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POMcycles

Template-Directed Assembly of Polyoxothiometalate Scaffolds into Nanomolecular Architectures[**]

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Polyoxometalate clusters (POMs) represent some of the largest non-biologically derived molecules so far synthesized as they occupy the 1–6 nm size range and exhibit a diverse variety of structures,[1–3] assembled from a large "virtual combinatorial library" of building blocks.[4] Whilst many tungsten POM clusters can be built in a controlled way, the designed assembly of giant molybdates is more difficult due to the inherent lability of the resulting compounds.[5] However, the thiometalate aqua cation $[Mo_2O_2S_2(H_2O)_6]^{2+}$ has been explored systematically by Cadot et al.[6,7] who showed that a large variety of planar ring clusters could be templated by organic ligands, and recently reported by us in the assembly of a Möbius strip.[5b]

The key problem with developing new approaches to nanosized clusters, especially in polyoxometalate chemistry, is due to the lack of structural stability of reactive building blocks. To address this we reasoned that the $[Mo_2O_2S_2]^{2+}$ cation, containing two Mo atoms could act as a highly effective linking unit, especially when templated by a highly symmetrical structure-directing anion such as squarate.[5d] Herein we show that in the presence of excess of molybdate with $[Mo_2O_2S_2]^{2+}$ and squarate, it is possible to cut the rings into fragments yielding much larger, protein-sized polyoxothiometalates, resulting in an unprecedented new family of compounds. Consequently, we deduced that this combination of building units would lead to a new family of architectures because, under reducing conditions, the molybdate-based building blocks can form a vast array of combinatorial units. This indeed proved correct since altering the pH value, the ratio of the starting material, and the counter cations resulted in a family of related structures, representing a new assembly type whereby "open" rings of $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (type A building blocks) can be combined with $[Mo_5O_{18}]^{6-}$ (type B building blocks) and in some cases $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ (type C building blocks) and $[Mo_2O_2S_2]^{2+}$ units (type D building blocks) to construct a library of new compounds (**1**–**5**, Figure 1); **1**: $\{Mo_{45}\} = \{A_5B_3\} = \{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_5(Mo_5O_{18})_3\}^{18-}$, **2**: $\{Mo_{47}\} = \{A_5B_3D_1\} = \{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_5(Mo_5O_{18})_3(Mo_2O_2S_2)(H_2O)_4]\}^{16-}$, **3**: $\{Mo_{55}\} = \{A_5B_3C_2D_1\} = \{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_5(Mo_5O_{18})_3[(Mo_2O_2S_2)_5(OH)_8(C_4O_4)_2]\}^{20-}$, **4**: $\{Mo_{96}\} = \{A_9B_6C_3\} = \{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_9[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]_3(Mo_5O_{18})_6\}^{36-}$ (previously reported in Ref. [11]). The assembly of the system is dependent on the nature of the alkali-metal cations used; under the same pH condition used in the synthesis of **4**, but in the presence of Cs^+ instead of K^+, compound **5** is formed exhibiting a highly symmetrical structure $\{Mo_{68}\} = \{A_8B_4\}$ $\{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_8(Mo_5O_{18})_4\}^{24-}$. This new assembly method is explained in Figure 2 which shows the formation of compound **5**.

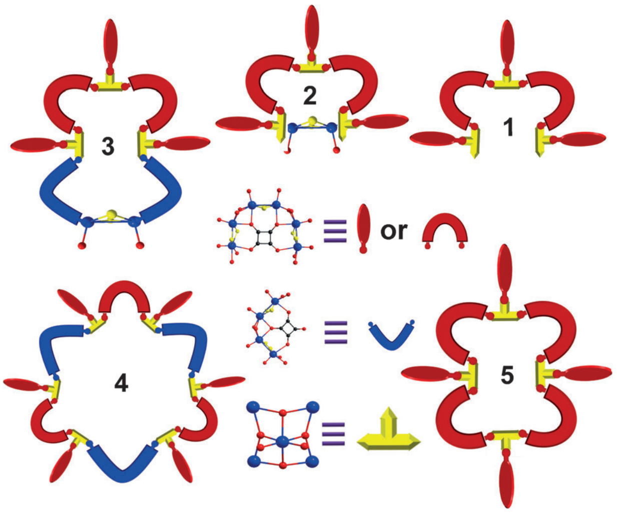

Figure 1. Representation of the polyoxothiometalate building blocks used for the construction of compounds **1**–**5**. The vertical view of the $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ building block (A) is represented by the red arc and the parallel view by the red ribbon. The $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ (C) is denoted by the blue angle while the $[Mo_5O_{18}]^{6-}$ synthon (B) by the yellow arrow (the squarate anions are omitted for clarity).

Notably the key building block is the unique isomer of the lacunary Lindqvist-type $[Mo_5O_{18}]^{6-}$ POM (Figure S3a and S3b in the Supporting Information) which is generated in situ and acts as a convergent scaffold linking unit. Further, it is important to note that the special geometry of the $[Mo_5O_{18}]^{6-}$ unit acts as a 90° "hinge" allowing rings to be connected both horizontal and perpendicular to the plane that defines the overall macrocyclic cluster structure,[8] and also that the orthogonal assembly seen here is also found in some biological systems.[9,10]

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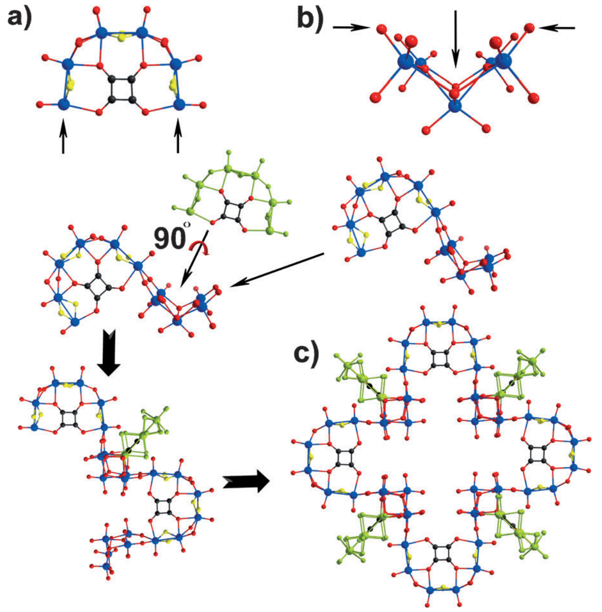

Figure 2. Representation of the assembly of the D_{4h} $\{Mo_{68}\} = \{A_8B_4\}$ (compound **5**). a) Generation of the type A $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ building block and b) type B $[Mo_5O_{18}]^{6-}$ building block. The key role of type B building block, as a 90° hinge connecting three type A building blocks, is shown to allow the connection of rings both in, and orthogonal to, the plane of the macrocycle. The construction of the macrocycle is also shown in the Supporting Information, Movie S1.

Table 1: Summary of the compounds, building blocks, total nuclearity and charge.

Building blocks		BB	Compounds				
			1	**2**	**3**	**4**[a]	**5**
$[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$		A	5	5	5	9	8
$[Mo_5O_{18}]^{6-}$		B	3	3	3	6	4
$[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$		C	0	0	2	3	0
$[Mo_2O_2S_2]^{2+}$		D	0	1	1	0	0
Nuclearity			45	47	55	96	68
Charge			18	16	20	36	24
BVS[b]	Mo_{av}	VI	5.9	5.9	6.1	5.9	6.0
		V	5.1	5.0	5.1	5.1	5.1
	S_{av}		2.0	2.2	2.0	2.0	2.0

[a] Compound **4** was recently reported in Ref. [11]. [b] BVS = bond valence sum.

Intriguingly, it can be seen that all these structures have a common characteristic: they undergo a sequential orthogonal self-assembly from low to high symmetry (from **1** to **5**), which is rarely seen (see Figure 1). For compounds **1**–**3**, the structures are similar due to the fact that: 1) the squarate anion templates the thiometalate dimer $[Mo_2O_2S_2]^{2+}$ forming the virtual building block $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ and 2) for compounds **1**–**3**, the pH values have a narrow range from 4.0 to 4.8, which presumably allows the $[Mo_5O_{18}]^{6-}$ anion to be stabilized. In compound **3** the $[(Mo_2O_2S_2)_5(OH)_8(C_4O_4)_2]^{2-}$ fragment exists in solution due to the higher concentration of $[Mo_2O_2S_2]^{2+}$ present combined with the higher pH value relative to compounds **1** and **2**. Then, when the pH value of the system is lowered to 3.4, and the amount of $Na_2MoO_4{\cdot}2H_2O$ is increased, compound **4** can be isolated (this was previously discovered in a continuous flow system).[11]

Additionally, the size of charge balancing cations can direct the assembly of the structures, so we investigated the effect of replacing the potassium cations with larger cesium cations. This approach gave rise to the discovery of compound **5** $\{Mo_{68}\}$. The building blocks, charge, and nuclearities of all the clusters presented in this work are summarized in Table 1.

Compound **1** (Figure S1) has an approximate C_{2v} symmetry crystallizing in the monoclinic system with space group $C2/c$. Five $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ subunits connect to three $[Mo_5O_{18}]^{6-}$ anions via Mo–O bonds (2.06(8)–2.51(8) Å). The $[Mo_5O_{18}]^{6-}$ (Figures S2 and S3) building unit consists of four corner-shared octahedra in an almost square-shaped configuration (3.67(1) × 3.80(1)) Å. An additional molybdenum polyhedron occupies the resulting cavity and lies 2.57(1) Å below the square-shaped plane, as defined by the four molybdenum corner-shared centers. There are no extra subunits coordinating to the two parallel $[Mo_5O_{18}]^{6-}$ anions because they are surrounded by the extra K^+ ions causing steric hindrance (Figure S1).

To the best of our knowledge, this is the first time that the $[Mo_5O_{18}]^{6-}$ anion[12] has been effectively used as the building block for the construction of large polyoxothiometalate architectures, although the $[Mo_5O_{18}]^{6-}$ geometry can be seen in the infinite compound $Na_6Mo_{10}O_{33}$ (see Figure S3c).[12c] When comparing $[Mo_5O_{18}]^{6-}$ unit reported here with the lacunary Lindqvist-type ion $[Mo_5O_{18}]^{6-}$, the coordination geometry of oxygen atoms to the Mo1 atom differs from *trans*-oxo to *cis*-dioxo groups coordinating to the Mo1* atom (Figure S3a and S3b). As such the $[Mo_5O_{18}]^{6-}$ unit presented here protrudes outwards while the $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ subunit coordinates to the $[Mo_5O_{18}]^{6-}$ unit through Mo–O interactions, 2.05(6)–2.49(5) Å, leading to a crucial linkage underlying the assembly of the structures. Also, the oxygen atoms of the $C_4O_4^{2-}$ anion coordinate to Mo^{VI} through Mo–O bonds. As for the thiometalate fragments, the $[Mo_2O_2S_2]^{2+}$ building blocks are bridged through double hydroxo bridging ligands, which exhibits long non-bonding Mo–Mo contacts, 3.344(2)–3.358(2) Å, alternating with short Mo–Mo bonding contacts within the building block $[Mo_2O_2S_2]^{2+}$, 2.845(2)–2.851(2) Å, as usually observed for the oxothiomolybdenum rings.[7] The shapes of the polyoxothiometalate fragments depend strongly on the squarate anion template.

Compound **2** (Figure S4), a crown-like structure, has C_{2v} symmetry and crystallizes in monoclinic system with space group $P2_1/m$. The structure is quite similar to **1**, and the only difference is that an additional $[Mo_2O_2S_2]^{2+}$ unit fills the vacancy in **1**. At the same time, the addition of $[Mo_2O_2S_2]^{2+}$ induces the conformation of the two end $[Mo_5O_{18}]^{6-}$ units distorted to form $\{Mo_5O_{18}(H_2O)_2\}$ (there is a description of the disorder in the Supporting Information, see Figure S4). Therefore the bridged fragment comprising the $[Mo_2O_2S_2]^{2+}$ and the two newly formed $\{Mo_5\}$ units can be formulated as $[(Mo_2O_2S_2)(Mo_5O_{18})_2(H_2O)_4]^{10-}$ (Figure S3d).

Compound **3** can be simply seen as a combination of compound **1** with the additional fragment $[(Mo_2O_2S_2)_5(OH)_8$-

$(C_4O_4)_2]^{2-}$ included. Additionally, the $[(Mo_2O_2S_2)_5(OH)_8(C_4O_4)_2]^{2-}$ fragment appears to be complexed with some potassium cations, with the two squarate anions being linked through K–O bonds, 2.67(0)–2.79(4) Å (Figure S5). The $[(Mo_2O_2S_2)_5(OH)_8(C_4O_4)_2]^{2-}$ fragment breaks the planarity of the whole structure, such that the molecule is forced to adopt a non-planar orientation to reduce the conformational hindrance. As a result, the molecule exhibits C_s symmetry. The fragment $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ in **3** also exists in compound **4**.

Cluster **4**[11] represents another example of an alternating orthogonal arrangement retaining D_{3h} symmetry with three basic building blocks A, B, and C. The nucleophilic $[Mo_5O_{18}]^{6-}$ unit (B) bonds with the $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (A) and the $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ (C) through Mo–O bonds, 2.08(8)–2.12(0) Å, resulting in the formation of the $\{[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]_3[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)](Mo_5O_{18})_2\}^{12-}$ repeating unit (see Figure S6). The repeating unit still contains the vacant nucleophilic position and the electrophilic position, which allows three identical repeating units to form a triangular ring cluster with a ca. 1.7 nm cavity, and 1D channels in the solid state. Figure S7 shows the packing structure of the $\{Mo_{96}\}$ wheels viewed along the *a*-axis, where the $\{Mo_{96}\}$ wheels are overlapped with respect to each other, forming an interdigitated molecular arrangement in the crystallographic *ab*-plane. Compound **5** (Figures 2 and 3) crystallizes in the triclinic system ($P\bar{1}$) and consists of $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (A) as well as $[Mo_5O_{18}]^{6-}$ (B) subunits. It has a very high symmetry D_{4h}, and the four $[Mo_5O_{18}]^{6-}$ units are symmetrically arranged around a central axis. The eight $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (A) subunits are orthogonally self-assembled in turn and the $[Mo_5O_{18}]^{6-}$ unit (B) links and supports them through Mo–O bonds, 2.09(9)–2.44(9) Å.

Comparing the five compounds (Figure 3), we found that they are composed of two common building blocks: $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ and $[Mo_5O_{18}]^{6-}$. The pH values and the ratio of the starting materials greatly influence the self-assembly process. The unique geometry of the $[Mo_5O_{18}]^{6-}$ unit organizes and links the polyoxothiometalate building blocks $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (A) and/or $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ (C) into alternating arrangements perpendicular to one another showing a type of "orthogonal" or alternating self-assembly pattern in and out of the plane (Figures 1 and 3). A prerequisite for molecular growth in the case of these clusters is the facile self-condensation and an increase in nucleophilicity on certain regions of the clusters' periphery, resulting in a subsequent capture of further electrophilic entities in a specific manner. The parameters such as pH, the ratio of the starting material, and the counter cations guide the self-assembly processes of the building blocks, resulting in the five related clusters **1**–**5** which contain common building blocks (A) and (B).

In summary, it was shown how to construct a new library of inorganic cluster scaffolds by integrating the inorganic $[Mo_2O_2S_2(H_2O)_6]^{2+}$ building block with an organic template. The five structures evolve in structural "completeness" from "incomplete" to gradually more "complete" moving from low to high symmetry. Thus, it would appear that the introduction of the squarate anion template is pivotal for the self-condensation of $[Mo_2O_2S_2(H_2O)_6]^{2+}$ to form the "open" ring (A). Since MoO_4^{2-} was used as the Mo^{VI} source to form the $[Mo_5O_{18}]^{6-}$ unit which is a unique isomer of the lacunary Lindqvist-type anion, the geometry of this unit $[Mo_5O_{18}]^{6-}$ controls the assembly of the polyoxothiometalate building blocks $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ (A) and/or $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$ (C) into alternating arrangements perpendicular to one another, allowing planar ring clusters to be cut and re-joined within and transecting the plane of the cluster. In future work we will explore this library aiming to expand the ring-size yet further and also determine the crucial parameters correlating template to linker in an effort to deduce a general route to expanding this class of clusters in a programmable way.

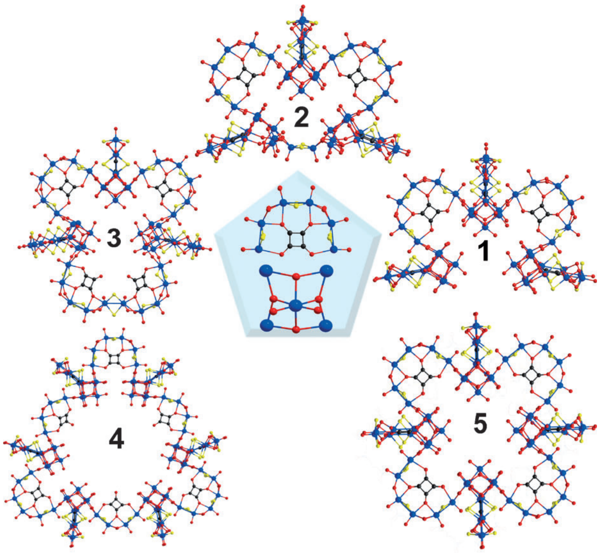

Figure 3. Ball-and-stick representation of the five clusters. The center pentagon shape displays the common building blocks A and B. Building block C is not shown here, it can be regarded as C=A–D) (Mo: blue, S: yellow, O: red).

Experimental Section

For detailed experimental conditions and crystallographic data for all the compounds, see the Supporting Information. Typical experimental procedure for the synthesis of compound **1**: Squaric acid $C_4O_4H_2$ (0.22 g, 1.9 mmol) was dissolved in 20 mL of distilled water and then the pH was adjusted to 7.6 with 1 M K_2CO_3 aqueous solution. $Na_2MoO_4\cdot 2H_2O$ (0.28 g, 1.2 mmol) was added to the above solution upon stirring followed by dropwise addition of 8 mL $[Mo_2O_2S_2]X_2$ (1 M, X: Cl^-, I^-) (tetramethylammonium cation also exists in this solution)[6b] diluted with 10 mL of distilled water containing KCl (0.25 g, 2.7 mmol). The pH of the solution was adjusted to 4.4 with 60% CH_3COOH. The rose red solution was stirred at room temperature for 1 h and then kept in an open vessel at 18 °C for six weeks. Orange block crystals suitable for X-ray crystallography were obtained. Yield: 60 mg (8.6% based on Mo^{VI}). Elemental analysis for $[N(CH_3)_4]_2K_{13}Na_3[C_{20}H_{20}Mo_{45}O_{124}S_{30}]\cdot ca.43\,H_2O$ ($C_{28}H_{130}K_{13}Mo_{45}N_2Na_3O_{167}S_{30}$, FW: 9019.89 g mol^{-1}; the elemental analysis was conducted on dried sample where nearly 83 lattice water molecules were lost compared with X-ray data) (%) calcd: C 3.73, H 1.45, N 0.31, S 10.63, Na 0.76, K 5.64, Mo 47.86; found: C 3.89, H 1.17, N 0.36, S 10.68, Na 0.85, K 5.69, Mo 49.46. IR (KBr): $\tilde{\nu}$ =3420.1 (m), 1619.9 (m), 1514.8 (sh), 1114.65 (w), 946.9 (sh), 847.6 (m), 753.1(m), 686.5 (m), 498.5 cm^{-1} (m).

Crystal data for **1**: $C_{28}H_{296}K_{13}Mo_{45}N_2Na_3O_{250}S_{30}$, MW = 10519.04 g mol^{-1}; monoclinic, space group *C2/c*, $a = 47.5953(14)$, $b = 21.8935(6)$, $c = 55.4035(16)$ Å, $\beta = 107.400(2)°$, $V = 55090(3)$ Å^3. Crystal data for **2**: $C_{28}H_{316}K_{10}Mo_{47}N_2O_{260}S_{32}$, MW = 10768.94 g mol^{-1}; monoclinic, space group $P2_1/m$, $a = 23.6561(11)$, $b = 19.3991(9)$, $c = 31.1718(13)$ Å, $\beta = 93.988(2)°$, $V = 14270.3(11)$ Å^3. Crystal data for **3**: $C_{36}H_{362}K_{18}Mo_{55}N_2O_{305}S_{40}$, MW = 12968.20 g mol^{-1}; triclinic, space group $P\bar{1}$, $a = 23.7158(8)$, $b = 24.8297(8)$, $c = 32.1743(11)$ Å, $\alpha = 107.994(2)$, $\beta = 92.788(2)$, $\gamma = 102.332(2)°$, $V = 17469.1(10)$ Å^3. Crystal data for **5**: $C_{48}H_{534}Cs_8K_{12}Mo_{68}N_4O_{411}S_{48}$, MW = 17342.07 g mol^{-1}; triclinic, space group $P\bar{1}$, $a = 19.9865(8)$, $b = 24.6627(11)$, $c = 24.7841(9)$ Å, $\alpha = 88.480(2)$, $\beta = 71.054(2)$, $\gamma = 78.984(2)°$, $V = 11333.6(8)$ Å^3. CCDC 909966 (**1**), 909967 (**2**), 909968 (**3**), 909969 (**5**), and 882568 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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