramolybdo complexes of dialkyl and diaryl arsinates.[6] However, this type of cluster unit differs significantly from the Mo_4O_{12} cluster in copper−Mo−$O_3PCH_2CH_2PO_3$ com-

Table 1. Selected bond lengths [Å] for compounds **1**−**3**

Compound **1**[a]			
Mo(1)−O(1)	1.697(4)	Mo(1)−O(5)	1.704(5)
Mo(1)−O(9)	1.929(4)	Mo(1)−O(11)	1.934(4)
Mo(1)−O(22)	2.289(4)	Mo(1)−O(13)	2.386(4)
Mo(1)−Mo(2)	3.1428(8)	Mo(2)−O(2)	1.689(4)
Mo(2)−O(8)	1.714(4)	Mo(2)−O(11)	1.912(4)
Mo(2)−O(12)	1.928(4)	Mo(2)−O(22)	2.258(4)
Mo(2)−O(13)	2.411(4)	Mo(3)−O(3)	1.705(4)
Mo(3)−O(6)	1.709(4)	Mo(3)−O(9)	1.910(4)
Mo(3)−O(7)	1.929(4)	Mo(3)−O(21)	2.287(4)
Mo(3)−O(13)	2.394(4)	Mo(3)−Mo(4)	3.1543(8)
Mo(4)−O(4)	1.705(4)	Mo(4)−O(10)	1.725(4)
Mo(4)−O(7)	1.909(4)	Mo(4)−O(12)	1.917(4)
Mo(4)−O(21)	2.282(4)	Mo(4)−O(13)	2.416(4)
K(1)−O(23)#1	2.564(5)	K(1)−O(12)#1	2.706(4)
K(1)−O(8)#2	2.831(5)	K(1)−O(8)	2.831(5)
K(1)−O(10)	2.949(5)	K(1)−O(10)#2	3.069(5)
Compound **2**[b]			
Mo(1)−O(8)	1.735(16)	Mo(1)−O(8)#1	1.735(16)
Mo(1)−O(6)#1	1.903(15)	Mo(1)−O(6)	1.903(15)
Mo(1)−O(10)	2.318(15)	Mo(1)−O(10)#1	2.318(15)
Mo(2)−O(1)	1.709(17)	Mo(2)−O(4)	1.710(16)
Mo(2)−O(2)	1.882(5)	Mo(2)−O(3)	1.945(16)
Mo(2)−O(9)#1	2.361(16)	Mo(2)−O(11)	2.380(14)
Mo(3)−O(5)	1.699(15)	Mo(3)−O(7)	1.726(15)
Mo(3)−O(6)	1.943(16)	Mo(3)−O(3)	1.968(16)
Mo(3)−O(11)	2.164(15)	Mo(3)−O(10)#1	2.360(14)
Hydrogen bonds:			
N(1)···O(3)#2	2.625(25)	N(2)···O(8)#3	2.743(28)
O(1W)···O(9)#1	2.820(24)	O(1W)···O(9)	2.820(24)
Compound **3**[c]			
Mo(1)−O(1)	1.711(5)	Mo(1)−O(2)	1.721(5)
Mo(1)−O(15)	1.911(5)	Mo(1)−O(11)	1.924(5)
Mo(1)−O(31)	2.318(5)	Mo(1)−O(22)	2.363(5)
Mo(2)−O(3)	1.711(5)	Mo(2)−O(4)	1.713(5)
Mo(2)−O(12)	1.900(5)	Mo(2)−O(11)	1.997(5)
Mo(2)−O(32)	2.194(5)	Mo(2)−O(22)	2.328(5)
Mo(3)−O(5)	1.700(5)	Mo(3)−O(6)	1.705(6)
Mo(3)−O(13)	1.938(5)	Mo(3)−O(12)	1.947(5)
Mo(3)−O(32)	2.327(5)	Mo(3)−O(23)	2.354(5)
Mo(4)−O(7)	1.699(5)	Mo(4)−O(8)	1.723(5)
Mo(4)−O(13)	1.882(5)	Mo(4)−O(14)	1.960(5)
Mo(4)−O(21)	2.272(5)	Mo(4)−O(33)	2.317(5)
Mo(5)−O(9)	1.696(5)	Mo(5)−O(10)	1.713(6)
Mo(5)−O(14)	1.956(5)	Mo(5)−O(15)	1.969(5)
Mo(5)−O(21)	2.202(5)	Mo(5)−O(31)	2.278(5)
Hydrogen bonds:			
N(1)···O(10)#3	2.710(10)	N(1)···O(14)#4	2.786(8)
N(2)···O(11)	2.768(8)	N(4)···O(2W)#5	2.783(9)
O(1W)···O(2W)#5	2.734(10)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1/2$, $-y + 1/2$, $-z + 1$; #2: $-x + 1/2$, $-y + 1/2$, $-z + 2$; #3: $-x$, $1 - y$, $1 - z$; #4: $-x$, y, $1/2 - z$. [b] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, y, $-z + 1$; #2: $1/2 - x$, $-1/2 + y$, $1 - z$; #3: $1 - x$, y, $-z$. [c] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1$, $-y$, $-z + 1$; #2: $-x$, $-y + 1$, $-z + 1$; #3: $x - 1$, y, z; #4: $-1/2 + x$, $1/2 - y$, $1/2 + z$; #5: $-1/2 + x$, $1/2 - y$, $-1/2 + z$.

pounds,[16] in that one Mo^{VI} ion in the latter cluster compounds is in a square-pyramidal geometry and the cluster units are noncyclic.

The $\{Mo_4O_{13}(SeO_3)\}^{4-}$ cluster units in compound **1** are bridged by K^+ ions through K−O(23) bonds to form a novel 1D double chain along the *c* axis (Figure 2). The K^+ ion is six-coordinate, with four terminal oxygen atoms from four cluster units, one bridging oxygen atom [O(12a)] from a cluster unit and one oxygen atom from a selenite group. The K−O distances are in the range 2.564(5)−3.069(5) Å (Table 1). The templates — the bipy ligands — are singly protonated. Packing of these templates forms cavities, which are occupied by $\{KMo_4O_{13}(SeO_3)\}^{3-}$ anionic chains (Figure 3).

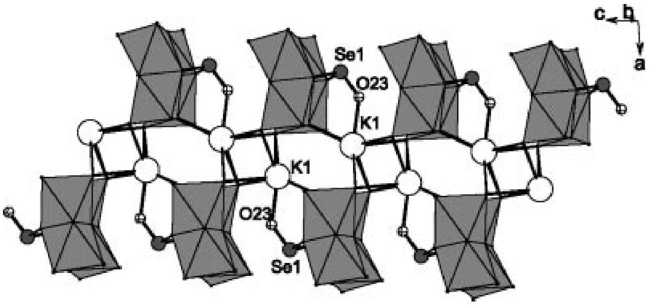

Figure 2. The 1D anionic chain of $\{KMo_4O_{13}(SeO_3)\}^{3-}$ moieties along the *c* axis in **1**; the MoO_6 octahedra are shaded in gray; the K, Se and O atoms are drawn as open, hatched and crossed circles, respectively

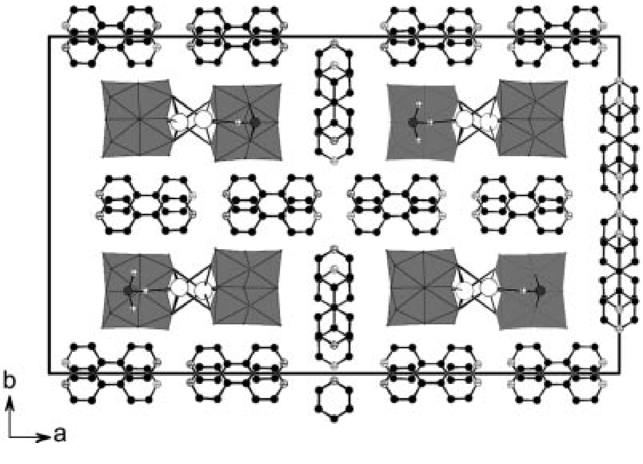

Figure 3. A view of the crystal structure of **1** along the *c* axis; the MoO_6 octahedra are shaded in gray; the K, Se, C, N and O atoms are drawn as open, hatched, black, octanded and crossed circles, respectively

Compounds **2** and **3** both contain a bicapped $\{Mo_5O_{15}(SeO_3)_2\}^{4-}$ anionic cluster unit (Figure 4). Five MoO_6 octahedra form a planar Mo_5O_{15} unit by sharing four edges and one corner. The corner-sharing occurs between two $Mo(2)O_6$ octahedra in compound **2**, and between $Mo(3)O_6$ and $Mo(4)O_6$ octahedra in compound **3.** The two opposite sides of the cluster unit are capped by two selenite groups (Figure 4). This type of bicapped Mo_5O_{15} cluster unit is similar to those reported previously in polymolybdophosphonates or -phosphates.[7] The Mo_5O_{15} cluster unit in compound **2** is less coplanar than the Mo_4O_{13} cluster unit in compound **1**. The mean deviation from the plane defined by Mo(1), Mo(2), Mo(3), and Mo(2a) and Mo(3a) is 0.1847 Å. The two Se^{IV} centers are 2.133 Å away from the Mo_5 plane. The Mo−O and Se−O distances are similar to those in compound **1** (Table 1). All Mo atoms are in the +6 oxidation state and the Se atoms are in the +4 oxidation state based on the results of bond-valence calculations.[15]

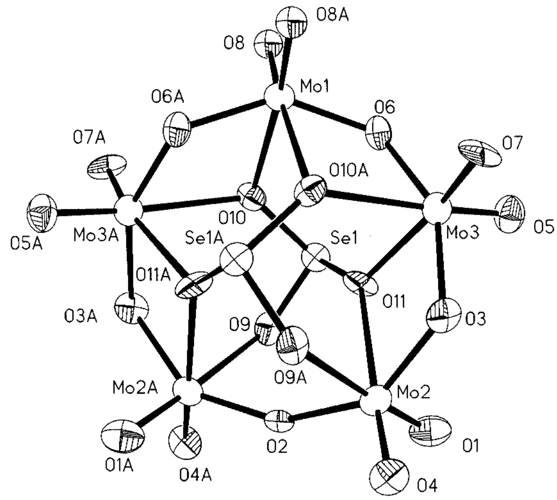

Figure 4. ORTEP representation of the $Mo_5O_{15}(SeO_3)_2{}^{4-}$ unit in **2**; the thermal ellipsoids are drawn at 50% probability; symmetry code for the generated atoms: a: $1 - x$, y, $1 - z$

The bicapped $\{Mo_5O_{15}(SeO_3)_2\}^{4-}$ anionic cluster units in compounds **2** are hydrogen-bonded with the templates, which in this case are doubly protonated bipy ligands, $\{H_2bipy\}^{2+}$, resulting in a hydrogen-bonded <201> 2D layer (Figure 5). The hydrogen bonds are formed between the amine groups of bipy and the terminal oxygen atoms of the cluster unit (Figure 5, Table 1). The lattice water mol-

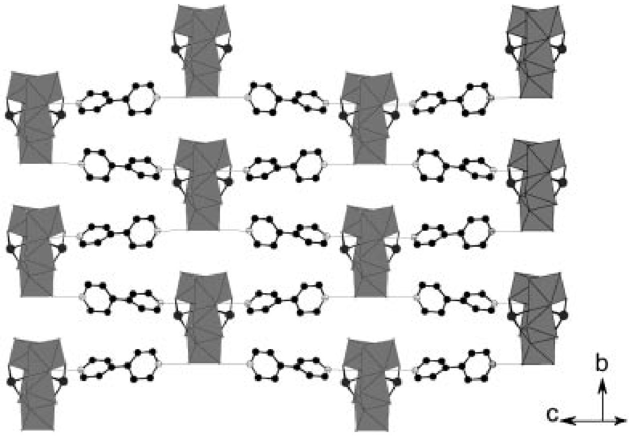

Figure 5. A <201> layer built from $Mo_5O_{15}(SeO_3)_2{}^{4-}$ units interconnected by $[H_2bipy]^{2+}$ cations through hydrogen bonding in **2**; the MoO_6 octahedra are shaded in gray; the Se, C, N and O atoms are drawn as open, black, octanded and crossed circles, respectively; hydrogen bonds are drawn as dotted lines

ecules are located between the layers and are involved in hydrogen bonding with the oxygen atom [O(9)] of the selenite group (Table 1).

Similar to compound **2**, the bicapped $\{Mo_5O_{15}(SeO_3)_2\}^{4-}$ anionic cluster units of compounds **3** are also interlinked by hydrogen bonds, although in this case to doubly protonated piperazines, containing atoms N1 and N2, resulting in a <040> corrugated layer (Figure 6, Table 1). The other doubly protonated piperazine molecules, containing N3 and N4, are located in the cavities formed by packing of the 2D layers, as are the lattice water molecules. These lattice water molecules are also involved in hydrogen bonding (Table 1).

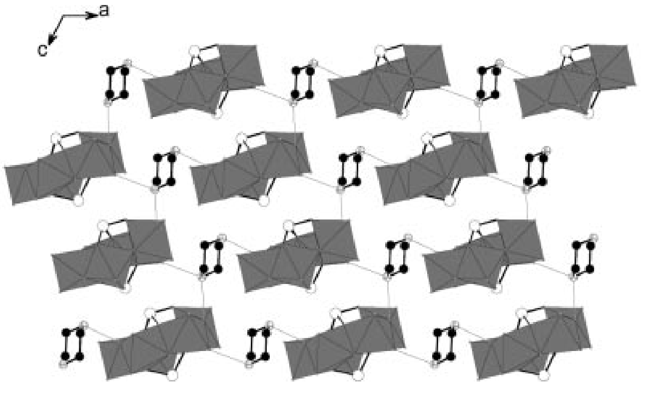

Figure 6. A <040> corrugated layer built from $Mo_5O_{15}(SeO_3)_2{}^{4-}$ units interconnected by $[H_2pip]^{2+}$ cations through hydrogen bonding in **3**; the MoO_6 octahedra are shaded in gray; the Se, C, N and O atoms are drawn as open, black, octanded and crossed circles, respectively; hydrogen bonds are drawn as dotted lines

The results of XRD powder-diffraction studies for compounds **1**−**3** indicate that all three compounds were isolated as single phases.

The IR spectra of compounds **1**−**3** all exhibit a strong band around 930−933 cm^{-1}, characteristic of ν(Mo=O). The bands around 720−730 and 438−457 cm^{-1} can be assigned to the vibrations of the selenite groups. The bands around 1614−1622 and 1403−1421 cm^{-1} originate from the templates — bipy in compounds **1** and **2**, and piperazine in compound **3**.

The TGA diagram of compound **1** indicates that it is stable up to 234 °C (Figure 7). The subsequent weight loss corresponds to the release of the template molecules and the decomposition of the cluster chain. The process is complete at 490 °C. Compound **2** starts to release its lattice water at 160 °C; the second weight loss corresponds to the release of the template bipy molecules and the decomposition of the cluster unit, which is complete at 487 °C. The TGA curves of compound **3** show two main weight losses (Figure 7). The first one starts at 143 °C and is complete at 202 °C, corresponding to the release of its three lattice water molecules. The unusually high temperature needed for the release of lattice water molecules may be due to the strong hydrogen bonds formed. The observed weight loss of 4.3% is in good agreement with the calculated value (4.5%). The second weight loss, covering a temperature range from 235 to 843 °C, corresponds to the loss of the piperazine molecules and decomposition of the compound. The residual solids were not identified due to insufficient samples collected.

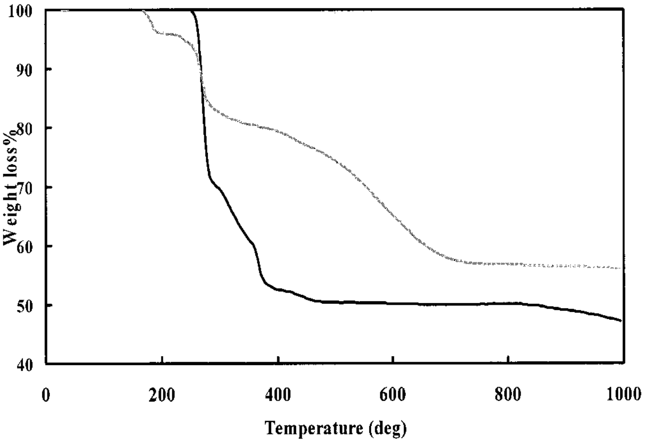

Figure 7. TGA curves for compounds **1** (black line) and **3** (grey line)

Conclusion

Three novel organically templated polymolybdates containing selenite groups as capping groups have been synthesized by hydrothermal reactions. These three examples demonstrate that the selenite group can be capped on many other polymolybdate cluster units in addition to the Mo_6O_{18} cluster reported previously.[9] Our future work will explore more organically templated selenite- or tellurite-containing polymolybdates.

Experimental Section

Materials and Methods: All chemicals were obtained from commercial sources and used without further purification. Mo, K and Se analyses were carried out with an ICPQ-100 spectrometer. IR spectra were recorded with a Magna 750 FT-IR spectrometer as KBr pellets in the range 4000−400 cm^{-1}. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 15 °C/min under nitrogen. The XRD powder patterns were collected with a Philips X'Pert-MPD diffractometer using graphite-monochromated Cu-K_α radiation in the angular range 2θ = 5−70° with a step size of 0.02° and a counting time of 3 s per step.

Preparation of $\{Hbipy\}_3\{KMo_4O_{13}(SeO_3)\}$ (1): A mixture of K_2MoO_4 (0.270 g, 1.0 mmol), SeO_2 (0.221 g, 2.0 mmol) and 4,4′-bipyridine (0.0792 g, 0.5 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL), and then heated at 160 °C for 6 d. The pH values before and after the reaction were 5.0 and 5.5, respectively. Colorless, needle-shaped crystals of **1** were collected in about 33% yield (0.101 g) (based on Mo). $C_{30}H_{27}KMo_4N_6O_{16}Se$ (1229.4): calcd. C 29.28, H 2.21, K 3.18, Mo 31.22, N 6.83, Se 6.42; found C 29.13, H 1.85, K 2.8, Mo 30.6, N 6.76, Se 6.7. IR (KBr): ṽ = 3435 br, 2047 m, 1614 s, 1595 s, 1567 m, 1526 m, 1489 s, 1407 m, 1326 m, 1213 s, 1065 m, 1009 m, 995 m, 930 s, 907 s, 894 s, 870 s, 807 s, 723 s, 685 s, 568 s, 539 m, 457 m cm^{-1}.

Preparation of {H_2bipy}$_2${$Mo_5O_{15}(SeO_3)_2$}·H_2O (2): A mixture of K_2MoO_4 (0.551 g, 2.0 mmol), SeO_2 (0.229 g, 2.0 mmol) and 4,4′-bipyridine (0.0792 g, 0.5 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL), and then heated at 160 °C for 6 d. The initial and final pH values for the reaction solution were 5.0 and 6.0, respectively. Colorless, plate-shaped crystals of **2** were collected in about 48% yield (0.251 g) (based on Mo). $C_{20}H_{22}Mo_5N_4O_{22}Se_2$ (1308.4): calcd. C 18.34, H 1.69, Mo 36.55, N 4.28, Se 12.07; found C 18.09, H 1.8, Mo 36.1, N 4.56, Se 11.8. IR (KBr): $\tilde{\nu}$ = 3089 br, 2080 m, 1622 s, 1557 m, 1514 m, 1489 s, 1404 m, 1371 m, 1204 s, 1001 m, 932 s, 904 s, 847 m, 803 s, 723 s, 684 s, 584 s, 553 s, 442 m cm^{-1}.

Preparation of {H_2pip}$_2${$Mo_5O_{15}(SeO_3)_2$}·$3H_2O$ (3): A mixture of $(NH_4)_6Mo_7O_{24}$ (0.355 g, 0.29 mmol), SeO_2 (0.339 g, 3.0 mmol) and piperazine (0.0896 g, 1.0 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL), and then heated at 110 °C for 5 d. The pH values before and after the reaction were 5.0 and 5.5, respectively. Colorless, brick-shaped crystals of **3** were collected in about 53% yield (0.132 g) (based on Mo). $C_8H_{30}Mo_5N_4O_{24}Se_2$ (1204.0): calcd. C 7.97, H 2.51, Mo 39.84, N 4.65, Se 13.12; found C 7.819, H 2.38, Mo 39.2, N 4.39, Se 12.7. IR (KBr): $\tilde{\nu}$ = 3017 br, 1615 s, 1579 s, 1454 s, 1421 s, 1382 s, 1329 w, 1307 m, 1205 s, 1086 m, 1075 m, 1059 m, 1004 s, 932 s, 902 s, 780 w, 730 s, 651 s, 578 s, 480 m, 438 m cm^{-1}.

X-ray Single-Crystal Structure Determination: Single crystals of compounds **1**−**3** were mounted on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were collected by the narrow-frame method at 293 K. All three data sets were corrected for Lorentz and polarization factors, as well as for absorption, with the SADABS program.[17a] The space groups of compounds **1** and **3** were determined uniquely to be *C*2/*c* and *P*2$_1$/*n*, respectively. For compound **2** the space group could be one *C*2, *C*2/*m*, or *Cm*. However, based on the E-value statistics, it is noncentrosymmetric, and furthermore, no reasonable solution was found for *C*2/*m* and *Cm*; thus, *C*2 was used for the subsequent refinements of compound **2**. All structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 with SHELX-97.[17b] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms and of amine groups were located at geometrically calculated positions and refined with isotropic thermal parameters. The hydrogen positions for the singly protonated bipy ligands in compound **2** were difficult to determine accurately and were not refined; neither were the hydrogen atoms of the lattice water molecules. Crystallographic data and structural refinements for compounds **1**−**3** are summarized in Table 2. Selected bond lengths are listed in Table 1. CCDC-234093 (**1**), -234094 (**2**) and -234095 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] *Polyoxometalate Chemistry for Nanocomposite Design* (Eds.: M. T. Pope, T. Yamase), Kluwer, Dordrecht, **2002**. [1b] *Polyoxometalates: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **2001**.

[2] [2a] D. Hagrman, P. J. Zapf, J. Zubieta, *Chem. Commun.* **1998**, 1283. [2b] Y.-S. Zhou, L.-J. Zhang, X.-Z. You, S. Natarajan, *J. Solid State Chem.* **2001**, *159*, 209. [2c] L. A. Meyer, R. C. Haushalter, *Inorg. Chem.* **1993**, *32*, 1579. [2d] R. S. Rarig Jr., J. Zubieta, *J. Solid State Chem.* **2002**, *167*, 370. [2e] R. S. Rarig Jr., L. Bewley, V. Golub, C. J. O'Connor, J. Zubieta, *Inorg. Chem. Commun.* **2003**, *6*, 539.

[3] [3a] C.-D. Wu, C.-Z. Lu, H.-H. Zhuang, J.-S. Huang, *Inorg. Chem.* **2002**, *41*, 5636. [3b] M. Yuan, E. Wang, Y. Lu, Y. Li, C. Hu, N. Hu, N. H. Jia, *Inorg. Chem. Commun.* **2002**, *5*, 505. [3c] C. du Peloux, A. Dolbecq, P. Mialane, J. Marrot, E. Rivière, F. Sécheresse, *Angew. Chem. Int. Ed.* **2001**, *40*, 2455. [3d] L. Xu, Y. Sun, E. Wang, E. Shen, Z. Liu, C. Hu, Y. Xing, Y. Lin, H. Jia, *New J. Chem.* **1999**, *23*, 1041. [3e] L. Xu, Y. Sun, E. Wang, E. Shen, Z. Liu, C. Hu, Y. Xing, Y. Lin, H. Jia, *J. Solid State Chem.* **1999**, *146*, 533.

[4] [4a] C.-D. Wu, C.-Z. Lu, H.-H. Zhuang, J.-S. Huang, *J. Am.*

Table 2. Crystal data and structure refinements for compounds **1**−**3**

	1	**2**	**3**
Empirical formula	$C_{30}H_{27}KMo_4N_6O_{16}Se$	$C_{20}H_{22}Mo_5N_4O_{22}Se_2$	$C_8H_{30}Mo_5N_4O_{24}Se_2$
Formula mass	1229.40	1308.4	1203.98
Space group	*C*2/*c*	*C*2	*P*2$_1$/*n*
a [Å]	42.480(3)	20.466(1)	12.0310(2)
b [Å]	24.841(2)	8.6581	21.5069(3)
c [Å]	7.040(1)	8.6581(6)	12.7401(1)
β [°]	98.476(3)	113.600(3)	117.723(1)
V [Å^3]	7347.5(8)	1754.3(2)	2918.08(7)
Z	8	2	4
$D_{calcd.}$ [g·cm^{-3}]	2.223	2.476	2.741
μ [mm^{-1}]	2.522	3.905	4.687
Reflections collected	22520	2700	8650
Independent reflections	6497 (R_{int} = 4.38%)	2420 (R_{int} = 5.34%)	5025 (R_{int} = 2.55%)
Observed data [$I > 2\sigma(I)$]	5112	2017	4506
GOF on F^2	1.123	1.212	1.101
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0490/0.1006	0.0722/0.1424	0.0401/0.0907
*R*1, *wR*2(all data)	0.0686/0.1087	0.0991/0.1640	0.0472/0.0956

[a] $R1 = \|F_o - F_c\|/|F_o|$; $wR2 = \{w(F_o^2 - F_c^2)^2/w(F_o^2)^2\}^{1/2}$.

Chem. Soc. **2002**, *124*, 3836. [4b] C.-Z. Lu, C.-D. Wu, H.-H. Zhuang, J.-S. Huang, *Chem. Mater.* **2002**, *14*, 2649. [4c] C.-D. Wu, C.-Z. Lu, X. Lin, H.-H. Zhuang, J.-S. Huang, *Inorg. Chem. Commun.* **2002**, *5*, 664. [4d] D. Hagrman, J. Zubieta, *Chem. Commun.* **1998**, 2005; E. Brukholder, J. Zubieta, *J. Chem. Commun.* **2001**, 2056.

[5] [5a] L. A. Mundi, R. C. Haushalter, *Inorg. Chem.* **1992**, *31*, 3050. [5b] M. Yuan, E. Wang, Y. Lu, Y. Li, C. Hu, N. Hu, H. Jia, *J. Solid State Chem.* **2003**, *170*, 192. [5c] Y. Zhou, L. Zhang, X. You, S. Natarajan, *Inorg. Chem. Commun.* **2001**, *4*, 699.

[6] [6a] K. M. Barkigia, L. M. Rajkovic, M. T. Pope, E. Prince, C. O. Quicksall, *Inorg. Chem.* **1980**, *19*, 2531. [6b] K. M. Barkigia, L. M. Rajkovic, M. T. Pope, C. O. Quicksall, *J. Am. Chem. Soc.* **1975**, *97*, 4146. [6c] K. Y. Matsumoto, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284.

[7] [7a] E. Burholder, V. Golub, C. J. O'Connor, J. Zubieta, *Chem. Commun.* **2003**, 2128. [7b] R. B. Fu, X. T. Wu, S. M. Hu, J. J. Zhang, Z. Y. Fu, W. X. Du, S. Q. Xia, *Eur. J. Inorg. Chem.* **2003**, 1798. [7c] U. Kortz, C. Marquer, R. Thouvenot, M. Nierlich, *Inorg. Chem.* **2003**, *42*, 1158. [7d] E. Burholder, V. Golub, C. J. O'Connor, J. Zubieta, *Inorg. Commun.* **2003**, *42*, 6729.

[8] [8a] U. Kortz, *Inorg. Chem.* **2000**, *39*, 625. [8b] D. G. Lyxell, D. Bostrom, M. Hashimoto, L. Pettersson, *Acta Crystallogr., Sect. B* **1998**, *54*, 424. [8c] K. F. Hsu, S. L. Wang, *Inorg. Chem.* **1998**, *37*, 3230. [8d] U. Kortz, M. T. Pope, *Inorg. Chem.* **1995**, *34*, 2160.

[9] U. Kortz, M. G. Savelieff, F. Y. A. Ghali, L. M. Khalil, S. M. Maalouf, D. I. Sinno, *Angew. Chem. Int. Ed.* **2002**, *41*, 4070.

[10] W. T. A. Harrison, M. L. F. Phillips, J. Stanchfield, T. M. Nenoff, *Angew. Chem. Int. Ed.* **2000**, *39*, 3808.

[11] [11a] A. Choudhury, D. Udaya Kumar, C. N. R. Rao, *Angew. Chem. Int. Ed.* **2002**, *41*, 158. [11b] D. Udayakumar, C. N. R. Rao, *J. Mater. Chem.* **2003**, *13*, 1635.

[12] I. Pasha, A. Choudhury, C. N. R. Rao, *Inorg. Chem.* **2003**, *42*, 410.

[13] Z. Shi, D. Zhang, S. Feng, G. Li, Z. Dai, W. Fu, X. Chen, J. Hua, *J. Chem. Soc., Dalton Trans.* **2002**, 1832.

[14] W. T. A. Harrison, L. L. Dussack, A. J. Jacobson, *Acta Crystallogr., Sect. C* **1996**, *52*, 1075.

[15] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

[16] [16a] R. C. Finn, J. Zubieta, *Inorg. Chem.* **2001**, *40*, 2466. [16b] R. C. Finn Jr., R. S. Rarig, J. Zubieta, *Inorg. Chem.* **2002**, *41*, 2109.

[17] [17a] G. M. Sheldrick, *Program SADABS*, Universität Göttingen, **1995**. [17b] G. M. Sheldrick, *SHELXTL, Crystallographic Software Package*, version 5.1, Bruker-AXS, Madison, WI, **1998**.

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