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Sulfite Anions as Structure-Directing Templates for the Engineering of Modular Polyoxometalates

CLUSTER ISSUE

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Dedicated to Professor Michael T. Pope on the occasion of his 80th birthday

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Polyoxometalates (POMs) are anionic metal oxides and encompass a diverse family of nanosized compounds with an unmatched range of architectures and physical properties. The use of the pyramidal sulfite anion, with its numerous coordination modes, has introduced structural diversity into the POM-based chemical systems, giving rise to the formation of novel synthons for the construction of unprecedented architectures ranging from low-nuclearity, isolable secondary building units to POM-based molecular nanoparticles, open-framework and 3D coordination materials, and the emergence of novel properties.

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1. Introduction

Polyoxometalates (POMs) are anionic metal oxide clusters of Mo, W, V and Nb. They have attracted the attention of researchers over the last two decades due to their remarkable archetypes and electronic structures,[1,2] as well as their diverse properties ranging from photochromism,[3] electrochromism[4] and magnetism[5] to applications in catalysis[6] and medicine.[7] Even though polyoxometalates have been known for more than 200 years, the major advances in the field have unravelled mainly over the last two decades. The vast growth observed in the field of POMs in terms of complexity of architectures and emergence of properties is associated with the technological developments in instrumentation; rapid single-crystal data collection and high-resolution spectroscopic techniques have allowed new discoveries to be made and new phenomena to be observed. This surge in research activity in the field of polyoxometalates is reflected in the observed exponential growth in the number of published articles, which becomes apparent in the main review articles dedicated to POM chemistry.[1,8]

Furthermore, the rapid development of the field has mainly been based on empirical observations and the fact that the formation mechanism of POM systems is governed by self-assembly processes involving the condensation of $\{MO_x\}$ units (M = W, Mo, V, Nb) directed by the fine adjustment of a long list of experimental variables such as 1) concentration/type of metal oxide anion, 2) pH, 3) ionic strength, 4) heteroatom type/concentration, 5) presence of additional ligands, 6) reducing environment, 7) temperature and pressure of reaction (e.g., microwave, hydrothermal, reflux), 8) counter-ion and metal-ion effects and 9) the processing methodology (one-pot, continuous-flow conditions).[9–14] Recently, considerable progress has been made towards understanding the underlying chemistry[15] and achieving better control over the self-assembly processes,[10] allowing the design and correlation of structure and observed functionality.[16] However, the continuous efforts of research groups to discover novel materials with new properties has mainly been based on previously reported examples and the fact that condensation reactions initiate the assembly process of the given chemical system. This means that the synthetic approaches relied more on serendipity and now we are actively trying to gain more control over the assembly processes. We hope this will lead to new libraries of synthetically available building blocks.[17,18] Consequently, the application of new synthetic approaches (hydrothermal and microwave processing, mixed solvents, ionic liquids, etc.) allows either control over the assembly of

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known building units for the engineering of materials with well-defined functionalities or the generation of fundamentally new synthons for the manufacturing of novel architectures as well as, potentially, the emergence of new properties.

In this review we will discuss the novel synthetic approaches employed recently by our groups and others for the generation of fundamentally new libraries of building blocks (Figure 1), which have given rise to a plethora of novel structural motifs and interesting properties. More specifically, we will show how the use of the pyramidal sulfite anion (SO_3^{2-}) as inorganic ligand, and which is also a mild base, reducing agent as well as structure-directing agent (due to the lone pair of electrons), introduces the necessary diversity into POM systems and allows access to new libraries of building blocks (Figure 1) as well as control of the associated assembly process and engineering of functionality. Moreover, we will discuss the origins of the observed constructive interaction of SO_3^{2-} with metal oxide systems based on the plethora of coordination modes available to the sulfite anion (Figure 2).

2. Novel Archetypes

2.1. Molybdenum and Tungsten Sulfite Chemistry – Bridging Fundamental Building Units

The first polyoxometalate compound that incorporated the sulfite anion appeared in 1976. Sasaki and co-workers reported a molybdenum-based pentanuclear cluster, bicapped by two sulfite anions.[19] The core consists of five *cis*-dioxido $\{Mo^{VI}O_2\}$ edge-sharing polyhedral units con-

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George I. Chilas was born in 1982 in Karpenisi, Greece and he received his B. Sc. degree in Chemistry from the University of Ioannina, Greece in 2003. He obtained his M. Sc. in Bioinorganic Chemistry in 2005 and his Ph. D. under the supervision of Prof. T. A. Kabanos from the University of Ioannina in 2009. His research activities focus on coordination chemistry, polyoxometalates and the bioinorganic chemistry of vanadium and molybdenum. At present, he is working for an international pharmaceutical company and enjoys keeping up-to-date with the latest developments of chemistry in his free time.

Lee Cronin is the Gardiner Professor of Chemistry at the School of Chemistry, University of Glasgow and he runs the Cronin 'Group in Glasgow. Lee was an undergraduate and D. Phil. student at the University of York, research fellow at the University of Edinburgh and an Alexander von Humbolt Research Fellow at the University of Bielefeld. From 2000 to 2002 he was a lecturer at the University of Birmingham and moved to the University of Glasgow in 2002. In 2006 he was promoted to Professor, became an EPSRC advanced research fellow in 2007 and was awarded the Philip Leverhulme Prize. In 2009 Lee was elected to the Royal Society of Edinburgh, awarded a Royal Society/Wolfson merit award and appointed to the Gardiner Professorship of Chemistry at the University of Glasgow. In 2011 he gave the opening lecture at TED-Global in Edinburgh called "inorganic biology" and was awarded the RSC Bob Hay Lectureship and in 2012 Lee was awarded the RSC Corday Morgan Medal and Prize. Cronin's work spans a range of fields and he is recognized for his creative studies in the field of inorganic chemistry, specifically the self-assembly and self-organization of inorganic molecules and the engineering of complex systems leading to the emergence of system-level behaviours. His pioneering contributions include the development of new techniques to control the assembly of nanoscale polyoxometalate clusters, some of the largest non-biological molecules known, the development of new cryospray and variable-temperature mass spectrometry (VT-MS) techniques for the elucidation of reaction mechanisms and the observation of highly reactive intermediates as well as the discovery of emergent nano/microstructures such as tubules, membranes and inorganic cells (based upon polyoxometalates). He is currently developing a range of new reaction formats and techniques to explore chemical reactions, including networked flow systems and 3D printing, and is developing systems, approaches and theories aiming at understanding and manipulating complex chemical systems, exploring systems chemistry and engineering evolution in chemistry outside the confines of biology.

Themistoklis A. Kabanos was born in Samos, Greece and he studied Chemistry at Thessaloniki University (1971–1975), before he moved to the University of Ioannina for his Ph. D. under the supervision of Prof. I. M. Tsangaris. In 1983 he was elected as a lecturer in the Chemistry Department of the University of Ioannina and in 2002 became a Full Professor. He carried out his postdoctoral studies with C. Hawkins (Brisbane, Australia), S. Cooper (Oxford, UK) and D. Woolins (London, UK). His research activities have focused on all aspects of the chemistry, structures and synthesis of polyoxoanion complexes of the early transition metals and the bioinorganic chemistry of vanadium and molybdenum.

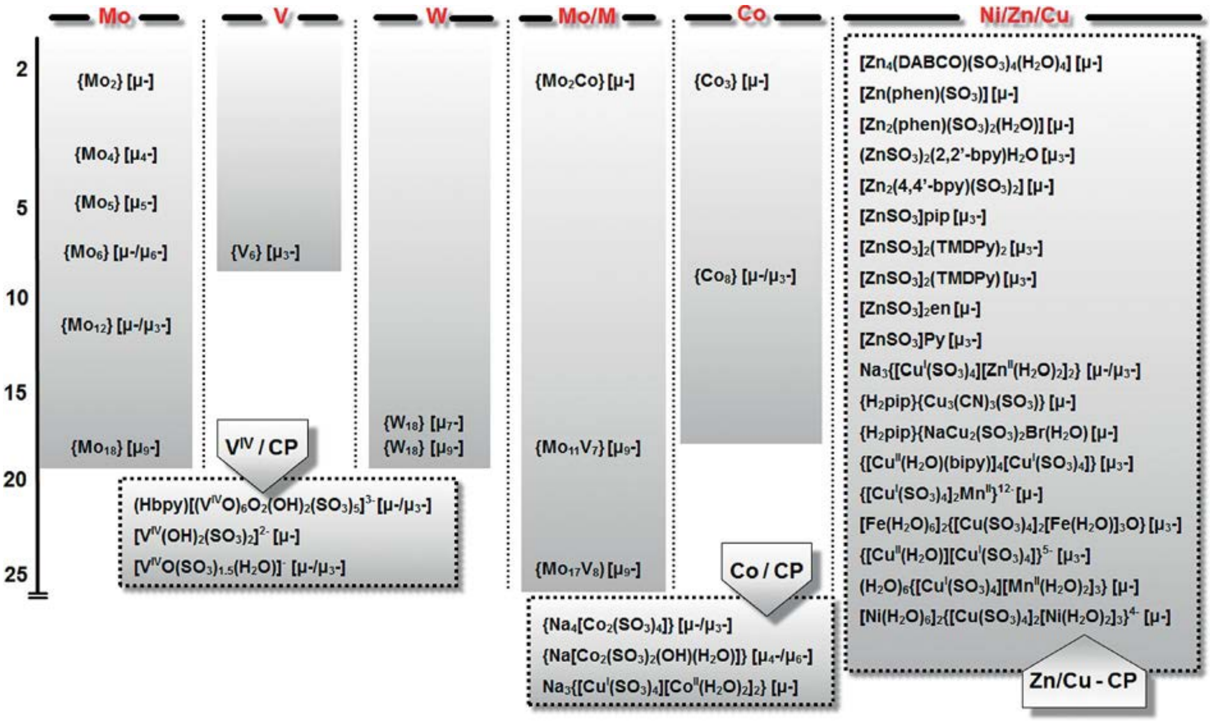

Figure 1. Observed nuclearities of the isolated compounds discussed in this review. The classification is based on their structural features and categorized as discrete molecules and coordination polymers (CP). The type of coordination mode(s) of SO_3^{2-} that contributed to the formation of the specific species is noted in brackets. Abbreviations: bpy: bipyridine; phen: 1,10-phenanthroline; en: ethylenediamine; py: pyridine; TMDPy: trimethylenedipyridine; DABCO: 1,4-diazabicyclooctane.

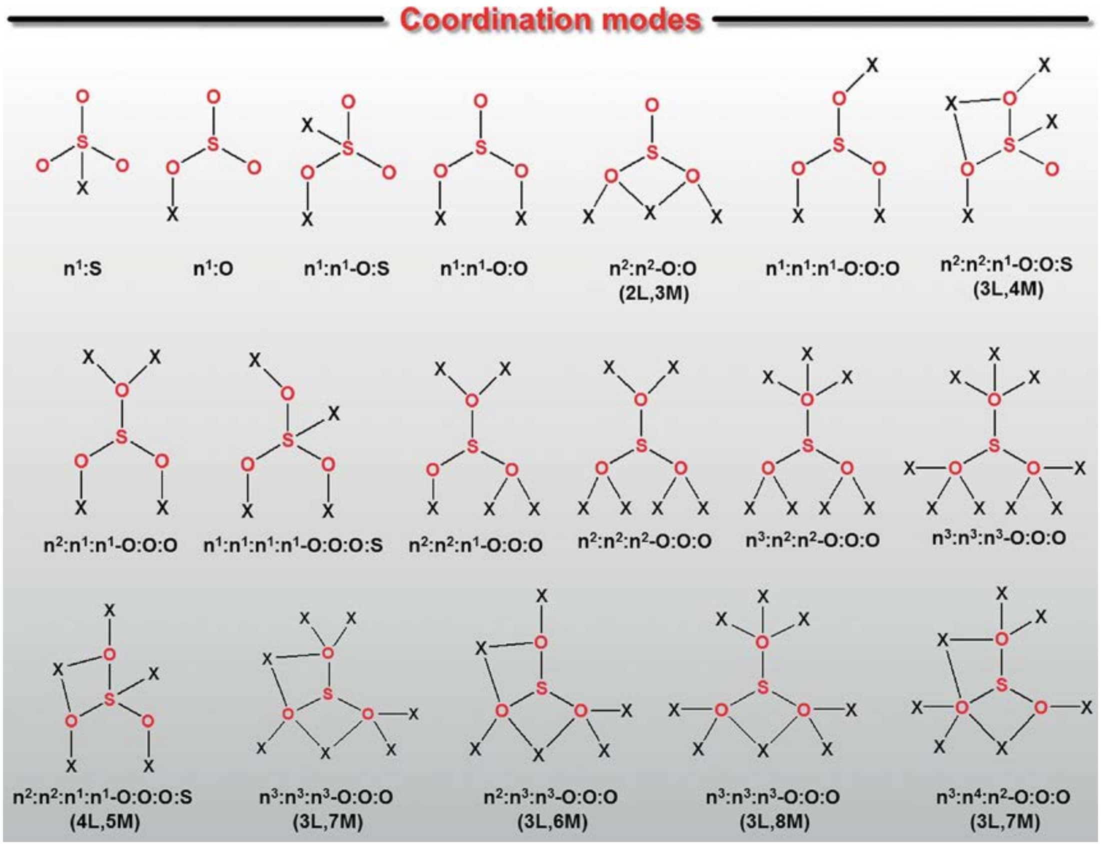

Figure 2. Representation of the observed coordination modes for the sulfite anion. X: transition metal and/or alkali metal.

nected by two sulfite anions in a cyclical fashion. Interestingly enough, the potential of the sulfite anions to act as synthons for the construction of unprecedented POM-based architectures was not realized until two decades later when Kabanos and co-workers reported in 2002 a series of Mo SO_3^{2-} compounds.[20] In this work, the isolation and crystallographic characterization of the dodecanuclear $[(Mo^{V}_2O_4)_6(\mu_2\text{-}SO_3)_{12}(\mu_3\text{-}SO_3)_4]^{20-}$ species (Figure 3, a) of the anion $\{Na[(Mo^{V}_2O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]_2\}^{15-}$ (Figure 3, b) consisting of two identical hexanuclear polyoxomolybdenum(V) sulfite anions $[(Mo^{V}_2O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]^{8-}$ (Figure 3, d) linked by a sodium cation and a dinuclear molybdenum(V) species decorated by five SO_3^{2-} anions (Figure 3, c) were reported. In addition, the multiple role of the sulfite anion in POM-based chemistry was demonstrated for the first time. The exploitation of the various coordination modes of the sulfite group in combination with the network of hydrogen bonds provided by the ammonium cations directed the self-assembly process towards the formation of a unique Keggin-like archetype (Figure 3, a) by bridging six dinuclear units $[Mo^{V}_2O_4]^{2+}$. Moreover, it has been shown that in the presence of alkali metals (Na^+ in this case), sulfite anions can template the formation of cyclic Mo^{V} compounds (Figure 3, d), which can be used as secondary building units (SBUs) for the construction of dimers of hexanuclear species (Figure 3, b). The dinuclear species $[(Mo^{V}_2O_4)(SO_3)_4(\mu_2\text{-}SO_3)]^{8-}$ (Figure 3, c) appears to be the isolable intermediate formed during the self-assembly of the Mo^{V}/SO_3^{2-} system and the structural progenitor of the $\{Mo_{12}\}$ and $\{Mo_6\}$ species. Finally, the crystallographic characterization of the above compounds revealed two new coordination modes for the sulfite anion (μ_3 and μ_6), demonstrating its potential to act as an inorganic ligand as well as to generate SBUs and give access to novel building-block libraries for the construction of high-nuclearity clusters with unprecedented archetypes.

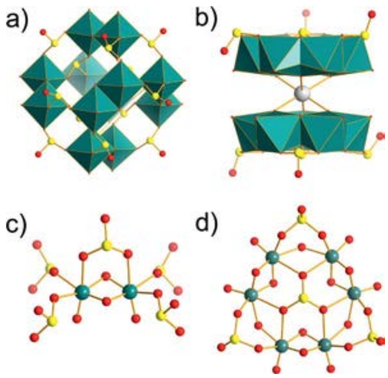

Figure 3. Polyhedral and ball-and-stick representations of the $(Mo^{V}_2O_4)^{2+}/SO_3^{2-}$ anions: a) $[(Mo^{V}_2O_4)_6(\mu_2\text{-}SO_3)_{12}(\mu_3\text{-}SO_3)_4]^{20-}$, b) $\{Na[(Mo^{V}_2O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]_2\}^{15-}$, c) $[(Mo^{V}_2O_4)(SO_3)_4(\mu_2\text{-}SO_3)]^{8-}$ and d) $[(Mo^{V}_2O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]^{8-}$. Colour code: Mo, teal polyhedral/spheres; O, red spheres; S, yellow spheres; Na, large grey sphere. Counter ions have been omitted for clarity.

Two years later, Cronin and co-workers[21] reported molybdenum sulfite species that adopt the Dawson archetype. More specifically, the mixed valence α-$[Mo^{V}_2Mo^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ (Figure 4, a) and the fully oxidized β-$[Mo^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ Dawson capsules were synthesized. Note that the two synthetic procedures employed led to the formation of two different isomers (α and β forms) of the same species; in both cases the capsules adopted a peanut-like shape in marked contrast to the traditional Dawson archetype (Figure 4, b).[22] Furthermore, the sulfite anions in these cases acted as templates in the formation of these novel capsules, with X-ray studies revealing two interesting features: 1) a new coordination mode (μ_9) for the sulfite anion establishing its efficacy as an inorganic ligand and 2) the incorporation of two adjacent sulfite anions into a configuration causing a short, yet non-bonding, intramolecular S···S interaction (ca. 3.2 Å) between the sulfite anions that is responsible for inducing intriguing functionality, as will be discussed later.

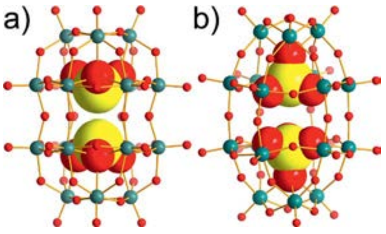

Figure 4. Ball-and-stick representation of the sulfite-based Dawson cluster: a) α-$[Mo^{V}_2Mo^{VI}_{16}O_{54}(SO_3)_2]^{6-}$ and b) the conventional a-type sulfate-based Dawson anion $[Mo_{18}O_{54}(SO_4)_2]^{4-}$[22] for comparison. The central anion templates are shown in space-filling mode. Colour code: S, yellow spheres; O, red spheres; Mo, teal spheres.).

One year later, the same group extended their investigations to the tungsten sulfite system and reported[23] the first two examples of polyoxotungstate clusters incorporating the sulfite anion, $[W^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ (Figure 5, a), the isostructural tungstate analogue of the Mo capsule, and $[W^{VI}_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$ (Figure 5, b).

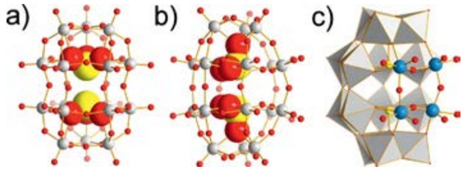

Figure 5. Ball-and-stick representations of sulfite-based Dawson clusters a) $[W^{VI}_{18}O_{54}(SO_3)_2]^{4-}$ and b) $[W^{VI}_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$. The central anion SO_3^{2-} templates are shown in space-filling mode. c) $[W^{VI}_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$ cluster in polyhedral mode in which the four tungsten metal centres exhibit two terminal oxido groups (shown as blue spheres). Colour code: W, light grey polyhedral/spheres; W (with two terminal oxido groups), blue spheres; O, red spheres; S, yellow spheres. Counter ions have been omitted for clarity.

Surprisingly, X-ray diffraction studies revealed considerable structural differences between the two tungsten sulfite species. This is because the species that is soluble in organic solvents, that is, the one with Bu_4N^+ as the counter ions, adopts a peanut-like structure like its Mo analogue (Figure 5, a). The structure consists of two $\{W_9(SO_3)\}$ units that contain six equatorial and three capping metal positions. These two units are joined by linking each of the six equatorial metal atoms of each unit through six bridging oxido ligands. The two trigonal-pyramidal SO_3^{2-} groups are centrally aligned and coordinate to all nine metal centres of each $\{W_9(SO_3)\}$ fragment in a μ_9-coordination mode. In the water-soluble case, in which K^+ and Na^+ are the counter ions, the two adjacent sulfite anions are tilted by approximately 45°, exhibiting an unusual μ_7-coordination mode and consequently only seven of the nine metal centres of each $\{W_9(SO_3)\}$ fragment are connected (Figure 5, b). This arrangement leaves four equatorial tungsten positions uncoordinated to sulfite anions. Instead, the two equatorial tungsten centres are coordinated to two terminal water molecules and the remaining two tungsten atoms appear as *cis*-dioxido species (Figure 5, c). This is the first example of a non-lacunary hetero-tungstate POM with two terminal oxido ligands linked to the same metal. This structural deviation from the typical Dawson archetype is expected to have a large influence on the observed properties, as will be discussed later in this article.

2.2. Vanadium-Sulfite Chemistry–Metallic Cores and 2D Networks

Shortly after demonstrating the constructive interaction of the sulfite-based synthons and fundamental molybdenum-based building units, Kabanos and co-workers extended their investigations to the interaction of the sulfite anion with vanadium. They reported the first two vanadium sulfite[24a,24b] POM compounds, specifically, the hexanuclear cluster $[(V^{IV}O)_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\mu_3\text{-}SO_3)_4(H_2O)_2]^{2-}$ (Figure 6, a) and the open-framework 2D material $[(V^{IV}O)(SO_3)_{1.5}(H_2O)]^-$ (Figure 6, b).

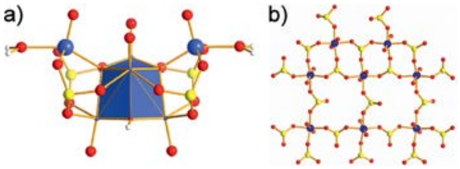

Figure 6. Ball-and-stick representations of a) $[(V^{IV}O)_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\mu_3\text{-}SO_3)_4(H_2O)_2]^{2-}$ and b) $[(V^{IV}O)(SO_3)_{1.5}(H_2O)]^-$ sulfite POMs. Colour code: V, light blue; O, red; S, yellow; H, white. Counter ions are have been for clarity.

The hexanuclear anion $[(V^{IV}O)_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\mu_3\text{-}SO_3)_4(H_2O)_2]^{2-}$ is constructed from a vanadium(IV) cubane $\{V^{IV}{}_4O_4\}$ metallic core stabilized by four sulfite bridges and two additional vanadium(IV) centres coordinated to the O corners of the cubane moiety. Interestingly, the same species was synthesized with ammonium and *tert*-butylammonium as the counter ions, generating different networks of hydrogen bonds and causing the same compound to crystallise in centrosymmetric (*tert*-butylammonium as counter ion) and non-centrosymmetric space groups (ammonium as the counter ion).

The layered net of the 2D open-framework material (Figure 6, b) consists of isolated VO_6 octahedra, each sharing four corners with four adjacent SO_3^{2-} trigonal pyramids. The connectivity between the VO_6 octahedra and the SO_3^{2-} pyramids creates eight- and four-membered ring-shaped windows. Each eight-membered window is formed by four VO_6 octahedra linked by four SO_3^{2-} anions. In a similar fashion, the four-membered windows are formed by two VO_6 octahedra and two SO_3^{2-} pyramidal units.

In 2005, the same group reported the synthesis and structure of a non-oxidovanadium(IV) {"naked"-V^{IV}} species,[24c] *trans*-$(NH_4)_2[V^{IV}(OH)_2(\mu\text{-}SO_3)_2]_\infty$ (Figure 7), under mild conditions consisting of V^{IV}/SO_3^{2-} polymeric 1D chains. X-ray diffraction studies revealed that the four equatorial V–O bonds are equivalent and equal to 1.996(4) Å; the two axial V–O bonds are also equivalent and equal to 1.988(8) Å. The vanadium octahedra are linked further through four μ_2-pyramidal sulfite bridges in 1D chains along the *c* crystallographic axis. The μ_2-sulfite bridges exhibit an O–S–O angle of 100.8(4)° keeping the vanadium(IV) octahedra in close proximity. The ammonium ions located between the chains are responsible for the stable packing of the chains. Note that even though the material was synthesized in an aqueous medium in the presence of air, the tight packing promoted by the network of hydrogen bonds created by the ammonium cations stabilized the "naked" form of vanadium(IV). The absence of the terminal oxido group in a vanadium(IV) species is extremely rare.[25]

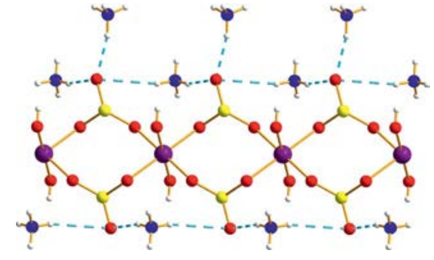

Figure 7. Ball-and-stick representation of *trans*-$(NH_4)_2[V^{IV}(OH)_2(\mu\text{-}SO_3)_2]_\infty$, depicting the hydrogen-bonded network. Colour code: V, violet; O, red; S, yellow; H, white.

2.3. Interaction of Sulfite with Mixed-Metal Mo/V Systems

Following the first series of studies on the self-assembly processes of molybdenum and vanadium sulfite chemistry, mixed-metal systems were investigated. The redox processes between the metal centres in combination with the differences in kinetics and reactivity could introduce diversity into the chemical system and the generation of novel building block libraries that could lead to the discovery of new architectures. Indeed, in 2008, Cronin, Kabanos and co-workers[26] reported the isolation and characterization of a new form of Dawson archetype, $[Mo^{VI}{}_{11}V^{V}{}_5V^{IV}{}_2O_{52}(\mu_9\text{-}SO_3)]^{7-}$ (Figure 8, a), which has been studied in detail in solution and the solid state. The new coordination mode for the sulfite anion in combination with the plethora of geometries and redox states exhibited by vanadium (octahedral $V^{IV/V}$ and tetrahedral V^{V}) and molybdenum [oxido- and *cis*-dioxidomolybdenum(VI)] led to the formation of an unprecedented version of the Dawson archetype (Figure 8).

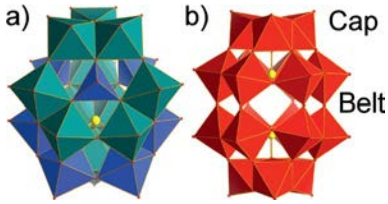

Figure 8. Polyhedral representations of a) the mixed-metal $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]^{7-}$ anion and b) the classical Dawson $[Mo_{18}O_{54}(\mu_9\text{-}SO_4)_2]^{n-}$ moiety. Colour code: Mo, teal/red polyhedra; V, light-blue polyhedra; S, yellow sphere.

The lower hemisphere is constructed from nine metal centres in octahedral geometry and the cavity formed is occupied by a $\mu_9\text{-}SO_3^{2-}$ anion and is structurally related to the classic Dawson archetype. In contrast, the upper hemisphere is constructed of six crystallographically localized molybdenum(VI) *cis*-dioxido atoms and three tetrahedral vanadium(V) centres. The adoption of a tetrahedral geometry by the vanadium(V) atoms reduced the size of the upper hemisphere and consequently the space of the internal cavity, which remained unoccupied. High-resolution cryospray mass spectrometry (CSI-MS) showed that the novel "Dawson" structure retains its integrity in solution, whereas EPR measurements showed surprisingly low A_z values, indicative of substantial crystallographic disorder of the vanadium(IV) atoms combined with electron hopping effects between the reduced and oxidized metal centres at higher temperatures. Investigation of the self-assembly of the previously discussed system led to the discovery of an unprecedented mixed-metal $\{M_{25}\}$ species that is structurally related to the $\{M_{18}\}$ Dawson-type species. In this work, Cronin and co-workers[27] reported the isolation and structural characterization of the largest metal sulfite species reported to date, $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}_{6}V^{V}O_{22})]^{10-}$ (Figure 9, b). Interestingly, the compound is the product of a molecular evolution process that takes place in the presence of the parent molecule (which acts as a transferable building unit), molybdenum and vanadium sources, followed by fine adjustment of the solution's acidity. In this case, the compound consists of the distorted form of the Dawson archetype, with its top decorated by a "crown"-shaped formation, $\{Mo^{VI}_{6}V^{V}O_{22}\}$. After careful investigation of the self-assembly of the chemical system, the authors demonstrated the self-assembly process leading to the formation of either a structurally related species through a molecular evolution process, $\{M_{18}\} \rightarrow \{M_{25}\}$ (Figure 9), or size-specific molecular POM-based nanoparticles by a "shrink wrapping"[28] and cation-effect process. More specifically, in the presence of sodium or potassium cations and triethanolamine (TEA) molecules as "shrink-wrapping" agents,[28] the self-assembly process is directed towards the formation of the 2.5 nm size Keplerate architecture $\{Mo_{72}V_{30}(SO_4)_{12}\}$.[29]

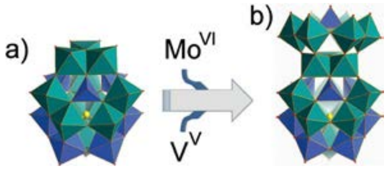

Figure 9. Polyhedral representations of a) $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]^{7-}$ and b) $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}_{6}V^{V}O_{22})]^{10-}$. Colour code: Mo, teal; V, light blue. The scheme represents the structural transformation between the POM species.

A couple of years earlier, Kabanos and co-workers initiated an investigation of the Mo/Co sulfite mixed-metal system. In this work, the synthesis and structural and physicochemical characterization of the trinuclear compound $[Co^{III}(Mo_2{}^{V}O_4)(NH_3)(SO_3)_6]^{7-}$ was reported[30] (Figure 10). Note that despite the reducing environment due to the presence of sulfites in the Mo/Co system, the cobalt(II) is oxidized to cobalt(III). In the absence of a cobalt(II) source in the Mo^{VI}/SO_3^{2-} system, no redox processes take place and the self-assembly process is directed towards the formation of the tetranuclear species $[Mo_4{}^{VI}SO_{16}]^{4-}$ upon addition of CH_3CN to the aqueous Mo^{VI}/SO_3^{2-} system and pentanuclear $[Mo_5{}^{VI}S_2O_{21}]^{4-}$ upon addition of 4,4′-bipyridine (4,4′-bipy) to the aqueous Mo^{VI}/SO_3^{2-} system (Figure 11).

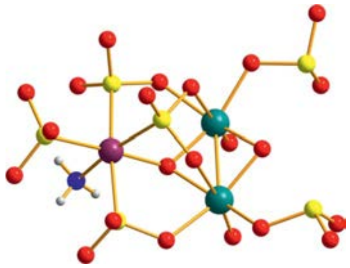

Figure 10. Ball-and-stick representation of the trinuclear anion $[Co^{III}(Mo_2{}^{V}O_4)(NH_3)(SO_3)_6]^{7-}$. Colour code: Mo, teal; Co, violet; S, yellow; O, red; N, blue; H, white.

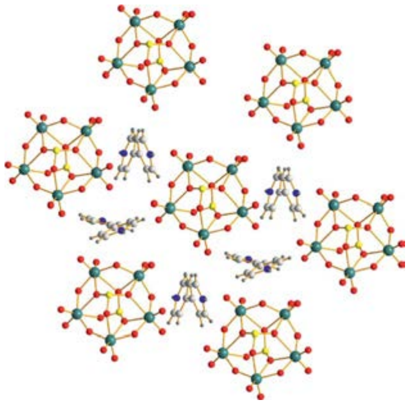

Figure 11. Ball-and-stick representation of the non-centrosymmetric packing of $(H_2bipy)_2[Mo_5{}^{VI}S_2O_{21}]$. Colour code: Mo, teal; S, yellow; O, red; N, blue; C, light grey.

2.4. Extrapolation of the Methodology to Thiometalate Chemistry

All the examples discussed above were focused on the investigation of interactions between the sulfite anion and the fundamental building units ($\{M_2\}$, $\{M_3\}$, $\{M_9\}$ etc.) that exist in typical POM-based chemical systems. In these systems at least, the initial driving force is based on the electrophilicity of the POM-based building units and the nucleophilicity of the sulfite anions combined with their ability to act as inorganic ligands through a multiple set of coordination modes. On the other hand, the fundamental building block in thiometalate chemistry for a wide range of compounds is the electrophile dinuclear species $[Mo_2O_2S_2]^{2+}$.[31] Taking into consideration the similarities between the two chemistries, Kabanos and co-workers used the synthetic approach employed in oxido(thio)metalate chemistry. In 2003 they reported[32] the first polyoxothiomolybdenum(V) sulfite species, $[\{Mo^V_2(\mu\text{-}S)_2O_2\}_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}]^{20-}$ (Figure 12).

Figure 12. Ball-and-stick representation of the $[\{Mo^V_2(\mu\text{-}S)_2O_2\}_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}]^{20-}$ anion. Colour code: Mo, teal spheres; S, yellow spheres; O, red spheres.

The reaction of the electrophilic dinuclear unit $[Mo^V_2O_2S_2]^{2+}$ with sulfite anions led to the formation of dodecanuclear compound $[\{Mo^V_2(\mu\text{-}S)_2O_2\}_6(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)_{12}]^{20-}$, which is the thio analogue of compound $[(Mo^V_2O_4)_6(\mu_2\text{-}SO_3)_{12}(\mu_3\text{-}SO_3)_4]^{20-}$.[20] In this case, six electrophilic dinuclear $[Mo^V_2(\mu\text{-}S)_2O_2]^{2+}$ moieties are connected to each other through 16 sulfite ligands, 12 of which exhibit a μ_2-coordination mode and the remaining four exhibit μ_3-coordination. The archetype of the reported compound can be considered the S derivative of the Keggin-type structural motif and is isostructural with the oxido-based species reported earlier by the same group.[20]

2.5. Non-POM Sulfite-Based Systems

The ability of the sulfite anion to act as a pyramidal inorganic ligand/template has been demonstrated in the case of molybdenum, tungsten and vanadium systems, which possess the inherent ability to form polyoxometalate structures.[33] The majority of the new sulfite-based POM structural motifs discussed above are based on traditional metals with only small variations and alterations. However, recently this area of research has shifted towards the discovery/design of new compounds beyond traditional POM frameworks (based upon Mo, W and V) in a bid to discover new architectures and the potential emergence of new functionalities.

In 2008, Kabanos and co-workers[34] reported the first mixed-valence cobalt-based sulfite compound with an interesting metalacycle archetype. In this case, redox processes between the cobalt(II) and a molybdenum(VI) source in the presence of sulfites led to the partial oxidation of the Co^{II} centres leading the self-assembly process towards the formation of the octanuclear Co sulfite species $Li\subset[Co^{II}_4Co^{III}_4(SO_3)_{16}(NH_3)_8]^{11-}$ (Figure 13).

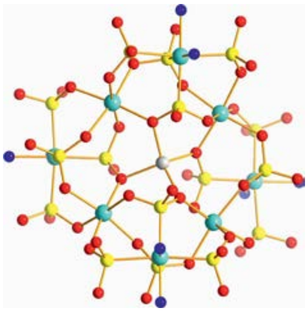

Figure 13. Ball-and-stick representation of the Co sulfite macrocycle $Li\subset[Co^{II}_4Co^{III}_4(SO_3)_{16}(NH_3)_8]^{11-}$ anion. Colour code: Co, aqua; S, yellow; O, red; N, blue; Li, white.

In the $Li\subset[Co^{II}_4Co^{III}_4(SO_3)_{16}(NH_3)_8]^{11-}$ cluster, four cobalt(II) centres form an almost ideal square-planar arrangement and a pair of symmetry-related Co^{III} dimers lie above and below the Co^{II}_4 plane grafted onto the tetramer through the 16 bridging sulfite groups. The $[Co_8(SO_3)_{16}(NH_3)_8]^{12-}$ cluster encapsulates a lithium cation, which lies at the centre of the Co^{II}_4 plane, and in combination with the four sulfite ligands forms an all-inorganic metallacycle.

Furthermore, synthetic chemists realized the potential of the pyramidal sulfite anion to act as an inorganic ligand and the structure-directing effect provided by the lone pair of electrons and investigated the interaction of sulfites with transition metals that are not used routinely for the construction of POM phases. Indeed, a few examples have been reported in which the use of Zn^{II}, Cd^{II} and Cu^{I} led to the formation of polymeric compounds with 2D and 3D morphologies. In 2006, Rao[35] reported the first series of Zn sulfite coordination compounds prepared under hydrothermal conditions. X-ray diffraction analyses revealed the following compositions: $[Zn(C_{12}H_8N_2)(SO_3)]$, $[Zn_2(C_{12}H_8N_2)(SO_3)_2(H_2O)]$, $[Zn_2(C_{10}H_8N_2)(SO_3)_2]\cdot H_2O$ and $[Zn_4(C_6H_{12}N_2)(SO_3)_4(H_2O)_4]$ [$C_{12}H_8N_2$: 1,10-phenanthroline; $C_{10}H_8N_2$: 4,4-bipyridine; $C_6H_{12}N_2$: 1,4-diazabicyclo[2.2.2]octane (DABCO)]. The use of different types of amine in the presence of SO_3^{2-} induced different structural features to form. The structure is one-dimensional in the case of phenanthroline, two-dimensional with 4,4-bipyridine and three-dimensional with DABCO as co-ligand.

In a similar fashion, Bu and co-workers[36] reported the influence of a different set of bifunctional organic amines on the Zn sulfite system. They demonstrated that Zn^{II} and SO_3^{2-} can form various neutral inorganic subunits ranging from 0D clusters to 1D chains and 2D sheets. Such inorganic subunits of different dimensionality connected further into extended frameworks with higher dimensionality [$(ZnSO_3)_2en$, $(ZnSO_3)pip$ and $(ZnSO_3)_2(TMDPy)_2$; en: ethylenediamine; pip: piperazine; TDMPy: 4,4-trimethylenedipiperidine] induced by the presence of organic ligands.

In an effort to extend their investigations, the same group[37] reported in 2007 another set of zinc(II) and manganese(II) sulfite polymeric structures, $(ZnSO_3)py$, (py: pyridine), $(ZnSO_3)_2(2,2\text{-bipy})H_2O$ (2,2-bipy: 2,2-bipyridine), $(ZnSO_3)_2(TMDPy)$ and $(MnSO_3)_2en$, which were synthesized hydrothermally. In these compounds, low-dimensional 1D and 2D inorganic subunits are assembled into higher 2D or 3D covalent frameworks through organic ligands. The authors demonstrated the tendency of the metal sulfite system to form polymeric inorganic units with structural features different to those commonly observed in metal coordination compounds and revealed the potential for developing framework materials with unique physical properties, such as low-dimensional magnetism and electronic properties that are characteristic of inorganic materials.

In 2007 and 2009, Mao and co-workers reported their studies on copper(I)[38] and Zn^{II}/Cd^{II} sulfite[39] systems. In the first case, the authors isolated the first layered copper(I) sulfite compounds, namely $\{H_2pip\}\{Cu_3(CN)_3(SO_3)\}$ and $\{H_2pip\}\{NaCu_2(SO_3)_2Br(H_2O)\}\cdot 2H_2O$ (pip: piperazine), templated by organic amines. In both cases, the compounds were synthesized under hydrothermal conditions and X-ray structure investigations revealed 2D layered structures. In the second case, the authors reported the hydrothermal preparation and characterization of two novel organically templated mixed-metal sulfites, namely $[H_2pip][NaZn_2Cu(SO_3)_4]$ and $[H_2pip][CdCu_4(SO_3)_4]$. In this case, both compounds exhibited a 3D mixed-metal inorganic framework with the organic template molecules occupying the pores in the inorganic skeleton. Moreover, the authors demonstrated the ability of the sulfite ligands to act as "hard" as well as "soft" ligands within the same structure.

Furthermore, in 2010, Kabanos and co-workers[40] reported the hydrothermal reaction of $[Co^{III}(NH_3)_6]Cl_3$ with Na_2SO_3 leading to the successful synthesis of cobalt(II) sulfite 2D and 3D inorganic coordination polymers $\{Na[Co^{II}_2(SO_3)_2(\mu_3\text{-}OH)(H_2O)]\}_\infty$ and $\{Na_4[Co^{II}_2(SO_3)_4]\}_\infty$, respectively. In this case, the fundamental dinuclear Co^{II}/SO_3^{2-} units are first formed in solution and then are connected through sulfite bridges to yield all-inorganic 2D and 3D open-framework structures. Note the absence of organic ligands in marked contrast to previously reported examples.

Finally, Robson and co-workers[41] reported the synthesis of the 1D $Na_3\{[Cu^I(SO_3)_4][Zn^{II}(H_2O)_2]_2\}\cdot H_2O$ and $Na_3\{[Cu^I(SO_3)_4][Co^{II}(H_2O)_2]_2\}\cdot H_2O$, and 2-D $[Na_4(H_2O)_{17}][Ni(H_2O)_6]_2\{[Cu(SO_3)_4]^{2-}[Ni(H_2O)_2]_3\}$ and $[Na_4(H_2O)_{17}][Co(H_2O)_6]_2\{[Cu(SO_3)_4]_2[Co(H_2O)_2]_3\}$ coordination polymers, demonstrating for the first time the efficacy of the $[Cu(SO_3)_4]^{7-}$ anion as a building block for the construction of novel polymeric architectures. Moreover, the same group reported recently[42] a family of mixed-valence $Cu^{I/II}/SO_3^{2-}$ coordination polymers based on the highly charged $[Cu(SO_3)_4]^{7-}$ anion; the authors demonstrated the reactivity of the nucleophilic $[Cu(SO_3)_4]^{7-}$ moiety towards first-row transition metals resulting in finite $\{[Cu^{II}(H_2O)(bipy)]_4[Cu^I(SO_3)_4]\}NO_3\cdot H_2O$, $Na_{12}\{[Cu^I(SO_3)_4]_2Mn^{II}\}\cdot 8H_2O$ and $Na_3(H_2O)_6[Fe^{II}(H_2O)_6]_2\{[Cu^I(SO_3)_4]_2[Fe^{III}(H_2O)]_3O\}\cdot H_2O$, and infinite $Na_5\{[Cu^{II}(H_2O)][Cu^I(SO_3)_4]\}\cdot 6H_2O$ and $(H_2O)_6\{[Cu^I(SO_3)_4][Mn^{II}(H_2O)_2]_3\}$ architectures. The reducing environment produced by the sulfite anion promoted the formation of mixed-valence species in solution as well as the self-assembly of the generated building blocks into either species with higher nuclearity or infinite coordination polymers.

3. Materials with Unique Properties

The previously discussed novel synthetic methodology and the efforts of synthetic chemists to move from serendipitous to designed approaches have led to a plethora of unprecedented architectures. In addition, a deep understanding of the underlying chemistry that takes place within a specific POM-based chemical system and identification of the available building block libraries is crucial because this allows better control of the self-assembly processes, the emergence of interesting properties and sets the scene for the engineering of materials with innovative functionalities. In this section we will discuss these issues.

3.1. Modular Magnetic Materials

The interaction of vanadium(IV/V) with the sulfite anion has led to a novel family of V/SO_3^{2-} compounds with novel architectures, as we discussed earlier. It has been demonstrated that it is possible not only to synthesize interesting redox-active metallic cores,[24] but also interesting modular magnetic materials.[43] Kabanos and co-workers reported in 2003 a hexanuclear $[(V^{IV}O)_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\mu_3\text{-}SO_3)_4(H_2O)_2]^{2-}$ (see Figure 6, a) species that exhibits an overall ferromagnetic behaviour.[24] Close inspection of the architecture led to the conclusion that the terminal water ligands coordinated to the peripheral vanadium(IV) centres as well as the two hydroxo bridges within the cubane core could be considered as "reactive" active sites because either can be easily removed and/or interact through hydrogen bonds with another moiety. Indeed, the same group demonstrated that it is possible to use the hexanuclear species as a secondary building unit to construct a new material with different properties.[43] The exploitation of both reactive sites of the $\{V_6\}$ species by replacing the terminal water molecules with sulfite bridges in the presence of an increased concentration of sulfite anions led to the formation of 1D chains of $\{V_6\}$ moieties. These chains are connected together to form an overall 2D layered material through a network of hydrogen bonds with a bifunctional organic ligand ($4,4'\text{-}Hbipy^+$: 4,4′-bipyridine; Figure 14). Variable-temperature magnetic susceptibility studies showed that the engineered intermolecular interaction created by bridging the ferromagnetic

$\{V_6\}$ cores led to switching of the overall magnetic behaviour to strongly antiferromagnetic with an $S_T = 0$ ground state.

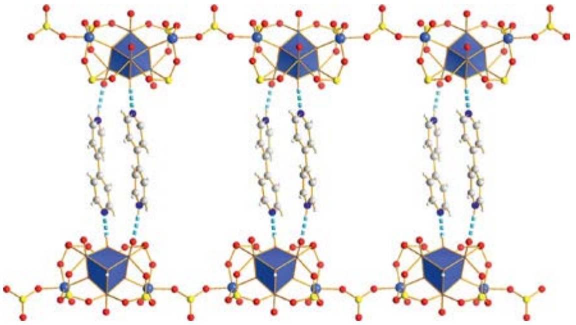

Figure 14. Polyhedral and ball-and-stick representation of the $(4,4'\text{-Hbpy})[(V^{IV}O)_6(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_2(\mu_3\text{-}SO_3)_4(\mu\text{-}SO_3)]^{3-}$ 1D chain. Colour code: V, light-blue spheres; S, yellow spheres; O, red spheres; N, blue spheres; C, light-grey spheres; H, small white spheres.

Note also the magnetic behaviour of the two Co^{II}/SO_3^{2-} coordination polymers, $\{Na[Co^{II}_2(SO_3)_2(\mu_3\text{-}OH)(H_2O)]\}_\infty$ and $\{Na_4[Co^{II}_2(SO_3)_4]\}_\infty$, which we discussed above and which were also reported by Kabanos and co-workers.[40] The difference in the reaction time for the hydrothermal synthetic procedure (1 day for $\{Na[Co^{II}_2(SO_3)_2(\mu_3\text{-}OH)(H_2O)]\}_\infty$ and 3 days for $\{Na_4[Co^{II}_2(SO_3)_4]\}_\infty$) allowed control of the materials' ground states ($S_T = 0$ for $\{Na[Co^{II}_2(SO_3)_2(\mu_3\text{-}OH)(H_2O)]\}_\infty$ and $S_T \neq 0$ for $\{Na_4[Co^{II}_2(SO_3)_4]\}_\infty$). In a similar fashion, the mixed-valence $Cu^{I/II}/SO_3^{2-}$ family of compounds[42] discussed above demonstrate the potential for generating materials in which the controlled assembly of the building blocks (by introduction of structure-directing ligands) or the availability of specific species (by controlling the ratio/concentration) in solution could modulate the observed magnetic behaviour and "switch" it from ferro- to antiferromagnetic. This interesting behaviour demonstrates the efficacy of the sulfite anions in the design of materials that exhibit useful cooperative electronic/magnetic effects, an important requirement for the construction of molecular electronic devices.

3.2. Optically Active Materials

The sulfite anion has C_{3v} symmetry and contains a nonbonding but stereochemically active pair of electrons, and therefore its non-centrosymmetric metal complexes may potentially display non-linear optical properties (NLO), which until now have only been observed in metal selenites/iodates, etc.[44] In this respect, it would be highly desirable to use sulfite anions as synthons for the construction of materials that exhibit non-linear optical properties (NLO). Recently, Kabanos and co-workers[30] reported a modified synthetic procedure for the isolation of the pentanuclear molybdenum(VI) sulfite compound $(NH_4)_4[Mo_5^{VI}S_2O_{21}]\cdot 3H_2O$, the main structural motif of which was reported earlier by Sasaki and co-workers[19] and crystallized in a centrosymmetric space group (orthorhombic, *Pbcn*). In this work, the authors demonstrated the engineering of asymmetry by use of a bifunctional organic ligand (4,4′-bipyridine) in the reaction mixture that produces the pentanuclear compound, which directed the orientation of the $\{Mo_5\}$ moieties within the crystal lattice (monoclinic, *C*2). The lack of centrosymmetry rendered the material a promising candidate for further investigations of its optical activity. Second harmonic generation (SHG) measurements were performed with a Nd:YAG laser at 1064 nm. The green light generated was analysed with a monochromator; the production of the second harmonic was verified by the observation of a single peak at 532 nm in the recorded spectra and its quadratic dependence on laser intensity.

3.3 Electronic Effects and Redox-Coupled Processes

As we discussed earlier, Cronin and co-workers[21,23] reported two Dawson capsules that host two sulfite anions in their cavities, their orientations varying considerably in the molybdenum and tungsten analogues. Interestingly, the authors demonstrated that the orientation of the pyramidal heteroanion (μ_9-coordination mode) has an interesting effect on the observed properties of the capsule. The molybdenum-based capsule, $\beta\text{-}[Mo^{VI}_{18}O_{54}(SO_3)_2]^{4-}$, presented a thermochromic response that has been attributed to the S···S interaction between the sulfur centres. Striking thermochromic behaviour was observed between 77 and 500 K (Figure 15), which represents the first observation of such behaviour in discrete polyoxometalate clusters. These initial investigations also showed that the colour change from pale yellow at 77 K to deep red at 500 K are gradual and completely reversible .

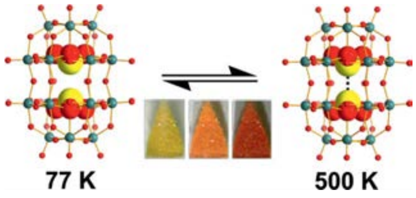

Figure 15. Ball-and-stick representation of the $[Mo_{18}O_{54}(SO_3)_2]^{4-}$ POM cage. As the temperature increases to 500 K, the colour gradually changes. Colour code: Mo, teal; O, red; S, yellow. Counter ions have been omitted for clarity.

On the other hand, X-ray studies revealed some striking differences in the case of the tungsten-based capsule $[W^{VI}_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$ (Figure 5). It was shown that the connectivity of the sulfite anions within the cavity of the capsule is different (μ_7-coordination mode) when there are two terminal water ligands coordinated to the tungsten centres of the capsule. Furthermore, the cluster anion $[W^{VI}_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$ undergoes a unique electron-transfer reaction when heated, which is associated with a structural rearrangement that allows the two embedded pyramidal sulfite ($S^{IV}O_3^{2-}$) anions to release up to four electrons to the surface of the cluster forming the reduced version of the sulfate-based cluster $[W_{18}O_{54}(SO_4)_2]^{8-}$. Although electron-transfer reactions and structural rearrangements are very well known for hetero-POMs,[45] this is the first example of an electron-coupled structural rearrangement in which the electrons are "provided" by the same material.

These unprecedented molybdenum- and tungsten-based Dawson sulfite capsules present a new class of "activated" metal oxide clusters and show potential for the development of novel functional metal oxides. More specifically, harnessing the versatile electronic properties of Mo/W-based POMs for use in electron-storage devices and molecular switches is highly desirable with implications for the engineering of functional materials.

4. Conclusions and Perspectives

The advances observed in the field of POM chemistry over the last few decades have now reached the point at which it is almost possible for synthetic chemists to design and control more confidently both the structures and properties of POM-based systems. In this review article we have shown that the use of the pyramidal sulfite anion with its numerous coordination modes (Figure 2) can introduce structural diversity into POM-based chemical systems, which consequently give rise to the formation of novel synthons for the construction of unprecedented architectures ranging from low-nuclearity, isolable secondary building units to POM-based molecular nanoparticles, open-framework and 3D coordination materials, and the emergence of novel properties. The structural and chemical diversity of the sulfite anions has helped research groups to gain access to novel libraries of building blocks and control their reactivity in a more sophisticated manner. Furthermore, it has been shown that a level of control over this library of building units and the associated self-assembly processes using redox reactions, metal-ion and ligand effects, temperature, pressure and crystallization conditions could direct the formation of specific architectures and fine-tune the observed properties of the materials. The examples discussed show the potential of this novel approach in POM chemistry and open the door to further discoveries and the emergence of novel properties, setting the scene for the development of design processes in nanotechnology applications. Finally, the paradigm of control over the observed properties is contributing to the predicted explosion in functionality and points towards a future of modular molecular devices and engineering of materials with desirable functionality.

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