From polyoxometalate building blocks to polymers and materials: the silver connection†

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Molecular growth processes utilizing polyoxometalate-based building blocks with silver connecting units have been used to produce four new materials: 1, [Ag4(bhepH)3(CH11.5Na0.5O6P)3]·8H2O (bhep = N,N′-bis(2-hydroxyethyl)piperazaine); 2, [Ag4(DMSO)3(MoO2O30)]·3, [Ag3[MnMoO18{(OCH2)2CNH2}2(DMSO)3]·3(DMSO)]·n; 4, [Ag3[MnMoO18{(OCH2)2CNH2}2(DMSO)3(CH2CN)2]DMSO]·n. The compounds were characterised using single crystal X-ray crystallography, elemental analysis, IR, TGA, DSC, and scanning electron microscopy. Compounds 1–4 were imaged on silicon substrates using scanning electron microscopy. Compound 1 represents a 0D dimer connected by silver ions but was also found to form channels facilitated by the hydrogen bonding between the protonated [bhepH]+ ligand and the cluster, and complex 2 forms 2D layered networks, whereas both compounds 3 and 4 form 1D networks; these networks are all connected by Ag(I) ions. Thermal studies show that the stabilities of compounds 2–4 are affected by the linking Ag(I) ions and the DMSO ligands and EM studies on compounds 3 and 4 showed the formation of fibres on silicon substrates.

Introduction

Polyoxometalate clusters (POMs) provide unrivalled structural diversity with clusters displaying a wide range of important physical properties and nuclearities, which range from 6 to 368 metal ions in a single molecule.1 In general, POM clusters are based upon metal-oxide building blocks with a general formula of MOx (where M is Mo, W, V and sometimes Nb, and x can be 4, 5, 6 or 7). POM-based materials have many interesting physical properties which result from their versatile structures, the ability to delocalise electrons over the surface of the clusters, the ability to incorporate heteroanions, electro-philes and ligands, and to encapsulate guest molecules within a metal-oxide based cage. POM clusters have been shown to exhibit catalytic activity,2 ionic conductivity,3 reversible redox behaviour,4 and cooperative electronic phenomena.5 Furthermore, during the last few years, POM chemistry has become multidisciplinary,6 interfacing with materials science,7–9 nanotechnology,9 and biology.10–13

We are interested in the ‘directed’ synthesis of new polyoxometalate-based clusters and in the construction of high dimensional architectures by the development of a building block approach that utilises synthetic equivalents or synthons that can be connected using pre-defined linkers.14

Whilst developing strategies towards this goal we recently reported a new family of POMs15–18 which appears to achieve the first part of this goal, and allows the isolation of a new structure type by virtue of the cations used to ‘encapsulate’ this unit, thereby limiting its reorganisation to a simpler structure. By using this approach we have isolated {Mo16}18 = [H2MoV2MoVI12O26]10–, {Mn16}16 = [Mn15O36(SO4)2]4– (M = Mo or W), {W19}17 = [H3W19O64]6– and {W36}18 = [H12W18O120]12– using bulky organo cations such as hexamethylenetetramine and triethanolamine. In previous work we were also able to combine the organo-cation directing approach and connect the POM-based building blocks to 1D polymeric chains, 2D grids and networks via coordination to electrophilic Ag(I) ions.14 As such these complexes represent rare examples of Ag-substituted POMs.14,19,20 By manipulating the organo counterion we could influence the overall architecture of a series of Ag–Mo POM based clusters.14 As a transition metal, silver(I) ions display a range of geometries and are able to form two to six coordination bonds, which make it a prime candidate to act as a linker.21,22

In this context we describe the synthesis, structure and physical properties of four new silver-bridged polyoxometalate containing compounds (characterised by single crystal X-ray analysis, elemental analysis, infra-red spectroscopy, TGA, DSC, and SEM): 1. [Ag4(bhepH)3(CH11.5Na0.5O6P)3]·8H2O (bhep = N,N′-bis(2-hydroxyethyl)piperazaine); 2. [Ag4(DMSO)3(MoO2O30)]·3, [Ag3[MnMoO18{(OCH2)2CNH2}2(DMSO)3]·3(DMSO)]·n; 4. [Ag3[MnMoO18{(OCH2)2CNH2}2(DMSO)3(CH2CN)2]DMSO]·n. Scanning electron microscopy studies on compounds 1–4 demonstrate that POM building blocks connected by silver ions can form interesting materials and thermal studies demonstrate the importance of the coordinating solvent and bridging Ag(I) linkers in dictating the overall stability of the materials. Compound 1 represents a rare example20 of Ag(I) ligated to a tungsten based POM, compound...
Results and discussion

Synthesis

Here we show that it is possible to generate Ag-POM-based clusters that can be constructed by utilizing synthetic equivalents and synthons as building blocks and silver(I) ions as linker groups. In compound 1, the formation of the dimer compound is directed by using the organic cation bhep. The Keggin clusters are connected through silver(I) ions and the 0D compound is directed by using the organic cation bhep. The O₄0P)₂⁺ comprises a two

view (C black, N blue, O red) and the Ag(I) ion is in light brown, and as very small spheres. The bhep ligands are shown in ball and stick purple polyhedron. The oxo ligands in the Keggin clusters are shown as green polyhedra, the central P atom as a

bridge, see Fig. 1: [Ag₃(bhepH)₆(W₁₁.₅Na₀.₅O₄₀P)₂⁺]. Colour scheme as in Fig. 2. The molecular structure of the bhep ligand is also shown.

Structural studies

The structure of compound 1, [Ag₃(bhepH)₆(W₁₁.₅Na₀.₅O₄₀P)₂⁺], comprises a two ζ-Keggin clusters bridged by a single Ag(I) via the terminal oxo ligands of the Keggin ion (O–Ag = 2.571(10) Å and O–Ag–O angle of 82.0(5)°). Although the complex is formulated as [Ag₃(bhepH)₆(W₁₁.₅Na₀.₅O₄₀P)₂⁺], a more accurate account is given by showing the mono-sodium substituted Keggin and full Keggin ion linked by the silver bridge, see Fig. 1: [Ag₃(bhepH)₆(W₁₁.₅Na₀.₅O₄₀P)](this

is because both crystallographic and elemental analysis indicates that the tungsten positions are under-occupied and may include sodium; this was confirmed by elemental analysis). The central bridging Ag(I) ion, located on a crystallographic two-fold axis, has a distorted octahedral geometry. The [Ag(O₄)₂] coordination motif in the equatorial plane is defined by two oxo ligands of the Keggin ion and the two –OH ligands from each of the two bhepH⁺ (Ag–O = 2.633(10) Å), while the axial sites of the Ag(I) ion are occupied by two nitrogen atoms from each of the bhepH⁺ ligands (N–Ag = 2.394(11) Å). In addition to the bridging Ag(I) ion, each Keggin is ligated to an additional non-bridging Ag(bhepH₂) motif where the Ag(I) ion has a distorted five coordinate geometry Ag–O(=W) = 2.552(9) Å, Ag–N is ca. 2.3 Å and the –OH groups of the bhepH⁺ ligand are ligated at longer distances that average ca. 2.724 Å. The cluster dimer units are also involved in an extensive hydrogen-bonded network which forms a channel-like structure containing a large amount of solvent water molecules, see Fig. 2.

Compound 2 can be formulated as [Ag₄(DMSO)₇]⁺ (Mo₈O₂₆)⁻ and related to the chain-like structures published previously containing polymers based on the {Ag–Mo₈–Ag} synthon. However, in this case, these synthons do not link together to form a chain-like arrangement but instead DMSO solvent is incorporated into the structure and also ‘pillars’ the Ag–Mo POM fragments, which ligate a total of four Ag(I) ions per cluster, providing essential support to the overall network. The {Mo₈–Ag₄} building block is arranged in such a way that it extends into a two-dimensional network via the coordinated DMSO molecules, see Fig. 3.

The {Mo₈} unit is ligated by Ag(I) ions on four of the six faces of the cluster and the clusters are connected via bridging DMSO solvents which are ligated to the Ag(I) ions present in the {Mo₈Ag₄} units and are coordinated alternately by S and O donor atoms.

Further, Ag(I) is bound to four oxygen atoms of the [Mo₈O₂₆]⁻ fragment and to two oxygens of two DMSO

blocks but also utilises DMSO as a directing and bridging ligand in the formation of a 2D net. Compounds 3 and 4 are based upon the Anderson cluster type, and have been connected to 1D chains using Ag(I) and bridging DMSO ligands but interact with the Anderson cluster via the tris ligand [[(tris(hydroxymethyl)amino)methane] which has three pendant hydroxyl groups that can replace the hydroxide groups on the surface of the Anderson cluster.

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molecules resulting in the Ag centre in an octahedral environment with a trigonally distorted geometry. The O–Ag–O angles and Ag–O bond distances fall within the expected ranges of 74.15(7) to 151.89(9)° and 2.296(3) to 2.581(2) Å respectively. In addition to this, one of the DMSO molecules is further coordinated to another silver (Ag(2)) ion through a Ag–S bond bringing the total number of silver ions in the asymmetric unit to two. The silver in this ‘linker’ unit links the Ag–Mo POM unit together in a two-dimensional array. The Ag(2) ion is also in an octahedral environment with trigonal distortion and on closer inspection is actually linked to a total number of four DMSO molecules either through Ag–O bonds or Ag–S bonds. The O–Ag–S angles are 76.96(6) to 119.56(6)° with Ag–O bond distances of 2.343(2) to 2.449(2) Å, see Fig. 3. In summary this 2D network comprises \{Mo8Ag4\} units that are connected by 4 DMSO ligands and also contain 4 non-bridging DMSO ligands.

Compound 3, \{Ag3[MnMo6O18{(OCH2)3CNH2}2(DMSO)5]\}_{n} forms a 1D chain in the solid state where the repeating unit in the chain is built from two tris-derived Anderson cluster \{MnMo6O18{(OCH2)3CNH2}2\}_{2}(DMSO)_{n}(CH3CN)_{2}\}_{n} units combined with Ag(I) and DMSO ligands. However in this case, the tris ligand on each side of the cluster (see Fig. 4) acts differently. The tris ligands on the right side of the cluster are defined as ‘tail’ groups and here are non-bridging instead of ligating \{Ag(CH3CN)2(DMSO)\}^{+}; the Ag(3) ion is in a 4 coordinate coordination mode and the Ag–N distance is 2.239 Å, see Fig. 5. The tris group on the left side of the cluster acts as a ‘head’ group and ligates to Ag(2) and the Ag–N distance is 2.258 Å. This Ag ion is itself part of a \{Ag2(DMSO)4\}^{2+}, see Fig. 5. Two DMSO ligands (via the oxo groups) bridge between Ag2 and Ag1 which itself is ligated to the side of the adjacent cluster in the 1D polymer with Ag–O(Mo) distances that fall in the range 2.414–2.680 Å.

Thermal studies
To investigate the stability of these silver-polyoxometalate-based materials a series of TGA and DSC experiments were
undertaken to see what effect the different building blocks would have on the stability of the materials produced. Both TGA and DSC studies were undertaken on compounds 1–4 and these results are summarised in Fig. 6.

The studies on compound 1 confirm the porous nature of the material with the initial weight loss of 13% corresponding to the loss of water from the solvent accessible cavity present. Both the TGA and DSC traces show the decomposition of the bhepH ligand in a series of steps. Compound 2 shows two well defined regions of solvent loss each corresponding to the loss of 4 DMSO molecules per event. The initial solvent loss appears to be the terminal DMSO ligands present and is well correlated with a sharp ‘melting’ link event in the DSC at ca. 150 °C. Compound 3 also shows a well defined series of events in the TGA associated with DMSO loss where the first two events correspond to the terminal and solvent DMSO being lost (5 DMSO) and the third event appears to be associated with the loss of the bridging ligands (3 DMSO). Again the DSC shows a ‘melting’ like event at ca. 150 °C associated with the first set of solvent loss. Compound 4 is also similar with loss of solvent DMSO, CH₃CN and terminal DMSO. The bridging DMSO ligands are lost next. Once again the DSC shows a ‘melting’ like event at ca. 150 °C.

It is interesting that all the silver-based coordination polymers demonstrated a degree of similar stability and behaviour despite the different types of polymer and bridging modes present. In particular the appearance of the sharp DSC ‘melting’ like event at ca. 150 °C for compounds 2–4 is intriguing. It would appear that the DMSO ligands present in 2–4 probably account for the similar results associated with the loss of solvent, terminal and bridging ligands with the solvent/terminal ligands being lost below 150 °C and the bridging DMSO ligands being lost at temperatures high than 200 °C.

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Concentrate on extending this molecular growth strategy to other POM-based structures linking the crystallographically determined building block principles to real materials.

**Experimental**

**Synthesis**

**Compound 1.** [Ag₄(bhepH)₆(W₁₁.₅Na₉.₅O₄₀P₂)₄]·8H₂O: Na₂WO₄·2H₂O (1.65 g, 5.0 mmol) was dissolved in water (20 mL) and acidified to pH 4 with 4 M HNO₃. To this solution was added N,N’-bis(2-hydroxyethyl)piperazine (0.84 g, 4.82 mmol) and the pH was increased to 7. Upon the addition of H₃PO₄ (0.44 g) the pH decreased to 6.47. Finally a solution of AgNO₃ (165 mg, 0.97 mmol) in water (1 mL) was added dropwise which resulted in the formation of a yellow precipitate. The solution was centrifuged several times and the clear solution decanted into a separate flask. The solution continued to precipitate but on leaving for several days produced clusters of white needles in sphalerite formation, which were suitable for single crystal X-ray diffraction. Yield: 300 mg (19% yield based on W). C₁₆H₆₈Ag₃N₁₆O₁₄P₂W₂₅Na: found (calc.) %: C 9.95 (10.30), H 2.14 (2.27), N 2.86 (3.00); IR (KBr, cm⁻¹): 3425 (b), 2996 (m), 2847 (w), 2721 (w), 1626 (w), 1457 (s), 1276 (w), 1190 (w), 1122 (w), 1078 (vs), 1034 (vs), 945 (vs), 851 (vs), 802 (vs), 727 (w).

**Compound 2.** [Ag₄(DMSO)₈(Mo₈O₂₆)]: Silver nitrate (23 mg, 0.14 mmol) in DMSO (2 mL) was added dropwise to a solution of [(H₂C₅H₁₁)₄N]₂Mo₈O₁₉ (102 mg, 0.069 mmol) in DMSO (5 mL) and then acetone was added (0.01 mL). The mixture was covered, and left for 48 hours to stir at room temperature. After this time the solution was still transparent yellow. Large colourless block crystals were successfully grown by diffusion of ethanol over 10 days. The crystals were suitable for single crystal X-ray diffraction. Yield: 48 mg (31%). C₁₆H₄₈Ag₄Mo₈O₃₄S₈: found (calc.) %: C 8.59 (8.59), H 2.17 (2.16); IR (KBr, cm⁻¹): 3432 (b), 2996 (w), 2960 (w), 2847 (w), 1719 (w), 1634 (m), 1435 (m), 1402 (m), 1311 (m), 1026 (s), 944 (s), 914 (s), 841 (s), 711 (s).

**Compound 3.** [Ag₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}₂(DMSO)ₓ]₃(DMSO)₉]: Silver nitrate (0.18 g, 1.06 mmol) in 10 mL of MeOH was added to Mn-Anderson cluster (0.5 g, 0.26 mmol) in 10 mL of DMSO. Yellow precipitates were formed immediately. The solution was kept stirring at 60 °C for 10 mins and another 10 mL of DMSO was added in. The solution was kept in dark for slow evaporation and yellow crystals were obtained after 3 days. Yield: 80 mg (15%). Elemental analysis: found (calc.) %: C 13.52 (13.70), H 3.45 (3.33), N 3.45 (3.35); IR (KBr, cm⁻¹): 3432 (b), 3009 (w), 2960 (w), 2847 (w), 1719 (w), 1634 (m), 1435 (m), 1402 (m), 1311 (m), 1026 (s), 944 (s), 914 (s), 841 (s), 711 (s).

**Compound 4.** [Ag₅[MnMo₆O₁₈{(OCH₂)₃CNH₂}₂(DMSO)ₓ]₉{(CH₃CN)₂}₉]: Mn-Anderson cluster (0.5 g, 0.26 mmol) was dissolved in 10 mL of MeCN, to which AgCF₃SO₃ (0.27 g, 1.06 mmol) in 10 mL of DMSO was added. Yellow precipitates were generated immediately. The solution was warmed to 50 °C and another 10 mL of DMSO was added.
added. A small amount of precipitate was filtered off and the solution was left in the dark for slow evaporation. Yellow crystals were obtained after one week. Yield: 98 mg (18%). Elemental analysis: found (%): C 15.20, H 3.26, N 16.02, O 53.82. The silicon substrates were cleaned and prepared by sonication in ethanol for 20 minutes. Then solutions of H2O2 were added. A small amount of precipitate was filtered off and the solution was left in the dark for slow evaporation. Yellow crystals were obtained after one week. Yield: 98 mg (18%).

X-Ray crystallographic studies

Data were measured on a Bruker Apex CCD diffractometer with graphite monochromator. Structure solution was with SHELXS-97 and refinement with SHELXL-97. Data were measured on a Bruker Apex CCD diffractometer with graphite monochromator. Structure solution was with SHELXS-97 and refinement with SHELXL-97. See Table 1 for summary crystallographic data.

Table 1: Crystallographic data for compounds 1–4

<table>
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<tr>
<th>Compound</th>
<th>Formula</th>
<th>Molar Mass</th>
<th>Space Group</th>
<th>Crystal System</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
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<td>24.737(15)</td>
<td>23.235(14)</td>
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<td>90</td>
<td>90</td>
<td>17566.5(19)</td>
<td>4</td>
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<tr>
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<td>C16H48Ag4Mo8O34S8</td>
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<td>P1</td>
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<td>13.3936(3)</td>
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<td>90</td>
<td>90</td>
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<td>12.8124(3)</td>
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<td>90</td>
<td>90</td>
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<td>4</td>
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References


Scanning electron microscope (SEM) measurements

The silicon substrates were cleaned and prepared by sonication in ethanol for 20 minutes. Then solutions of H2O2 were added. A small amount of precipitate was filtered off and the solution was left in the dark for slow evaporation. Yellow crystals were obtained after one week. Yield: 98 mg (18%). Elemental analysis: found (%): C 15.20, H 3.26, N 16.02, O 53.82. The silicon substrates were cleaned and prepared by sonication in ethanol for 20 minutes. Then solutions of H2O2 were added. A small amount of precipitate was filtered off and the solution was left in the dark for slow evaporation. Yellow crystals were obtained after one week. Yield: 98 mg (18%).

Thermal analysis data

TGA data were collected on a TA instruments Q 500 thermal analyzer under nitrogen carrier gas. The ramp rate was 2 °C min⁻¹ to 200 °C and then 10 °C min⁻¹ to 1000 °C. The DSC measurements were done on a TA instruments DSC Q 600. The ramp rate was 5 °C min⁻¹ and the sample was placed in an aluminium pan.

Acknowledgements

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