Struct Bond (2018) 176: 1–30
DOI: 10.1007/430_2017_5

Building Block Libraries and Structural Considerations in the Self-assembly of Polyoxometalate and Polyoxothiometalate Systems

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Abstract Inorganic metal-oxide clusters form a class of compounds that are unique in their topological and electronic versatility and are becoming increasingly more important in a variety of applications. Namely, Polyoxometalates (POMs) have shown an unmatched range of physical properties and the ability to form structures that can bridge several length scales. The formation of these molecular clusters is often ambiguous and is governed by self-assembly processes that limit our ability to rationally design such molecules. However, recent years have shown that by considering new building block principles the design and discovery of novel complex clusters is aiding our understanding of this process. Now with current progress in thiometalate chemistry, specifically polyoxothiometalates (POTM), the field of inorganic molecular clusters has further diversified allowing for the targeted development of molecules with specific functionality. This chapter discusses the main differences between POM and POTM systems and how this affects synthetic methodologies and reactivities. We will illustrate how careful structural considerations can lead to the generation of novel building blocks and further deepen our understanding of complex systems.

Keywords Chalcogenides • Clusters • Polyoxometalates • Polyoxothiometalates • Self-assembly

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1 Introduction

Today, Polyoxometalates (POMs) [1] are a key emerging area that promises to allow the development of sophisticated designer based materials and devices that exploit developments in instrumentation, nanoscale science and material fabrication methods. POMs are constructed by combinations of early transition metal-oxide units (e.g. M = Mo, W, V and Nb) at their high oxidation states. POMs are large frameworks, where the transition-metal oxyanions are linked together by the sharing of oxygen atoms to form structures with the general formula $\{MO_x\}_n$ [2] They may contain tens to hundreds of metal atoms that reach nuclearities as high as 368 metal atoms in one single cluster molecule forming nanosized architectures approaching the sizes of small protein molecules [3]. Over the last decade, a number of reviews have addressed different aspects of POM science; including new structures, biomedical applications, catalysis, theoretical calculations and perspectives for new materials [4, 5].

POMs have a rich history and have been known for more than two centuries, but due to a lack of appropriate analytical methods, the field remained for long one of the most underdeveloped disciplines in inorganic chemistry. Their discovery dates back to 1826, when the first synthesized POM system was reported. The compound isolated was ammonium phosphomolybdate and contained the $[PMo_{12}O_{40}]^{3-}$ anion. However, it was not until almost a century later, when in 1933, Keggin determined the structure of $H_3[PW_{12}O_{40}]$ by powder X-ray diffraction [6]. Since then, the ongoing development of synthetic methodologies and spectroscopic techniques has led to an eruption of structurally characterized POM compounds, see Fig. 1 [7]. In terms of technique development, fast and high-resolution single crystal data collection has allowed the area to blossom in an unimaginable way. The observed explosion of POM chemistry attracted the attention of various research groups who demonstrated the desire to develop the field further by focusing their efforts on understanding the underlying chemical processes masked by the self-assembly which govern these chemical systems. These efforts were mainly associated with fine manipulation of a long list of experimental variables which affect the self-assembly process to different extents (Fig. 1), in marked contrast to the oxo-chalcogenide chemistry, which is the key factor for the observed diversity in architectures and functionalities of POM-based species. Consequently, the rational utilization of this set of variables introduces an element of design in complex chemical processes which facilitates a degree of control during the self-assembly process.

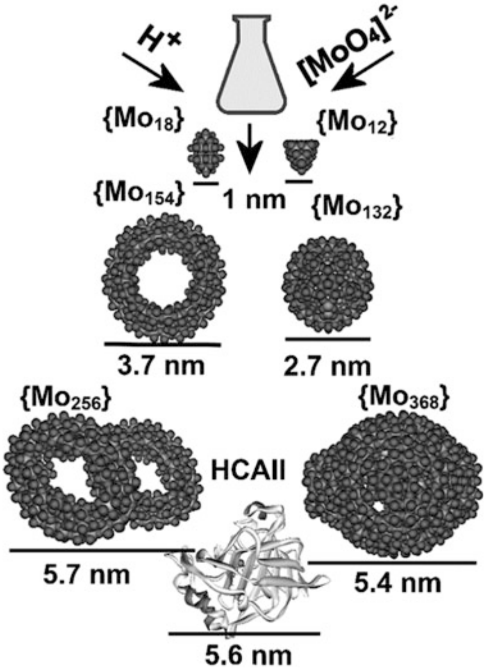

Fig. 1 Representations of the structures of some polyoxometalate (POM) clusters, all synthesized under 'one-pot' – 'one-step' reaction conditions (space filling: Mo *large grey spheres*, and O *smaller grey spheres*) from the well-known and studied $\{M_{12}\}$/$\{M_{18}\}$ Keggin/Dawson ions to the $\{Mo_{154}\}$/$\{Mo_{132}\}$ and $\{Mo_{256}\}$/$\{Mo_{368}\}$ clusters. These clusters are compared (to scale) with the protein Human Carbonic Anhydrase II (a medium-sized protein with 260 residues, MW 29.6 kD) to demonstrate their macro dimensions

The development of novel synthetic approaches over the last decades has helped synthetic chemists realize the correlation between experimental variables and complexity of the generated building block libraries. This observation is the driving force which renders POM chemistry a key emerging area that promises to allow the development of highly complex modular molecule-based materials and molecular devices with predefined functionality. Moreover, advances in other spectroscopic techniques such as electrospray-ionization mass spectrometry (ESI-MS) and heteronuclear NMR have allowed researchers to bridge the gap between solution and solid state complex self-assembled chemical systems and reveal mechanistic aspects of the underlying chemistry [8]. However, despite all the efforts, the increase in the number of reported species and the investigation of their physical properties, it is frustratingly difficult to reveal crucial information regarding the selection rules that trigger the organization of the generated building blocks in a controlled fashion and even more difficult to design specific routes leading to predefined functionality or emergence of new properties and phenomena. Therefore, given the enormous challenge in understanding and controlling the self-assembly processes for a range of self-assembled cluster-based architectures, numerous research groups have focused their efforts on the development and/or discovery of new selection rules. These efforts trigger the formation of highly diverse and complex building block libraries which will allow to shine light upon the underlying processes of high nuclearity POMs as well as the construction of new architectures [9].

Interestingly, Polyoxothiometalates (POTMs), a closely related family of compounds similar to POMs, have attracted the attention of researchers due to their seemingly similar chemical behaviour. Recent interest surrounding POTMs has proved fruitful. The insertion of soft donating centres such as sulphur atoms in molecular structures has provided access to various unique properties. The properties of this new class of molecular clusters can be attributed directly to the addition of sulphur, as in addition to its own properties of softness and polarization, it presents intense redox activity different from that of oxygen. This provides access to a plethora of interesting building blocks and molecular clusters with chemistries differing to that of POMs.

2 Classification of Polyoxometalates

POMs exhibit a diverse array of structural types exhibiting an abundance of structural features, compositions and sizes ranging from 1 to 5.6 nm [3]. In this way, many thousands of POMs are known to exist, which may be functionalized and exploited to suit particular design criteria. Thus, attempting to understand the relationships between different cluster types can often seem daunting and on occasions perplexing. In order to aid the researchers' understanding of different cluster types, a very general approach has been adopted to make the connections between different building block types, archetypes and physical properties. This has been done by dividing the family of POMs into three domains:

1. The first general subset consists of *Heteropolyanionic* species which are metal-oxide species that are formed by incorporation of an oxoanion of another element, notable p- and d-block oxoanions such as PO_4^{3-}, SO_4^{2-}, SiO_4^{2-}, etc. As a result of the huge amount of structural variety possible from the various combinations of POM moieties with other fragments, this subgroup is by far the most explored subset of POM clusters. Archetypical examples of this category include Keggin $[XM_{12}O_{40}]^{n-}$, Dawson $[X_2M_{18}O_{62}]^{n-}$ and Anderson $[XM_6O_{24}]^{n-}$, see Fig. 2.

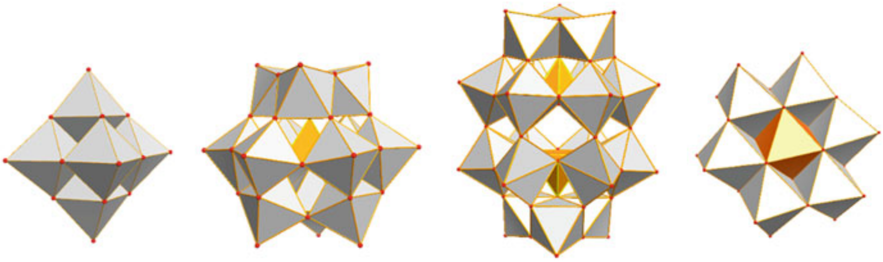

Fig. 2 Archetypical POM structures: left to right, Lindqvist, Keggin, Dawson and Anderson

2. *Isopolyanions* are metal-oxide frameworks lacking the addition of a heteroanion/heteroatom. For example, Lindqvist anions $[M_6O_{19}]^{n-}$ are part of this subset, as only one metal type is present in the framework. Subsequently, these clusters are often structurally less robust than their heteropolyanion counterparts [10]. However, they also exhibit interesting physical properties, such as high charges and strongly basic oxygen surfaces, which means that they are attractive units for use as building blocks [11].
3. *Molybdenum-blue* and *Molybdenum-brown* reduced Mo-based POM clusters are related to molybdenum blue type species, which was first reported by Scheele in 1783 [12]. Their composition was largely unknown until Müller et al. reported, in 1995, the synthesis and structural characterization of a very high nuclearity cluster $\{Mo_{154}\}$ crystallized from a solution of Mo-blue, which has a ring topology [13]. The interest generated by this result is partly due to its high nuclearity and partly because of the size of this cluster; with an outer diameter of ca. 34 Å, an inner diameter of 25 Å and with a thickness of 14 Å, it is a truly nanoscopic molecule. Using reaction conditions of pH ~1, with a concentration of Na_2MoO_4 of ca. 0.5 M and a degree of reduction of between 1 and 20%, the solution yields the 'Giant-Wheel' $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ in over 80% yield in 24 h [14]. The building up principle does not stop there, a series of mixed-valence Mo-blue (containing delocalized Mo^V-Mo^{VI}) clusters (e.g. $[Mo_{256}Eu_8O_{776}H_{20}(H_2O)_{162}]^{20-} \equiv \{Mo_{256}\}$) [15] have been reported as well as a class of spherical Mo-brown (containing localized Mo^V-Mo^V units) clusters (e.g. $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}(H_2O)_{72}]^{42-} \equiv \{Mo_{132}\}$) [16] and the highest nuclearity cluster reported to date, a 'lemon'-shaped cluster ($[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-} \equiv \{Mo_{368}\}$) [3], see Fig. 3.

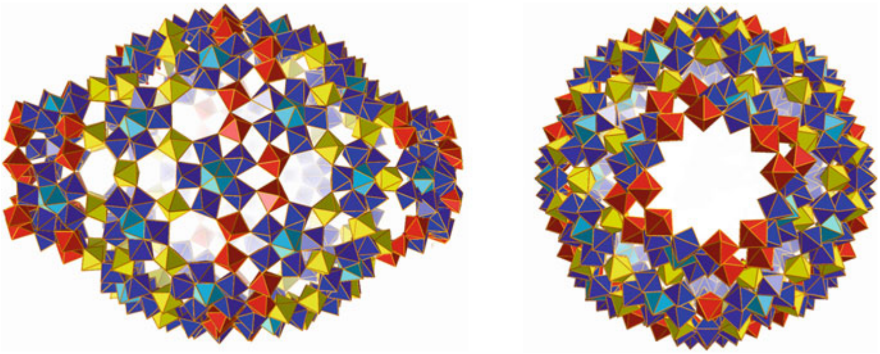

Fig. 3 Structure of the $\{Mo_{368}\} \equiv [H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$ cluster shown with polyhedral plots. The transferable building blocks are highlighted in different colours according to the scheme: $\{Mo_1\}$ *yellow*, $\{Mo_2\}$ *red*, $\{(Mo)Mo_5\}$-pentagon *blue/cyan*

3 The Building Block Approach

At first sight, the synthesis of POMs species can often appear to be trivial, as reported POM-based studies frequently use ill-defined and vague terms such as ‘one-pot’ or self-assembly synthesis. The use of such terms evades discussing the complex nature and sequence of events that occur along the reaction pathway. Instead, it is common only to focus on the outcome, providing a false sense of simplicity and serendipitous nature of the underlying chemical events. Generally, the approach used in the synthesis of POMs requires in most cases just one step. This usually involves the acidification of a solution of molybdates, tungstates or vanadates leading to an initial condensation process forming low nuclearity metal-oxide species (primary BBs) which react to form larger architectures. This sequence of events is influenced by a variety of experimentally controlled variables, such as: (a) concentration/type of metal-oxide anion, (b) pH, (c) ionic strength, (d) heteroatom type/concentration, (e) presence of additional ligands, (f) reducing environment, (g) temperature and pressure of reaction (e.g. microwave, hydrothermal and refluxing), (h) counter-ion and metal-ion effect and (i) processing methodology (one-pot, non-equilibrium conditions). Careful consideration of the above experimental variables in combination with experimentally observed outcomes has not only led to the discoveries of new clusters and emergence of new functionalities but also to understanding the relationship between the starting materials (metallic salts of tungsten, molybdenum, etc.), the generated library of building blocks, the architecture of the isolable POM-based compounds and finally the potential functionality of the POM-based material. The realization and understanding of the first steps of building block formation is crucial for the further development of POM chemistry; the primary constituents of the reaction mixture as well as the isolated species could act as a set of transferable building blocks that can be reliably utilized in the formation of larger architectures and potentially give rise to new properties and finally new functional materials. The first key point at this stage is the use of reliable synthetic routes for the regeneration of previously observed synthons at sufficient concentration and utilize them for the construction of new architectures.

Considering the inherent difficulties in terms of understanding and controlling the assembly processes, researchers have based most of the work on known structural archetypes of this family of clusters. Members from each of the structural archetypes discussed above can then be further modified and functionalized to form derivative structures. For instance, removal of at least one metal centre from the above (*plenary*) structures forms *lacunary* anions. More specifically, lacunary species of the Keggin structure are obtained when one or more addenda atoms are removed along with their oxo ligands unshared with other addenda. In this manner, mono- [17], di- [18] or trilacunary [19] clusters have been isolated. These polyanions are fairly reactive and tend to fill these vacant positions with other addenda metals or a wide range of electrophiles capable of octahedral coordination.

The lacunary Keggin clusters can be prepared by two different routes. Firstly, they can be formed in solution by controlled hydrolysis of the parent Keggin cluster. In monolacunary Keggin derivatives, an $[MO]^{4+}$ unit is removed by careful addition of base. This method was employed to isolate the first lacunary species. However, they can also be prepared more efficiently from solutions of simple addenda metal and heteroanion salts under strict pH control. More specifically, monolacunary clusters such as $[SiW_{11}O_{39}]^{8-}$ and trilacunary species such as $[SiW_9O_{34}]^{10-}$ are prepared in this manner whilst di-lacunary $[SiW_{10}O_{36}]^{8-}$ is obtained from the monolacunary precursor [20]. For example, the clusters $\{Ln_2As_3W_{29}\}$ and $\{(UO_2)_3As_3W_{29}\}$ result from the reaction of $\{XW_9\}$ lacunary anions where lanthanide anions are used as linkers. In another example, the anion $[Ln_2(H_2O)_7As_3W_{29}O_{103}]^{17-}$ (Ln^{III} = La, Ce) [21] contains three $\{AsW_9\}$ fragments bridged by two additional tungsten atoms and two Ln^{III} cations [22]. Clusters based on four linked $\{XW_9\}$ have also been identified. The cluster $[As_4W_{40}O_{140}]^{28-}$ [22] is a cyclic anion, being composed of four $\{\alpha\text{-}AsW_9\}$ units linked by additional tungsten atoms; the structure shown in Fig. 4 is a dicobalt derivative [19]. Derivatives of $[As_4W_{40}O_{140}]^{28-}$ have also been produced with lanthanide cations [22].

Following the same approach, Pope et al. have synthesized a massive heteropolytungstate anion which is a dodecamer of the $\{XW_9\}$ units, $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$ [23]. The 12 $\{XW_9\}$ units are linked by Ln^{III} cations (Ln = La, Ce, Nd, Sm) and additional tungsten atoms to produce a folded cyclic cluster with a D_{2d} idealized symmetry. The anion is completed by the four $\{W_5O_{18}\}$ lacunary fragments and the structure is shown in Fig. 5. This anion is extremely interesting and exhibits interesting topology and high nuclearity of metal ions.

In a similar manner, stable lacunary derivatives can be generated by Dawson or Lindqvist structures which can be used further as building blocks to construct larger

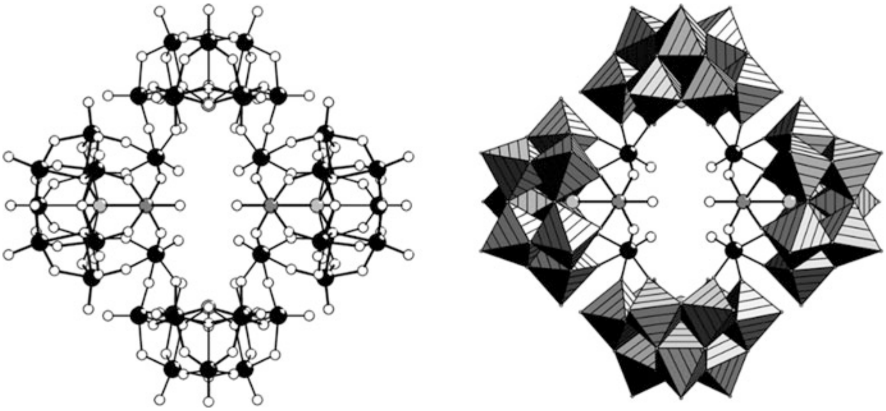

Fig. 4 The structure of the cyclic anion $[As_4W_{40}O_{140}]^{28-}$. A ball-and-stick representation is shown on the LHS and a polyhedral representation is shown on the RHS with the linking units shown in *ball* and *stick*. The W atoms are shown as *black spheres*, the As atoms as *grey spheres* and the O atoms as *white spheres*

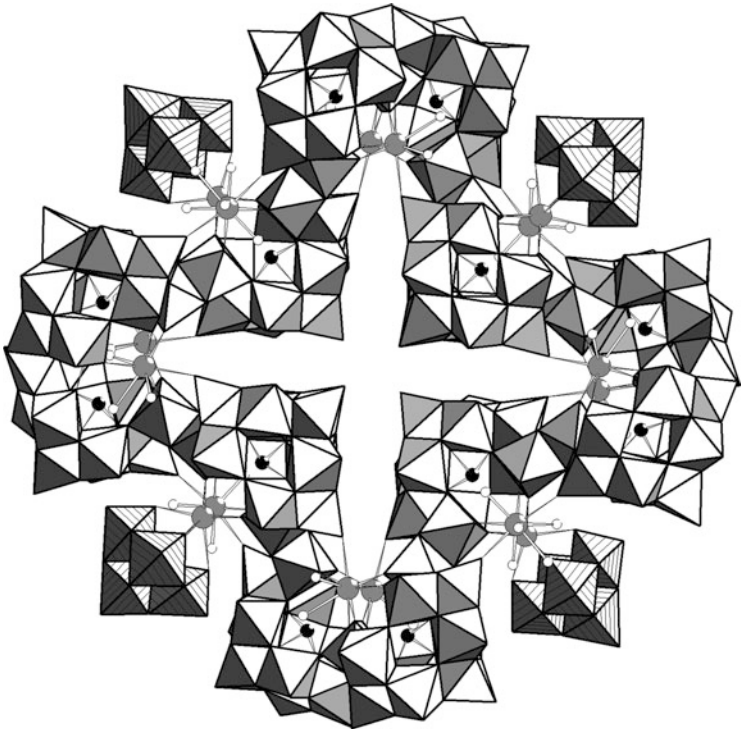

Fig. 5 Structure of the anion $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$ as a folded cyclic assembly of 12 {B-α-AsW_9} groups linked by additional W centres, all shown as polyhedral representations and four {LnW_5} groups. Ce(La) centres as *large grey spheres* and As centres as *small black spheres*. Finally, the water ligands are shown as *white spheres*

structures. The formation of lacunary Dawson clusters is driven by a controlled increase of the pH in solutions of the plenary cluster. Unlike the lacunary Keggins, the Dawson equivalents cannot be directly obtained from the condensation of the $[MO_6]$ units and templating heteroanions. Mono-, di-, tri- and hexalacunary species have been isolated [24].

Many new compounds have been constructed recently using lacunary building units, which have been increasingly used as rigid inorganic ligands to stabilize multinuclear metallic cores that could significantly alter the overall functionality of the isolated material [25]. For example, Cronin et al. demonstrated successfully the stabilization of a multinuclear $\{Fe_{12}(OH)_{18}\}$ core, utilizing the trivacant polyanion {α-$P_2W_{15}O_{56}$} and form an inorganic tetramer cluster $[KFe_{12}(OH)_{18}$(α-1,2,3-$P_2W_{15}O_{56})_4]^{29-}$ [26]. Recently, a novel planar $\{Mn_{19}\}$ magnetic cluster $[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-}$ have been isolated by Kortz et al. adopting a similar approach and utilization of the Keggin tungstosilicate lacunary fragment instead [27]. The planar $\{Mn_{19}(OH)_{12}\}^{26+}$ core is incorporated in the centre of six $\{SiW_{10}\}$ fragments. Lately, our group developed this field further by combining the stabilization effect offered from the lacunary fragments and redox process of the manganese centres (Mn^{II} to Mn^{III}) and reported an unprecedented Mn-mixed-valence architecture with the formula: $[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]^{18-}$ [28]. The in situ isomerization and partial reorganization of the starting lacunary $\{\gamma\text{-}SiW_{10}O_{36}\}$ species to $\{B\text{-}\beta\text{-}SiW_8O_{31}\}$ and $\{B\text{-}\beta\text{-}SiW_9O_{34}\}$ units led to the entrapment of a mixed-valence $\{Mn_5O_6\}$ cubane core, which is structurally relevant to the oxygen evolving centre of the biological photosystem II (PSII) (Fig. 6) [29]. These results demonstrate the vast possibilities and potential for the preparation of the many known multinuclear magnetic cores embedded within a POM framework where they can be finely tuned and magnetically isolated by altering their overall functionality. Furthermore, it is also possible following relatively simple synthetic procedures to prepare nanosized redox active assemblies using simple metal salts.

Many lacunary derivatives of the $\{P_2W_{18}\}$ cluster have been isolated. The two isomers of the monolacunary $\{\alpha\text{-}P_2W_{17}\}$ differ in the position of the vacancy. They are labelled as α_1 and α_2 for clusters where the vacancy is in a 'polar' position or in a 'belt' position, respectively [30]. The existence of $\{P_2W_{16}\}$ is still much debated yet the As analogue has been isolated [31]. Both α and β isomers have been isolated of the trilacunary derivative $\{P_2W_{15}\}$ [32]. In both cases, an entire polar triad is

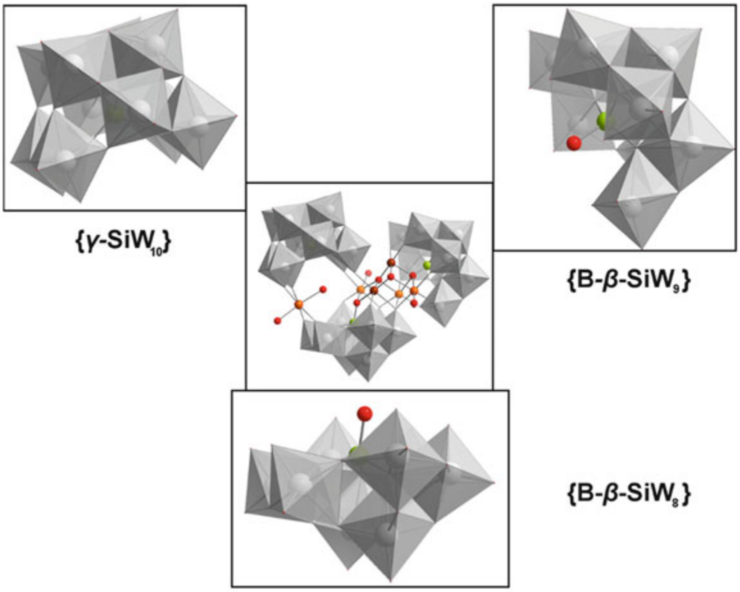

Fig. 6 Polyhedral/ball-and-stick representation of the $[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})\text{-}(\gamma\text{-}SiW_{10}O_{36})]^{18-}$ anion, showing the three inequivalent silicotungstate Keggin fragments $\{SiW_8\}$, $\{SiW_9\}$ and $\{SiW_{10}\}$ and the $\{Mn_4O_4\}$ cubane core with an appended 'pendant' Mn ion very similar to that found in the structure of photosystem II (PSII). Colour code: WO_6, *grey polyhedral*; Mn^{III}, *red-brown spheres*; Mn^{II}, *orange spheres*; Si, *green spheres* and O, *red spheres*. Counter ions and solvent molecules have been omitted for clarity

removed to form a reactive heptadentate inorganic ligand. In the hexalacunary derivative, {α-P_2W_{12}}, six adjacent addenda centres are removed from one side of the plenary cluster (see Fig. 7). Another highly relevant lacunary fragment based on the Wells–Dawson structure is the hexavacant {P_2W_{12}}. The structure of this cluster has been indirectly elucidated from elemental analysis and NMR spectroscopy. The occupation of the vacant positions by six Mo centres and the spectroscopic characterization of these heterometals have provided additional support for a 'boat-like' structure in {P_2W_{12}}. This lacunary fragment has proven to be an exceptional building block for the assembly of dimeric, trimeric and tetrameric structures. A cyclic tetrameric assembly of this hexalacunary fragment, {P_8W_{48}}, is also known [26].

The largest polyanion cluster isolated so far constructed using Dawson lacunary synthons, $[Mn^{III}{}_{40}P_{32}W^{VI}{}_{224}O_{888}]^{144-}$ ({$Mn_{40}W_{224}$}), is linked by Mn^{III} precursors and the hexavacant phosphotungstate $[a\text{-}H_2P_2W_{12}O_{48}]^{12-}$ ({P_2W_{12}}) [33]. The structure of {$Mn_{40}W_{224}$} shows how different archetypal building blocks can be assembled via a network of Mn-O = W bridges (Fig. 8) into an unprecedented architecture. The core of the architecture is based on the {P_8W_{48}} unit, which acts as scaffold for the organization of the remaining building blocks giving rise to the final structure. It is worth noting that the discussed synthetic approach is transferrable and can be extrapolated to a wide range of other POM architectures in principle, which demonstrates the exciting potential using a cluster-built-on-cluster design approach to expand the size of the POM clusters way beyond the current state of the art.

The obtained knowledge has prompted researchers to go a step further and adopt a synthetic approach which utilizes preformed POM clusters as a set of transferable building blocks that can be reliably used in the formation of new materials under controlled experimental conditions [11, 34]. A representative example of this effort is the utilization of the $[P_8W_{48}O_{184}]^{40-}$ ring-shaped macrocyclic POM cluster as building unit, with an integrated 1-nm pore as an 'aperture synthon', with manganese linkers yielding a vast three-dimensional extended framework architecture

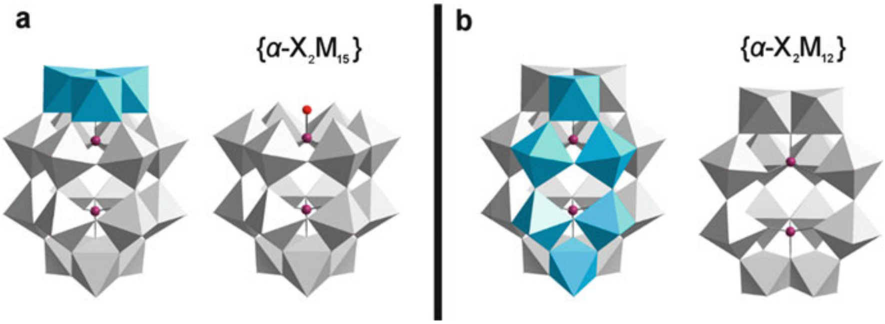

Fig. 7 Representation of the {α-X_2M_{15}} (**a**) and {α-X_2M_{12}} (**b**) lacunary isomers of the Wells–Dawson structure. Two representations of the plenary {α-X_2M_{18}} structures, which highlight the removed [MO_6] octahedra, are included to the left of each lacunary fragment

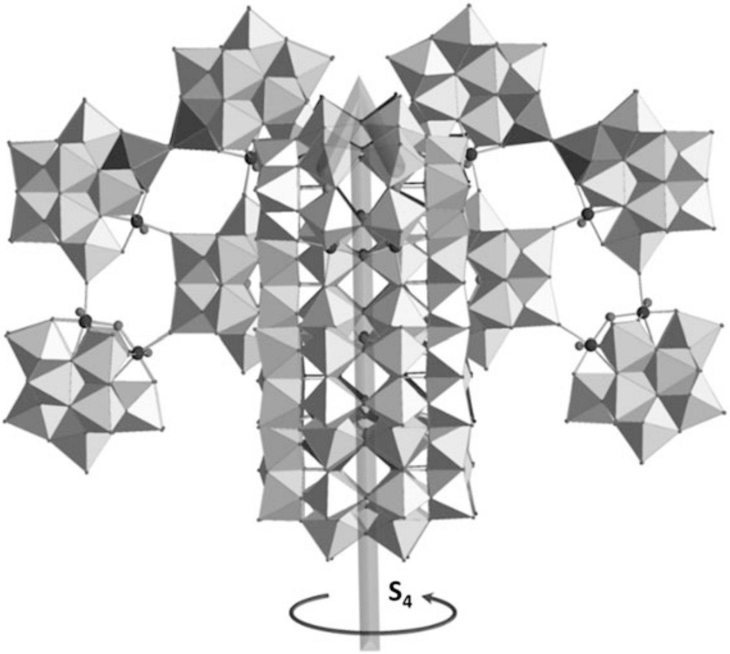

Fig. 8 Polyhedral representation of $[Mn^{III}_{40}P_{32}W^{VI}_{224}O_{888}]^{144-}$ shows that all the fragments are joined together through Mn^{III}-O = W bridges. The entire cluster adopts an idealized S_4 symmetry, with the principal axis coinciding with the fourfold axis of the central $\{P_8W_{48}\}$ wheel. The WO_6 units are shown in *light grey polyhedra* and the W/Mn disordered positions are in *dark grey polyhedra*. Counter ions and solvent molecules have been omitted for clarity

based on a truncated cuboctahedron (Fig. 13) [35]. The 1-nm-diameter entrance pores of the $\{P_8W_{48}\}$ structural building unit lead to approximately spherical 7.24 nm^3 cavities containing exchangeable alkali-metal cations that can be replaced by transition-metal ions through a cation exchange process (Fig. 9). The whole process can be controlled either via electrochemical switching of the overall framework charge by manipulating the oxidation state of the manganese linker ions or by physically gating the pores with large organic cations, thus demonstrating how metal–organic framework-like structures with integrated pores and new physical properties can be designed. In this way, cluster-based building blocks are assembled either through M-O-M′ oxo bridges or by the use of metal–organic complexes as linkers. However, the quest for deeper understanding of the assembly of POM-based chemical systems should not be confined by the predictability of a ‘fully controlled’ assembly process which could limit our horizons and minimize the chances of ground-breaking discoveries. The field of POMs is still expanding exponentially due to the obtained information in regard to the complex underlying chemistry which now can be better understood and controlled to an extent. The following sections will be devoted to discussing the similarities and differences observed in the closely related family of POTM clusters and the various synthetic

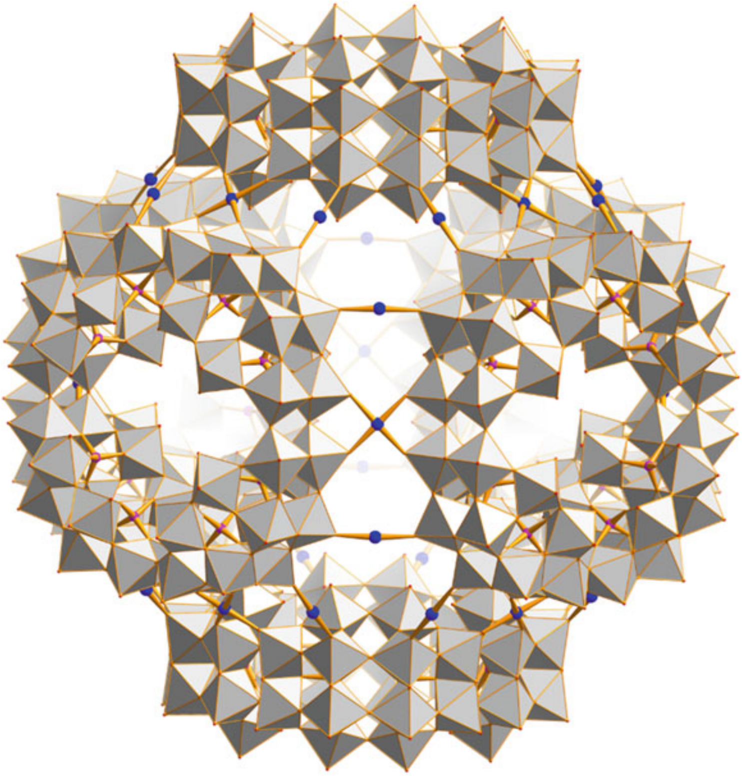

Fig. 9 Polyhedral representation of the face-directed assembly of the $[P_8W_{48}O_{184}]^{40-}$ molecular building unit, combined with electrophilic manganese linkers; colour code: WO_6, *grey polyhedra*, O, *red spheres*, Mn, *blue spheres* and P, *pink spheres*. Counterions and solvent molecules are omitted for clarity

methodologies which have been adopted in this case in order to improve our understanding and trigger a structural and information explosion similar to the one observed in POM chemistry.

4 Polyoxothiometalates

The transition-metal thioions of early transition metals have long been of interest due to their broad range of colours. In their highest oxidation state, V, Nb, Ta, Mo, W and Re form tetrahedral species that exhibit a plethora of interesting properties [36]. Initial investigation into thiometalates dates to the beginning of the nineteenth century where Berzelius noted their formation by passing H_2S gas into an aqueous solution for $Mo_4{}^{2-}$ and $WO_4{}^{2-}$. However, it was not until the turn of the twentieth century that the true composition of these compounds was established. In contrast to POMs, the chemistry of thiometalates remained a somewhat underexplored domain and only in the past 20 years has the field attracted the interest of researchers and shown signs of development [38]. Today, interest in thiometalates is due predominately to their implications in catalysis and bioinorganic chemistry because of the vital role of MoS_2 and WS_2 as catalysts for the hydrosulfurization, deoxygenation and denitrogenation of oil fractions [37]. In bioinorganic chemistry, their interest is directly related to their key role in molybdoenzymes [38]. Thus, the efforts to prepare appropriate synthetic models for the proper investigation of the active sites of molybdoenzymes led to the development of various sulfido and disulfido complexes; this group of clusters remains the most widely developed family of thiometalate compounds.

The introduction of sulphur in POM frameworks is expected to significantly modify the structural and electronic properties of POMs in an effort to develop complementary properties at the molecular level; such as the electrocatalytic function of the {M-S} core combined with the electron storage capacity of POMs. The study of the acidification of the basic thioanions $[MS_4]^{2-}$ (M = Mo, W) revealed that the condensation process of thiometalates is much more complex than oxometalates since it is systematically accompanied with intramolecular redox processes [39–43].

Different attempts to functionalize POMs by direct addition of sulphide by hydrogen sulphide failed because of facile and rapid reduction of the metallic framework and subsequent degradation into metal thio-species. However, the replacement of oxygen by sulphur has proved possible in less reducible POMs. Klemperer et al. reported the first example of a mixed Nb(Ta)-W Lindqvist $[W_5MO_{19}]^{3-}$ (M = Nb^{V} or Ta^{V}) succeeding to incorporate an M = S group and form the first thio-POM $[W_5MSO_{18}]^{3-}$. The methodology has successfully been transposed to the Keggin $\{PW_{11}MO_{40}\}^{4-}$ species allowing to isolate and characterize the first sulphur-containing Keggin derivative $[PW_{11}MSO_{39}]^{4-}$ [44]. In 1978, Müller et al. reported the novel $[(S_2)_2Mo(S_2)_2Mo(S_2)_2]^{2-}$ anionic complex and explicitly stated that $S_2{}^{2-}$ anions can reduce Mo^{VI} to Mo^{V} and further form Mo–Mo bonds which may possibly lead to interesting magnetic properties [45]. Later, Müller and Sécheresse developed synthetic routes for the preparation of $[Mo_3S_4]^{4+}$ and $[Mo_2O_2S_2]^{2+}$ precursors, respectively. Similarly, Cohen and his co-workers reported the synthesis of $[W_2S_6]^{2-}$ based compounds in DMF instead of aqueous solution [46], whilst Sécheresse and co-workers adopted the preparation of the $[Mo_2O_2S_2]^{2+}$ building block from DMF and transferred it successfully to aqueous media (see Fig. 10) [47]. The $[Mo_3S_4]^{4+}$ cluster core belongs to the family of the general formula $\{M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3\}$ (Q = S, Se, Te) which contains a triangular metal cluster M_3 and four chalcogenide ligands (one μ_3-Q and three μ_2-Q). The previously reported pseudo-cuboidal fragment $[Mo_3S_4]^{4+}$ tends to form low nuclearity clusters. It can react with transition metals or noble metal ions to form dimeric structures [48, 49]. On the contrary, $[Mo_2O_2S_2]^{2+}$ proved to be a lot more versatile and chemically suitable to interact constructively with a variety of organic and inorganic ligands including POM-based species [50]. Thus, Sécheresse and Cadot set about the challenge to develop a synthesis for POTMs in water.

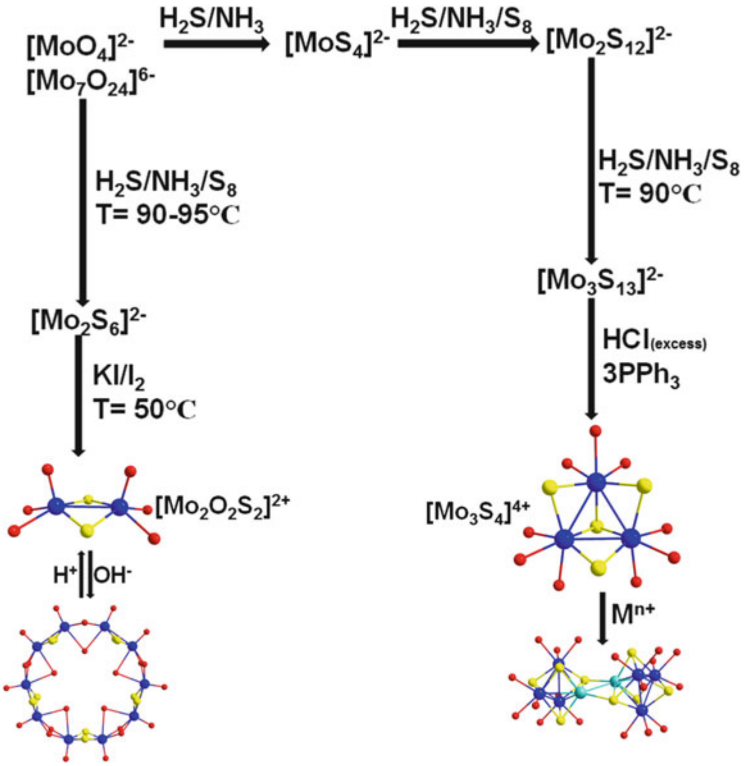

Fig. 10 Reaction pathways for the formation of the two archetypical electrophilic building blocks $[Mo_2O_2S_2]^{2+}$ and $[Mo_3S_4]^{4+}$

4.1 Fundamental Oxothiometalate Building Blocks

The choice of precursor for the core design of POTMs remains somewhat limited. For a precursor to be suitable, it should ideally display a reasonable degree of thermodynamic stability along the condensation process, an adapted electronic structure and its initial geometry should be suitable with respect to the target molecule. At present, there exist only two primary building block units for the synthesis of POTMs; these are the dimeric dication species $[M_2O_2S_2(H_2O)_6]^{2+}$, where M = Mo or W. The molybdenum (M = Mo) analogue of the dication has been most widely explored due to its ability to remain stable in aqueous medium. The $[Mo_2O_2S_2]^{2+}$ unit has acido-basic properties and polycondensation ability. The two Mo^V centres are equivalent and linked by a double sulfido bridge (Mo-S = 2.3 Å) with a metal–metal bond ($d(Mo^V \cdots Mo^V) = 2.8$ Å) improving the cohesion of the unit and leading to its excellent stability. The double sulfido bridges and the metal–metal bond confer to these building block specific coordination properties producing a unique class of compounds which are not observed with the full oxo analogue [51]. The coordination requirements are mainly restricted to the equatorial and axial sites of the two equivalent Mo^V atoms leading to the highly predictable assembly. A common feature of this family of compounds is the ring-shaped topology, but the symmetry associated with the obtained structure is dependent on the geometry of the template, which gives rise to host–guest properties such as anion recognition and anion-templated synthesis. Additionally, the specific coordination ability and excellent stability of $[Mo_2O_2S_2]^{2+}$ make it superior to other oxothioanions.

The self-condensation of POTMs follows an opposite general trend to that observed in POM synthesis in terms of the pH range. Generally, the formation of POM species results from the acidification of a solution containing monomeric oxoanions $[MO_4]^{2-}$ (M = Mo, W). Conversely, the assembly of POTM species is triggered by addition of base which generates oleosis and oxoleosis products which can be spontaneously assembled further to larger architectures. It is worth noting that the self-condensation process is susceptible to the presence of structure directing agents (e.g. counter ions and metal ions) in a similar fashion to POM chemistry [51, 52].

Following these general reactivity and chemical behaviour trends, Cadot and co-workers have made great efforts to investigate the self-condensation process with and without templates (see Fig. 11). The first series of cyclic compounds, $[Mo^V{}_8S_8O_8(OH)_8(HMo^{VI}O_5(H_2O))]^{3-} = \{Mo_9\}$, [53] $[I_2Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]^{2-} = \{Mo_{10}\}$ [47] and $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6] = \{Mo_{12}\}$ [51], were obtained in the absence of templates at different pH values ranging from 5.0 to 2–3 and 1.5, respectively. Additionally, a gradual molecular growth has been indicated by a rational interconversion between $\{Mo_{10}\}$ and $\{Mo_{12}\}$ rings via self-rearrangement processes. The $\{Mo_9\}$ ring is the first example of mixed valent POTMs where a monomeric oxoanion $[MO_4]^{2-}$ templates the formation of the ring [53]. The isolation of this cluster highlighted the potential of using organic templates of various lengths, flexibility and coordination ability to influence the self-condensation process of $[Mo_2O_2S_2]^{2+}$ units. Indeed, Cadot and co-workers using a templated synthesis approach have reported the constructive utilization of organic carboxylate ligands to template the self-condensation of $[Mo_2O_2S_2]^{2+}$ [54]. More specifically, a family of ring-shaped POTM clusters exhibiting a variety of nuclearities, shapes and symmetries have been synthesized and characterized as host–guest assemblies (see Fig. 12). The host–guest covalent and H-bond interactions [52, 55] between the fundamental building blocks $[Mo_2O_2S_2]^{2+}$ and polycarboxylate and (poly) phosphate ligands proved to be crucial for directing the self-condensation as well as defining the overall nuclearity of the obtained cluster. Another interesting feature of some members of this family is their ability to act as either anionic or cationic receptors depending on the pH value of the reaction mixture. For example, the addition of a strong base to the neutral inorganic ring $[Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5]$ in aqueous medium leads to partial deprotonation of the inner H_2O molecules and/or Mo-OH-Mo bridges. In the presence of Cs^+ cations, a reorganization occurs and a dianionic eight-membered ring capped by two Cs^+ cations with the formula $[Cs_2Mo_8O_8S_8(OH)_{10}(H_2O)]\cdot 33H_2O$ forms [56]. This class of compounds is mainly orchestrated by mutual adaptability between the host and guest components. To

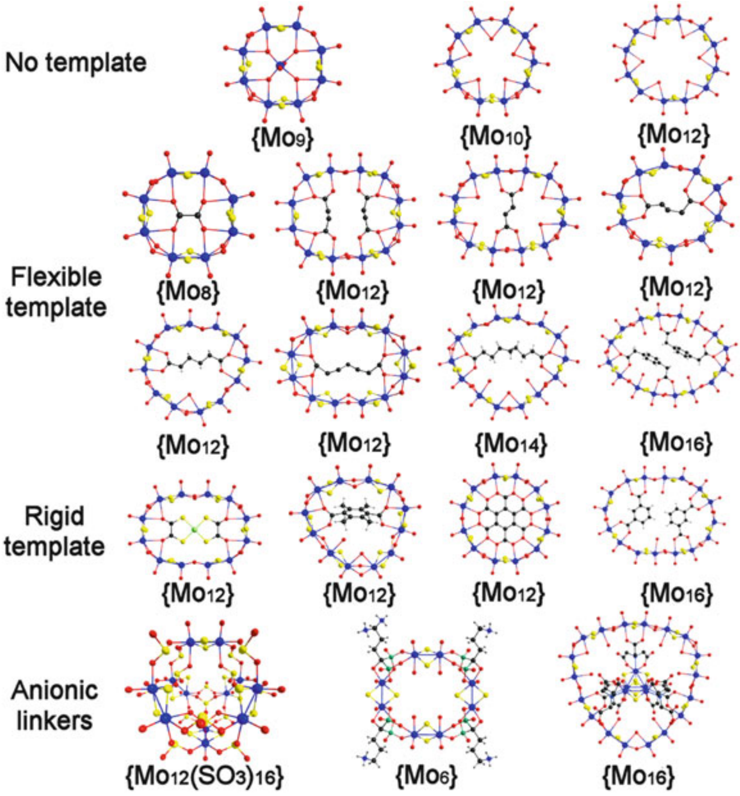

Fig. 11 Ball-and-stick representation of polyoxothiometalate (POTM) ring-shaped clusters templated by ligands or small clusters

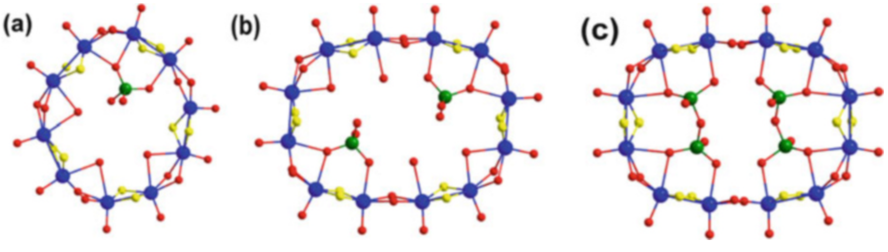

Fig. 12 Ball and stick representation of phosphate templated POTM rings: (**a**) $[(H_2PO_4)Mo_{10}S_{10}O_{10}(OH)_{11}(H_2O)_2]2-$; (**b**) $[(H_2PO_4)_2Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_2]4-$ and (**c**) $[(P_2O_7)_2Mo_{12}S_{12}O_{12}(OH)_{12}]6-$

date, the largest organic ligand templated macrocycle is an $\{Mo_{18}\}$ cluster [57]. The fluxional behavior of the organic ligand templated rings has been investigated by NMR and identified the presence of conformational isomers in solution [58]. An interesting observation is that flexible organic ligands direct the assembly of macrocycles with high flexibility, whilst rigid templates favour the formation of rings that have limited conformational transformations. Additionally, heteroanions can act as templates or linkers in a similar fashion. For example, phosphate anions can act as templates in the case of PO_3^{2-}, mono- and di-phosphato rings (see Fig. 12). When a single mono-protonated phosphate $[HPO_4]^{2-}$ anion was used, a decanuclear ring $\{Mo_{10}O_{10}S_{10}(OH)_{10}(HPO_4)\}$ was obtained. A dodecanuclear ring can also be formed containing two $[HPO_4]^{2-}$ or two $[P_2O_7]^{4-}$ anions [59].

An interesting deviation from the ring-shaped structural archetype was reported recently by Cadot and co-workers when they isolated two nanosized $\{Mo_{84}\}$ and Keplerate-type $\{Mo_{132}\}$ clusters, in concentrated acetate buffer (pH 3.6) solution (see Fig. 13) [60]. Müller et al. also employed the $[Mo_2O_2S_2]^{2+}$ fragment to combine $\{W_6O_{21}\}$ pentagonal building block in an effort to form the 'soft' analogue of a tungsten based Keplerate $\{W^{VI}{}_{72}Mo^{V}{}_{60}\}$ cluster [61]. The $\{Mo_{84}\}$ structure is quite interesting due to the fact that it incorporates a new triangular POTM building block $\{Mo_6S_6O_6(OH)\}^{5+}$. The $\{Mo_{84}\}$ molecular cube exhibits six open faces with the diameter ca. 9 Å. Interestingly, the cluster incorporates 24 outward-oriented acetate ligands which can be substituted by specific organic moieties, which paves the way for post-functionalization and design tailored for specific applications.

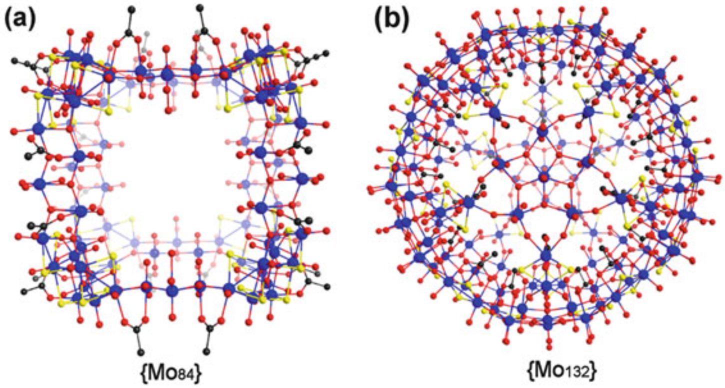

Fig. 13 (**a**) Representations of $[H_{32}Mo_{84}S_{48}O_{200}(AcO)_{24}]^{32-}$ which comprise two kinds of building blocks: $\{Mo^{VI}{}_3O_{11}\}^{4-}$ units forming the edges and $\{Mo_6S_6O_6(OH)\}^{5+}$ units located at the corners of the molecular cube; (**b**) representation of the sulphurated Keplerate-type anion $\{Mo_{132}\}$

4.2 Design of New Building Block Libraries

4.2.1 The Squarate Anion as Template

According to previously reported examples, hydrolytic condensation of the $\{Mo_2O_2S_2(H_2O)_6\}^{2+}$ cation produced a rich class of cyclic host–guest compounds, with the shape and size of the host cyclic rings being dependent on the size of flexible organic carboxylates [54]. However, this approach led to limited structural diversity due to the lack of a building block library of sufficient complexity. The only exception was the isolation of the nanosized $\{Mo_{84}\}$ molecular cube Fig. 13a, due to the generation of additional constituents, $\{Mo_6S_6O_6(OH)\}^{5+}$, that could be used for the construction of a larger structure. Intrigued by this observation, our group focused on the potential of generating a new and more diverse library of building blocks using a template of appropriate rigidity and symmetry. The choice of template candidate was the squarate anion which offers sufficient coordination sites whilst its planarity would introduce the appropriate rigidity necessary to stabilize the formation of new building blocks. Indeed, the first effort led to the generation of new building block which gave us the opportunity to isolate chiral clusters following a 'symmetry-breaking' strategy (Fig. 14).

More specifically, we showed how this symmetry breaking is manifested in a stepwise manner from $(NMe_4)_4[(Mo_2S_2O_2)_7(OH)_{14}(C_4O_4)_2(H_2O)_2]\cdot 13H_2O$ $\{Mo_{14}\}$, **1** a planar molecule, to $K_8[(Mo_2S_2O_2)_6(OH)_8(C_4O_4)_2(Mo_2O_8)_2(H_2O)_4]\cdot 15H_2O$ $\{Mo_{16}\}$, **2** a non-planar molecule formed by the addition of $\{Mo_2O_8\}$ anions into the system and finally to $KH[NMe_4]_2[(Mo_2S_2O_2)_4(OH)_6(Mo_2O_8)(C_4O_4)]\cdot 10H_2O$ $\{Mo_{10}\}$, a chiral ring-shaped structure. Furthermore, it is possible to isolate the non-chiral version of the **3a** ring, **3b**, which contains a mirror plane within the ring (see Figs. 15 and 16) [62].

4.2.2 The Role of the Lindqvist-Based Building Unit $[Mo_5O_{18}]^{6-}$

Following on from the identification of the above compounds, the building blocks A and B have been utilized to synthesize an array of new compounds with unprecedented architectures and in doing so, the additional building block C ($[Mo_5O_{18}]^{6-}$, Fig. 17, centre) has been identified [63]. C is an isomer of the lacunary Lindqvist

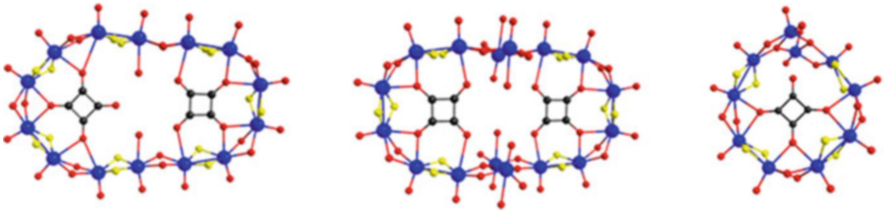

Fig. 14 *Left* – $\{Mo_{14}\}$; *middle* – $\{Mo_{16}\}$ and *right* – $\{Mo_{10}\}$ chiral

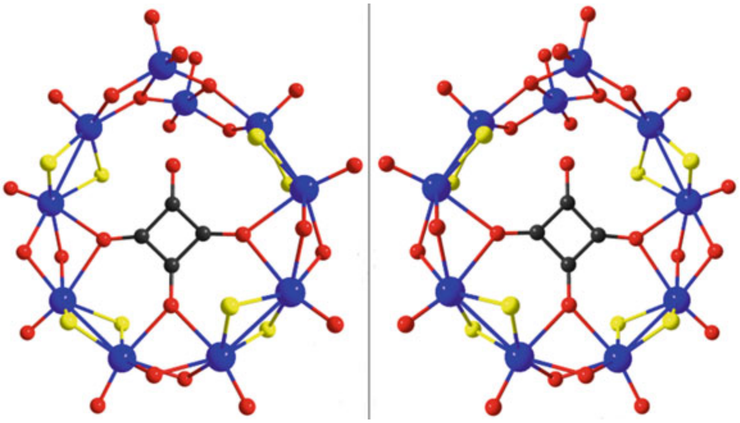

Fig. 15 The absolute configurations of the left- and right-handed $\{Mo_{10}\}$ clusters. This is a very interesting observation because even though the structural features of this series of clusters did not deviate from the ring-shaped topology, it was possible to generate new building blocks with increased complexity, leading to the manifestation of spontaneous chiral resolution and control of the interaction of the available constituents

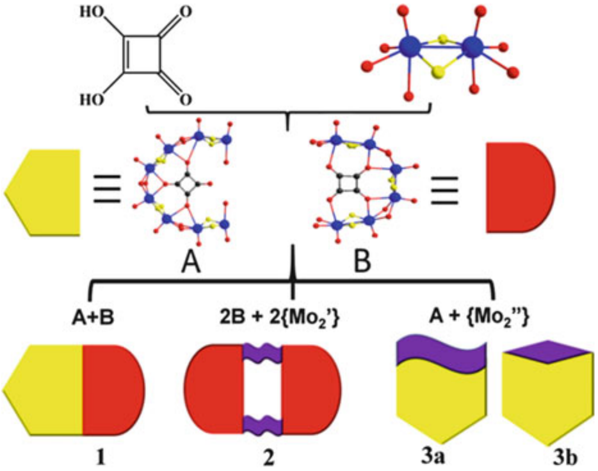

Fig. 16 Schematic representation of the new virtual building blocks A and B, and the constructive interaction for the construction of new species

anion which acts as a linking unit in these structures. Compared with the configuration of the traditional $[Mo_5O_{18}]^{6-}$, the coordination environment of the Mo^{VI} atom is greatly distorted which directly influences coordination mode considering the structural deviation from the traditional lacunary anion. The distortion leads to the active oxygen coordination atoms of the $[Mo_5O_{18}]^{6-}$ anion pointing further outwards, decreasing the steric hindrance, and allowing the subunit

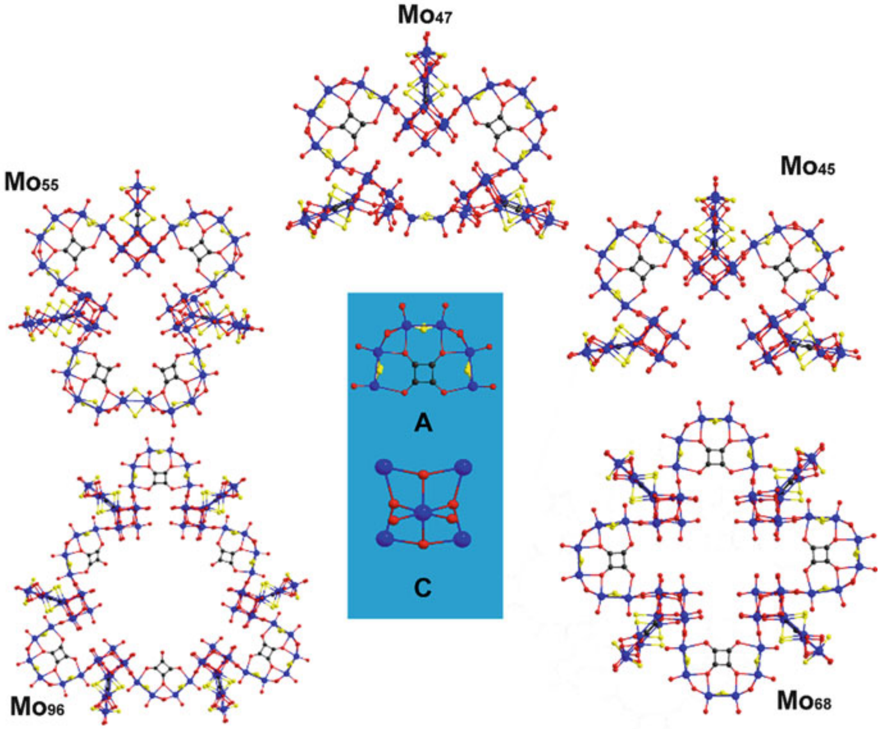

Fig. 17 Ball-and-stick representation of the new family of nanosized clusters and representation of the pentagonal common building blocks (Mo: *blue*, S: *yellow* and O: *red*)

$[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ to coordinate to the $[Mo_5O_{18}]^{6-}$ anion via Mo–O bonds (2.05(6)–2.49(5) Å). More specifically, the unit has three distinct sites to which A and B can bind: two of which are coplanar and are located on the exterior of the molecules, whilst the third, which is perpendicular to the others, resides on the inner surface. A, B and C can interact in several ways, with sequentially increasing size as more building blocks are incorporated, as shown in Fig. 17. The key points from the synthetic chemists point of view are that self-assembly can be directed by specifying the parameters such as pH, ratio of starting material and counter cation, and that molecular growth is facilitated by both fast self-condensation and subsequent increase in reactivity at certain regions of the clusters' periphery.

It is worth noting that the $\{Mo_{96}\}$ cluster is the largest POTM reported to date that possesses a D_{3h} symmetry and incorporates three building blocks: $[Mo_5O_{18}]^{6-}$, $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$ and $[(Mo_2O_2S_2)_2(OH)_2(C_4O_4)]$, which assemble in an alternating orthogonal arrangement. Additionally, the molecule exhibits a 1.7-nm cavity; Fig. 18 shows the packing structure of $\{Mo_{96}\}$-wheel viewed along the *a*-axis, where the $\{Mo_{96}\}$-wheels are overlapped with respect to each other, forming an interdigitated molecular arrangement within the crystallographic *ab*-plane.

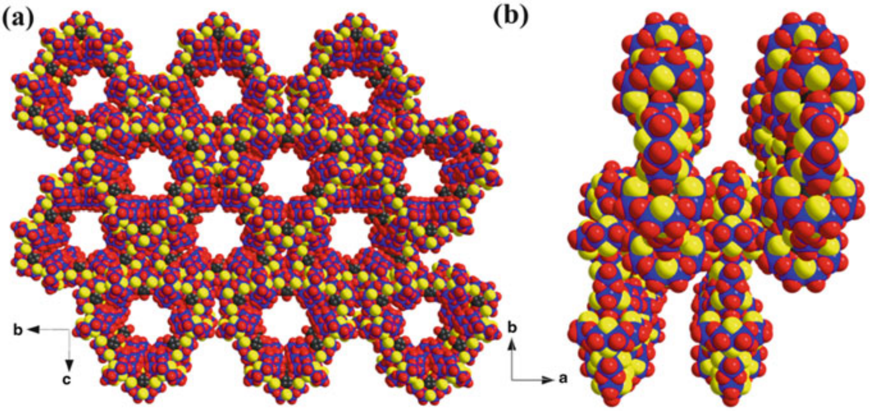

Fig. 18 (**a**) View along crystallograhic *α*-axis of the nanosized $\{Mo_{96}\}$ cluster's packing structure; (**b**) Interdigitated molecular arrangement within crystallographic *ab*-plane

4.2.3 The Role of the Elusive Pentagonal Building Unit $\{\mathbf{Mo(Mo_5)}\}$

It has been widely reported that lacunary POMs can be linked by transition metals into extended giant clusters and even high dimensional frameworks. However, such self-assembly systems are, to some extent, out of control because of the versatile coordination modes and configurations available to transition metals. For complex systems, using well-defined precursors to induce self-condensation into giant clusters has indubitable advantages for the study of self-assembly mechanisms. Interestingly, Müller and co-workers developed synthetic approaches based on libraries of virtual building blocks that allow target-driven self-assembly via the expression of the appropriate/necessary constituents for all possible components, resulting in high yield syntheses of inorganic superfullerenes and giant ring-shaped, electron-rich, mixed-valence polyoxomolybdates under appropriate conditions [64–66].

To date, there are only a few examples of lacunary POMs that have been used constructively in POTM chemistry for the construction of new topologies. Recently our group reported the first system that combines successfully the newly discovered POTM building block $\{(Mo_2O_2S_2)_3(OH)_4(C_4O_4)\}$ with the elusive virtual lacunary POM fragment – pentagonal $\{Mo^{VI}(Mo^{VI}_5)\}$ which has been described, as the fundamental component for the generation of a family of nanosized POTM–POM clusters (see Fig. 19). The $\{(Mo_2O_2S_2)_3(OH)_4(C_4O_4)\}$ building block has unsaturated Mo^V centres resulting in a positively charged unit, which is susceptible to nucleophilic attack by the negatively charged pentagonal unit to generate a novel intriguing family of thiometalate 'butterfly-shaped' clusters, $(N(CH_3)_4)_3K_{11.5}Na_{0.5}[(Mo_2O_2S_2)_3(C_4O_4)(OH)_4]_6(OH)_2[Mo^{VI}_6O_{21}(H_2O)]_2I\cdot 19H_2O$ $\{\mathbf{Mo_{48}}\}$. $[N(CH_3)_4]_3K_{11}[(Mo_2S_2O_2)_3(C_4O_4)(OH)_4]_6(OH)_2[Mo^{VI}_6O_{21}(DMF)]_2\cdot 2DMF\cdot 33H_2O$ $\{\mathbf{Mo_{48}}\}$, $[N(CH_3)_4]_4K_{18}[(Mo_2O_2S_2)_3(C_4O_4)(OH)_4]_6(OH)_2(Mo^{VI}_6O_{21}(H_2O))_2[Mo^{VI}_{12}O_{36}(C_4O_4)_4]\cdot 79H_2O$ $\{\mathbf{Mo_{60}}\}$ and $K_{16}[(Mo_2O_2S_2)_3(C_4O_4)(OH)_4]_4(Mo^{VI}_5O_{19}(H_2O)_2)_2\cdot 42H_2O$, $\{\mathbf{Mo_{34}}\}$ (see Fig. 20).

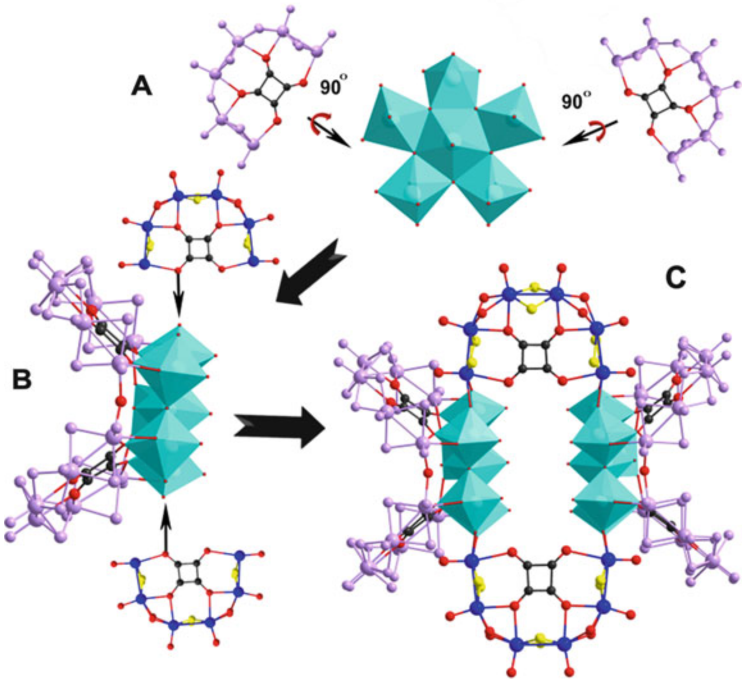

Fig. 19 Representation of the stepwise trapping of pentagonal {Mo_6} assemblies in POTM systems: Two building blocks [$(Mo_2O_2S_2)_3(OH)_4(C_4O_4)$] (*light violet*) rotate 90° to coordinate to the pentagonal unit via Mo–O bonds to form unit B and then two more [$(Mo_2O_2S_2)_3(OH)_4(C_4O_4)$] link two B units to construct the {Mo_{48}} (C) (pentagonal unit {Mo (Mo_5)}: *cyan polyhedra*; ball-and-stick representation for C: *black*; Mo^V: *blue*; S: *yellow* and O: *red*)

4.2.4 The Role of the SeO_3^{2-} as Template and Linker

The family of small and flexible XO_3^{2-} (X = S or Se) anions with pyramidal geometry was envisaged as very promising template candidates and assembly directing agents due to the numerous coordination modes and their lone pair of electrons which can potentially induce interesting electronic properties. The combination of structurally diverse POM synthons and tuneable chalcogen-based ones could give rise to unprecedented architectures and the emergence of unique properties. Indeed, our group investigated recently the potential variation induced by the generation of novel synthons (POM and POTM building block libraries) and demonstrated the effect of non-conventional heteroanions on the self-assembly processes and final structural motifs in thiometalate chemistry. The selenite anion template revealed a variety of coordination modes leading to the generation of different building blocks. Additionally, the SeO_3^{2-} anion proved to be a highly diverse unit since it can act as template as well as a linker. The SeO_3^{2-} anion

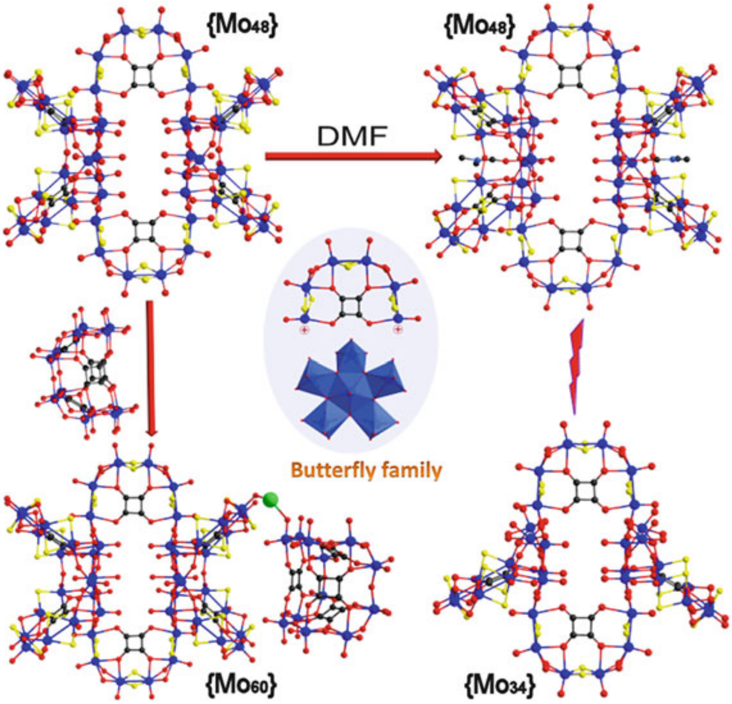

Fig. 20 Ball-and-stick representation of the 'butterfly' family; all the family members are based on the same building block library

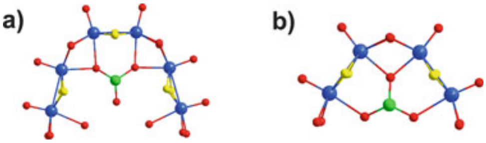

Fig. 21 SeO_3^{2-} templated POTM subunits (**a**) $[(Mo_2O_2S_2)_3(OH)_4(SeO_3)]$ and (**b**) $[(Mo_2O_2S_2)_2(OH)_2(SeO_3)]$

templates the self-condensation of $[Mo_2O_2S_2]^{2+}$ units giving two types of subunits $[(Mo_2O_2S_2)_3(OH)_4(SeO_3)]$ and $[(Mo_2O_2S_2)_2(OH)(SeO_3)]^+$, depending on the coordination mode of selenite anions (Fig. 21).

Investigation of the parameter space of the $\{Mo_2O_2S_2\}/XO_3^{2-}$ system and constructive use of the new building blocks led to the formation of new family of nanosized clusters with high nuclearities ranging from $\{Mo_8\}$ to $\{Mo_{36}\}$ and diverse architectures Fig. 22 [67, 68].

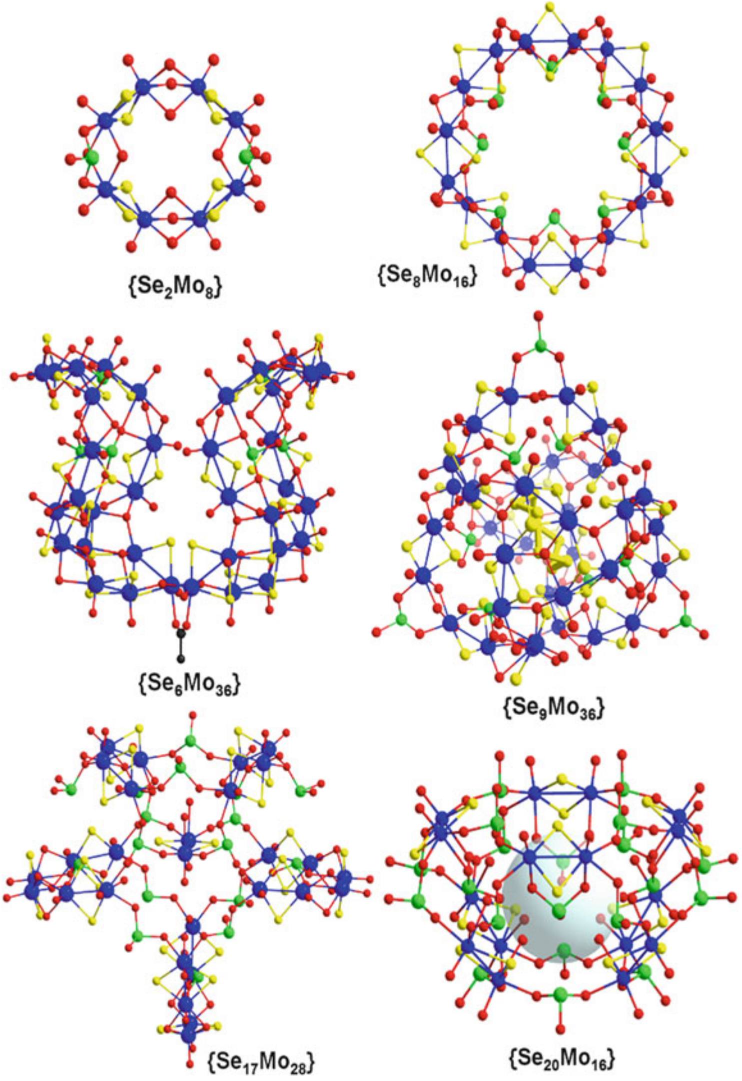

Fig. 22 Ball-and-stick representation of the SeO_3^{2-} templated POTMs family of six clusters with varying Mo: chalcogen ratios

5 Conclusions and Perspectives

The vast development in the field of POTM chemistry is in part due to recent synthetic approaches adopted by researchers. More specifically, the assembly of the fundamental $[Mo_2O_2S_2]^{2+}$ building block using templates of different rigidity and coordination ability led to the generation of new and more complex building block libraries. The use of squarate anions as the template led to the formation of building blocks, e.g. $[(Mo_2O_2S_2)_3(OH)_4(C_4O_4)]$, able to retain their structural integrity over a wide range of pH values and used constructively for the construction of nanosized clusters with architectures which deviate from the archetypical ring-shaped topology. Also, it was shown that the building block libraries can be further diversified by the in situ generation of virtual building blocks observed in POM chemistry such as $[Mo_5O_{18}]^{6-}$ and the pentagonal $[Mo_6O_{21}]^{12-}$ observed mainly in Mo-Blue chemistry but have never been identified and regenerated in POTM systems. In a similar manner, the assembly of $[Mo_2O_2S_2]^{2+}$ units was influenced by the presence of the $SeO_3{}^{2-}$ anion in a different way due to the flexibility, geometry and multiple coordination modes of the selenite anions. The coordination ability differs to organic carboxylate ligands, as the small size of the selenite anion acts as template as well as linker. This led to the formation of a fundamentally new building block library which was used for the construction of species with unprecedented topologies.

The POTM family is proved to be governed by similar selection rules which drive the assembly of the available constituents, with the only exception being the range of pH values where this condensation takes place. However, the field did not expand as rapidly as their POMs relatives. We showed that this bottleneck was mainly due to the fact that there was no available building block library of high enough diversity which will allow the system to 'evolve' from the ring-shaped topology and limited range of nuclearities to unprecedented architectures of increased complexity and nuclearities ranging from 16 to 96 metal centres. The above realization reveals an opportunity for further development of the oxothiometalate chemistry based upon the building block ideas discussed above; using these ideas, it should be possible to work towards designer nanomolecules of ever increasing size and complexity. Such clusters, for instance, are being proposed for the design of catalysts and molecule-based devices that could be used in molecular electronics. Potentially such systems could be used to probe the behaviour and even discover new physics in relation to the 2D metal chalcogenides or understand better the molecular growth processes. We are confident that the observed structural explosion in the area of POMs and recently in oxothiometalates will pave the way for the design and engineering of supramolecular systems with unprecedented properties and functionalities.

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