Compounds 1–7

Introduction

The self-assembly of polyoxometalate-based coordination compounds provides a convenient approach to molecular metal oxide architectures based on molybdenum, tungsten, or vanadium. Indeed, their versatile nature originates from the ability to link oxo-anions into a range of clusters including ultra-large clusters containing several hundred metal ions in a single molecule. Given the range of accessible structures, and their attractive and almost unmatched range of electronic and molecular properties, polyoxometalates (POMs) have been the subject of an immense number of studies in many fields including catalysis,3,4 magnetism,5,6 medicinal chemistry,7,8 and materials science.9,10 Thus research towards understanding and manipulation of the self assembly processes that underpin the formation of POM clusters has to be an attractive route to enable the design of designer clusters and multi-functional materials, which take advantage of the unique physical properties associated with this extraordinary class of molecules.11

The routes to synthesize POM clusters (large or small) often employ ‘one-pot’ reactions.1,3 As such, the manipulation of some of the many reaction parameters often represents a straightforward, but rather serendipitous, route to new, self-assembled POM architectures.1 A potential avenue of investigation that may allow the design of larger architectures based on clusters uses POM building blocks as synthons.12 This is because the ability to assemble large cluster systems from smaller known building blocks could be a direct way to systematically control the overall cluster architecture and properties while retaining the geometries of the building blocks. Thus, such building blocks of well-defined shape and connectivity might form the basis for work towards the growth of nanoscopic clusters of predetermined structure and function. However, the major problem with this approach lies in establishing routes to produce reactive building blocks present in solution in significant concentrations that can be reliably utilized in the formation of larger architectures, without re-organizing to other unknown fragments. Access to such building blocks has been the major limitation in stepwise growth of Mo-based POM clusters compared to the more kinetically inert W-based clusters.12 Such limitations may be circumvented by adopting an approach that kinetically stabilizes the building block in solution, thereby effectively preventing its reorganization to other structure types.

One possible route to this goal is to use bulky organic cations to isolate new structure types by virtue of the cations used to ‘encapsulate’ the new building blocks, thereby limiting their reorganization to simpler structural types. By trapping clusters during the self-assembly process it may be possible to restrain the cluster from reorganizing into other well-known structure types. Also, in many cases, synthetic strategies toward Mo-based cluster systems are guided by the fact that structures of polyoxomolybdate clusters are frequently derived from highly stable, low-nuclearity structural archetypes such as the Os-symmetric Lindqvist21 anion [Mo12O40]$^{4-}$ and the various isomers of the Keggin structure,22 [Mo12O40(XO4)]$^{3-}$, or the Dawson structure,23 [Mo12O40(XO4)]$^{3-}$ (X = S, P, As, Si etc.) Templated or non-templated by main-group hetero anions, these anions generally adopt a spherical shape, and so are the very few known polyoxomolybdate anions of {Mo$_n$} nuclearity. For example, [NaMo$_{4n}$OH$_n$]$_2$O$_{2n}$$^{-n}$ and [H$_2$Mo$_{4n}$O$_{2n}$]$_{2n}$ exhibit cluster structures based on the fully reduced ε-Keggin [Mo$_{12}$] motif with four capping [Mo$^6$O$_{4n}$] units.

Previously, by using protonated hexamethylenetetramine (HMTAH$^+$) as counter ions, we were able to stabilize and isolate a highly charged polyoxomolybdate anion, [H$_2$Mo$_{20}$Mo$_{20}$O$_{20}$]$^{12-}$ 1a, which represents a new structural type.24 The anion 1a displays an unusual flat shape and can itself be formally decomposed into a highly condensed {Mo$_{20}$} building block which incorporates two pairs of Mo$^+$ centres and to which two edge-sharing {Mo$_7$} groups are attached via corners. As we previously reported, 1a is stable in the solid state as the salt (C$_2$H$_4$N$_5$)$_2$[H$_2$Mo$_{20}$O$_{20}$]·3H$_2$O (1) since the highly negative cluster anion is virtually completely wrapped by the organic HMTAH$^+$ cations. In an extension to this approach we also recently isolated a family of sulfite-based Dawson-type mixed-valence polyoxomolybdates [Mo$_{16}$O$_{40}$(SO$_4$)$_{18}$]$^{16-}$, using the same type of synthetic approach. Furthermore these [Mo$_{16}$O$_{40}$(SO$_4$)$_{18}$]$^{16-}$ clusters possess unusual electronic properties and display S–S interactions between the lone pairs of the two sulfite anions inside the cluster.25 Thus, the use of bulky
organic cations in the formation of Mo-based POMs appears to restrict aggregation to the more highly symmetrical cluster types, allowing a fundamentally more diverse set of clusters and cluster-based building blocks to be isolated, that display unprecedented structural or physical features. Herein, we report a full investigation into the \([\text{H}_2\text{Mo}^V_8\text{Mo}^VI_{16}\text{O}_{52}\text{O}_{86}]^{30-}\) system and its reactivity towards electrophiles, as well as investigations into the magnetic and electronic properties. Our results demonstrate that the \([\text{H}_2\text{Mo}^V_8\text{Mo}^VI_{16}\text{O}_{52}\text{O}_{86}]^{30-}\) structure is indeed kinetically stabilized by the presence of a surrounding sheath of the bulky HMTAH cations, and also can be stabilized further after it coordinates two divalent metal cations to two specific binding sites.

**Experimental**

**General procedures**

All reagents and chemicals were purchased from commercial sources and used without further purification. Infrared spectra were recorded using a Perkin-Elmer paragon 1000 PC or Nicolet Magna 560 series II FTIR spectrometer. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-SQUID magnetometer. Variable temperature (2–290 K) susceptibilities were recorded at 0.5 Tesla. In addition, field-dependent (0.1–5.0 Tesla) measurements of all compounds at 10 K showed linear \(M \propto H\) behaviour and excluded the presence of a significant amount of magnetic impurities. Susceptibilities were corrected for diamagnetic and temperature-independent paramagnetism (TIP) contributions that were derived from a combination of Pascal's constants and the experimentally determined diamagnetic susceptibility of compounds 1 with \(X_{\text{Zanipe}}(T) = -1.03 \times 10^{-6} \text{ emu mol}^{-1}\) (for compounds 2–4) and 5 with \(X_{\text{Zanipe}}(5) = -3.38 \times 10^{-6} \text{ emu mol}^{-1}\) (for compounds 6 and 7). This approach is necessary as the simple addition of Pascal's constants does not incorporate TIP effects and thus largely overestimates \(X_{\text{Zanipe}}\) values for most polyoxomolybdate compounds.

Density functional theory calculations (including Löwdin and Mulliken population analysis) using the TURBOMOLE 5.6 program suite required TZVPP (cc-pVTZ polarization functions) basis sets and hybrid B3-LYP exchange–correlation functionals to converge. All structures were based on crystallographic coordinates that were allowed to equilibrate without functional to converge. All structures were based on crystallographic coordinates that were allowed to equilibrate without functional to converge. The solution slightly changed from brown to reddish brown. Dark brown block crystals were obtained overnight. Yield: 0.24 g, 23%. IR (KBr disk): 3426, 1631, 1432, 1314, 1041, 993, 843, 660 cm\(^{-1}\); elemental analysis calcd. for \(\text{C}_9\text{H}_6\text{Mo}_3\text{Mo}_7\text{O}_{24}\text{Na}_2\text{H}_2\text{O}_3\); C 7.79, H 1.18, N 6.94%; found: C 7.71, H 1.12, N 6.78%.

**Synthesis of (C\(_6\)H\(_13\)N\(_4\))\(_2\left(\text{H}_2\text{O}\right)\text{Mo}_7\text{O}_{24}\)·2H\(_2\)O 6.** Crystals of 6 were produced as follows: The brown reaction solution obtained during the synthesis of 1 was kept undisturbed for 4 h. After this period it was quickly mixed with a solution of \(\text{FeSO}_4\cdot7\text{H}_2\text{O}\) (0.90 g, 3.2 mmol) or \(\text{HNO}_3\cdot6\text{H}_2\text{O}\) (0.18 g, 0.75 mmol), which was acidified previously using hydrochloric acid (37%, 0.20 ml). The mixture was stirred for 2 minutes and quickly filtered. The solution colour slightly changed from brown to reddish brown. Dark brown block crystals were obtained overnight. Yield: 0.24 g (26%). IR (KBr disk): 3207, 1637, 1420, 1372, 1255, 1023, 979, 934, 892, 841, 660 cm\(^{-1}\); elemental analysis calcd. for \(\text{C}_8\text{H}_8\text{Fe}_2\text{Mo}_7\text{O}_{24}\text{Na}_2\text{H}_2\text{O}_3\); C 8.75, H 2.94, N 6.60; found: C 8.85, H 2.55, N 6.81%.

**Synthesis of (C\(_6\)H\(_13\)N\(_4\))\(_2\left(\text{H}_2\text{O}\right)\text{Mo}_7\text{O}_{24}\)·2H\(_2\)O 7.** Crystals of 7 were produced in a synthesis route analogous to that of 6. The initial brown reaction solution obtained in the synthesis of 1 was kept undisturbed for 6 h. After this period it was quickly mixed with a solution of \(\text{Na}_2\text{S}_2\text{O}_4\cdot6\text{H}_2\)O (0.18 g, 0.65 mmol) in \(\text{H}_2\)O (50 ml), which was acidified previously using hydrochloric acid (37%, 0.20 ml). The mixture was stirred for 2 minutes and quickly filtered. A grey precipitate was obtained and light green crystals were obtained after 6 h. Yield: 0.35 g (38%). IR (KBr disk): 3211, 1637, 1466, 1372, 1255, 1255, 1214, 1024, 934, 959, 856, 680 cm\(^{-1}\); elemental analysis calcd. for \(\text{C}_{8}\text{H}_{8}\text{Fe}_2\text{Mo}_7\text{O}_{24}\text{H}_{2}\text{O}\); C 7.86, H 2.94, N 6.81; found: C 7.86, H 2.97, N 6.99%.

**Synthesis of (C\(_6\)H\(_13\)N\(_4\))\(_2\left(\text{H}_2\text{O}\right)\text{Mo}_7\text{O}_{24}\)·8H\(_2\)O 8 and (C\(_6\)H\(_13\)N\(_4\))\(_2\left(\text{H}_2\text{O}\right)\text{Mo}_7\text{O}_{24}\)·8H\(_2\)O 9.** Powder samples of 8 and 9 were produced in the same procedure as used for synthesis of 2 by replacing \(\text{FeSO}_4\cdot7\text{H}_2\text{O}\) with \(\text{ZnCl}_2\) (0.12 g, 0.85 mmol) or \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) (0.18 g, 0.76 mmol), respectively.
Grey precipitates were formed immediately after zinc and nickel salt solutions were mixed into the molybdate solution. These precipitates were filtered off and dried under vacuum. For 8, yield: 0.32 g (36%). IR (KBr disk): 3205, 1636, 1404, 1382, 1258, 1219, 1065, 1010, 980, 960, 918, 875 cm⁻¹; elemental analysis calcd. for C₉H₁₃N₄O₄·Mo₂O₇·H₂O: C 31.34, H 1.62, N 15.78; found: C 31.45, H 1.70, N 15.62%. For 9, yield: 0.25 g (28%). IR (KBr disk): 3423, 1638, 1463, 1401, 1261, 916, 980, 937, 870, 794, 651 cm⁻¹; elemental analysis calcd. for C₁₀H₁₂N₄O₄·Mo₃O₁₄·H₂O: C 39.86, H 4.11, N 13.05; found: C 39.94, H 4.13, N 12.92%.

Structural analysis

The crystal structure of 1 comprises discrete centrosymmetric anions [H₂Mo²⁺Mo⁶⁺O₁₂²⁻] in a Keggin anion [Mo₁₂O₃₉H₂O]³⁻ that is either produced during the formation of 1 in a competing reaction that involves Na⁺ cations or by decomposition of 1 in the presence of the mother liquor; this decomposition appears to be accelerated upon heating. The two compound 8 and 7 were originally designed for synthesising similar cluster compounds of 2 and 3 but with more Fe²⁺ or Mn²⁺ ions attached to the molybdate cluster [H₂Mo₁₆O₅₂]³⁻. However, 1 decomposed when the Fe²⁺ or Mn²⁺ ion concentrations are increased, yielding metal complexes of heptamolybdate. Medium Fe²⁺ concentrations result in mixtures of 2 and 6 as confirmed by X-ray powder diffraction or 3 and 7 for Mn²⁺. Bridging anions such as acetate and sulfate have occasionally been reported to involve in the formation of polyoxomolybdates ²⁶⁻²⁸ To explore their effect in the present system in the presence of protonated HMTA, we have probed the use of sulfuric acid or a combination of hydrochloric and acetic acid (complete acidification by acetic acid results in the rapid precipitation of an unknown compound), but this approach yields the same product of 1 rather than products containing acetate or sulfate.

Results and discussion

Synthetic strategy

Crystals of [C₉H₁₃N₄][H₂Mo₁₆O₅₂]·3H₂O 1 were obtained from a buffered solution with a pH of around 4.0 that utilises protonated HMTA as counter ions. Normally, medium- and high-nuclearity polyoxomolybdates are formed at lower pH values such as 1 to 2. However, it was observed that the combination of HMTA and molybdate in a solution at a pH value of 4 and below produces a white precipitate that is not able to form soluble ‘molybdenum blue’-type solutions.²⁹ Therefore, the reaction was carried out at the lowest possible pH (before precipitation occurs) of around 4. Also, the reducing agent Na₂S₂O₇ was added simultaneously with the addition of sodium molybdate which allows the quick formation of soluble reduced polyoxomolybdate species. Following the formation of [H₂Mo₁₆O₅₂]³⁻, further acidification of the solution causes the [Mo₉O₄] cluster to decompose and causes precipitation. This precipitate was confirmed to be the same phase as compound 5 by X-ray powder diffraction analysis. Furthermore, it was observed that compound 5 is either produced during the formation of 1 in a competing reaction that involves Na⁺ cations or by decomposition of 1 in the presence of the mother liquor; this decomposition appears to be accelerated upon heating.

Structural motifs of each Mo₉O₄ group are bridged via a µ-oxo and a µ₂-hydroxo function and coordinate to two terminal and two µ₂-oxo positions of the Mo₉O₄ fragment building blocks. Although [Mo₉O₄]⁻ type building blocks are abundant in various other large polyoxomolybdates such as clusters based on the doughnut-shaped [Mo₁₂O₄²⁻] structural type or the giant ring clusters of the type [Mo₉O₆]⁻ and [Mo₉O₈]⁻ and their derivatives, these consist of either two corner-shared MoO₄ octahedra (found in the giant ring molecules) or comprise reduced Mo₆ centres. [Mo₉O₄]⁻ building blocks consisting of edge-sharing MoO₄ octahedra, on the other hand, are seen for the first time in the [Mo₉O₄]⁻ structural motif. For the complete cluster, terminal Mo=O bonds with bond lengths in the range of 1.6 to 1.7 Å are found, while the bridging Mo−O bond lengths of bridging oxygen centres range from 1.7 to 2.2 Å. Further, some of the terminal oxygen centres form hydrogen bonds with solvated water molecules and the protonated HMTA cations.

Interestingly, the arrangement of the sixteen Mo positions bears similarities to the metal skeleton found for the cluster molecule [M₈O₄]²⁻ [M₈O₄(OMe)₃(OAc)₃(MeOH), (H₂O)] 6H₂O, see Fig. 2.²⁶ although both molecules differ in the coordinating modes of their ligands.
Table 1  Crystallographic data collection, intensity measurements and structure refinement parameters for 1–7 (note that structures 1 and 2 have been reported by us in an earlier publication and are included here for comparative proposes)²

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Fig. 1 Left: Ball-and-stick representation of the molecular structure of $[\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10}\text{−}$ 1a (Mo$V$ centres of the central $\{\text{Mo}_{12}\}$ building block: bright blue; Mo$V$ (belonging to the $\{\text{Mo}_5\}$ building block): dark blue; Mo$V$ centres of the two $\{\text{Mo}_5\}$ groups: pink; O: red; H: bright grey; Mo–Mo bonds indicated by dotted lines). Right: Polyhedral representation of 1a. The four oxygen positions to which a $\{\text{Mo}_5\}$ group attaches are encircled in green.

Fig. 2 Schematic comparison of the mixed-valence $\{\text{Mo}_{12}\}$ (a) and $\{\text{Mn}_{16}\}$ (b) frameworks, for clarity only the metal and the bridging oxo positions are shown. Both structures comprise a central fragment of four face-sharing, incomplete Mo$_4$ cubanes, highlighted by dark grey bonds and dark blue (Mo) or dark grey (Mn) metal centres. In the case of the $\{\text{Mo}_{12}\}$ cluster this central $\{\text{Mo}_{12}\}$ fragment contains the four formal Mo$^\circ$ centres that are arranged to form two $\{\text{Mo}^V\}$ pairs with short Mo···Mo contacts of 2.6 Å, indicated by dashed lines; in the case of the $\{\text{Mn}_{16}\}$ cluster these central metal positions represent the $\{\text{Mn}^{IV}\}$ core. These central $\{\text{M}_i\}$ fragments are surrounded by a $\{\text{Mo}^V\}$, and $\{\text{M}^{III}\}$ ring, respectively.

Besides compounds 2, 3 and 4, which can be produced as crystals suitable for single crystal X-ray analysis, crystalline powders were precipitated for the nickel(II) and zinc(II) analogues. X-Ray powder diffraction data indicate that these products represent isomorphous derivatives of compounds 2–4.

The inherent reactivity of the highly charged cluster anions 1a causes gradual decomposition and rearrangement reactions when crystals of compound 1 are kept in the reaction solution for some days, after which they re-dissolve and a different solid, $\text{(C}_6\text{H}_7\text{N}_4\text{H})\text{[Mn}_7\text{O}_{24}\text{(H}_2\text{O})_5\text{]}\text{·}8\text{H}_2\text{O}$ 3 and $\text{(C}_6\text{H}_7\text{N}_4\text{H})\text{[Co}_7\text{O}_{24}\text{(H}_2\text{O})_5\text{]}\text{·}8\text{H}_2\text{O}$ 4 can be isolated in good yield. The cluster anions in 2–4 are of approximate C$_2$ symmetry and are based on a $\{\text{Mo}_{12}\}$ fragment where two $\text{[H}_2\text{Mo}_{16}\text{O}_{52}]^{10}\text{−}$ (M = Fe, Mn, Co) groups are coordinated to inversion symmetry-related sites. Each M$^\circ$ centre binds to two terminal oxo positions of the $\{\text{Mo}_{12}\}$ building block, one of a Mo$^\circ$O, and one of an adjoining Mo$^\circ$O$_4$ octahedron (M = O(Mo$V$): 2.129(4) Å; M = O(Mo$^{IV}$): 2.116(4) Å), see Fig. 3.

Fig. 3 (a) Representation of the isostructural $\{\text{M}_{2}\text{Mo}_{16}\}$-type clusters in 2, 3, and 4. The $\text{[H}_2\text{Mo}_{16}\text{O}_{52}]^{10}\text{−}$ fragment is shown in polyhedral representation with the four Mo$^\circ$O coordination polyhedra hatched, and the $\text{[M}^\circ\text{(H}_2\text{O})_6]^{1+}$ groups in ball-and-stick mode. (b) Potential magnetic exchange pathways in $\{\text{M}_{2}\text{Mo}_{16}\}$ involving the two $\{\text{Mo}^V\}$ dimers. Mo–Mo bonds within these dimers are represented by black lines.

Compound 1 is reasonably stable, both in the solid state and in solution, and it forms metal complexes with diverse transition metal cations and the compounds (C$_6$H$_7$N$_4$H)$_6$[Fe$_2$(H$_2$O)$_8$H$_2$Mo$_16$O$_{52}$]·8H$_2$O 2, (C$_6$H$_7$N$_4$H)$_6$[Mn$_7$(H$_2$O)$_5$H$_2$Mo$_{16}$O$_{52}$]·8H$_2$O 3 and (C$_6$H$_7$N$_4$H)$_6$[Co$_7$(H$_2$O)$_5$H$_2$Mo$_{16}$O$_{52}$]·8H$_2$O 4 can be isolated in good yield. The cluster anions in 2–4 are of approximate C$_2$ symmetry and are based on a $\{\text{Mo}_{12}\}$ fragment where two $\text{[H}_2\text{Mo}_{16}\text{O}_{52}]^{10}\text{−}$ (M = Fe, Mn, Co) groups are coordinated to inversion symmetry-related sites. Each M$^\circ$ centre binds to two terminal oxo positions of the $\{\text{Mo}_{12}\}$ building block, one of a Mo$^\circ$O, and one of an adjoining Mo$^\circ$O$_4$ octahedron (M = O(Mo$V$): 2.129(4) Å; M = O(Mo$^{IV}$): 2.116(4) Å), see Fig. 3.

The inherent reactivity of the highly charged cluster anions 1a causes gradual decomposition and rearrangement reactions when crystals of compound 1 are kept in the reaction solution for some days, after which they re-dissolve and a different solid, (C$_6$H$_7$N$_4$H)$_6$[Na$_2$Mo$_{10}$O$_{24}$H$_2$O$_5$]·4H$_2$O 5, is formed. 5 comprises a zigzag-shaped, one-dimensional anionic coordination polymer of heptamolybdate [Mo$^{VI}$O$_5$O$_2$]$^{2−}$ units linked by [H$_2$O]Na$(μ$_2$O$_2$)Na[Na$_2$H$_2$O$_5$] units linked via two bridging water molecules with a Na···Na distance of ~3.5 Å. The dimer binds to the two $\{\text{Mo}_5\}$ fragments in two coordination modes, with one sodium position coordinated to two and the other to three terminal oxo groups of the $\{\text{Mo}_5\}$ fragments with Na···O(Mo) distances of 2.450(4) to 2.466(6) Å. One and two terminal water ligands, respectively, complete the slightly distorted octahedral coordination environments of the two sodium cations. In the solid-state structure of 5, the polymeric [Na$_2$Mo$_{10}$] strands are sandwiched between layers of HMTA-based cations, see Fig. 5. Interestingly, the cations present in 5 are twofold protonated HTMA and/or an alkylated derivative of HMTA, N-((H$_2$NCH$_2$)HMTA, which again is protonated (such an alkylation reaction has been reported by Ojha et al.) and presumably originates from the acid.
catalysed decomposition of some HTMA cations and subsequent alklyation of intact HMTA cations present in solution). For 5, a ratio of 3 : 1 has been established from elemental and X-ray structure analysis results between the HMTAH$_2^{+}$ and $\text{Na}(\text{H,NCH}_2\text{-})$-HMTAH$_2^{+}$ species. Interestingly, a similar {Na$_2$Mo$_7$}$_n$ compound has been described by Yang et al.$^{19}$ using a different synthetic strategy that employs MoCl$_3$ and sodium molybdate as starting materials.

The {Mo$_n$} cluster anion 1a also decomposes in the presence of divalent transition metal cations in high concentrations, around 5–10 times higher than the concentrations used to produce the {M$_2$Mo$_n$}$_n$-based compounds 2–4 (see Scheme 1). Under such conditions the isostructural {Mo$_n$M$_l$}_n-type compounds (C$_{6}$H$_{13}$N$_4$)$_2$[Fe$_2$(H$_2$O)$_9$Mo$_7$O$_{24}$]$\cdot$$\text{H}_2\text{O}$ and (C$_{6}$H$_{13}$N$_4$)$_2$[Mn(H$_2$O)$_6$Mo$_7$O$_{12}$]$\cdot$2H$_2$O 7 are formed which again are based on individual heptamolybdate fragments that now coordinate to two M$^{2+}$ cations. In the molecular cluster anions 6a and 7a, one of the two Fe$^{0}$ or Mn$^{n}$ centres binds to a terminal oxo position of the [Mo$_7$O$_{24}$]$^{6-}$ fragment, the other one coordinates to one terminal and one bridging oxo position of a neighbouring MoO$_6$ octahedron. Correspondingly, five and four terminal water ligands complete the octahedral coordination environments of both M$^{2+}$ centres, see Fig. 6. In addition, compounds 6 and 7 show hydrogen bonding between coordinated water molecules and other terminal oxygen atoms on the molybdate fragment and the protonated HMTA cations, cf. Fig. 7.

**Magnetic properties**

The magnetism of compounds 1–7 was characterized by susceptibility measurements. Weak yet significant antiferromagnetic coupling is observed for all compounds containing spin centres despite the large intramolecular M···M distances of ca. 11.81 Å in {M$_2$Mo$_n$}$_n$-based and ca. 6.90 Å in {M$_2$M$_l$}_n-based compounds; this illustrates the efficiency of polyoxomolybdates in mediating magnetic superexchange. In the {M$_2$Mo$_n$}$_n$-type compounds 2–4 the shortest superexchange pathways are of the type M$^{IV}$–O–Mo$^{V}$–Mo$^{V}$–O–Mo$^{V}$ (assuming a metal–metal bond between the Mo centres of a {Mo$_5$}$_2$ dimer), Fig. 3b, while M$^{IV}$–O–Mo$^{V}$–O–Mo$^{V}$–O–M$^{IV}$ pathways, Fig. 5b,
are present in the \{M\textsubscript{2}Mo\textsubscript{7}\} anions, and the HMTAH\textsuperscript{+} cations in the crystal structure of 6 and 7, seen along the c axis. The dimensions of one unit cell are emphasized. The heptamolybdate fragments are represented by blue polyhedra with the appended Fe\textsuperscript{II}/Mn\textsuperscript{II} centres in green. C: black; N: bright grey.

Electronic properties

In order to explore the reactivity of the highly charged cluster anion 1\textsubscript{a} density functional theory calculations were performed on both 1\textsubscript{a} and its Zn(II) derivative [Zn\textsubscript{2}(H\textsubscript{2}O)\textsubscript{8}H\textsubscript{2}Mo\textsubscript{16}O\textsubscript{52}]\textsuperscript{6-}. Overall, the surface charge distribution as defined by the atomic net charges of the terminal oxo positions shows pronounced charge maxima and minima. Class-2 (Löwdin) atomic charges of these 26 positions differ by up to 22% from the average of −0.532, and by up to 26% from the average of −0.494 for the 14 μ\textsubscript{2}-oxo positions, compared to the maximum differences of 8% from the average of −0.493 for the 12 μ\textsubscript{2}-oxo positions, see Fig. 7. It is interesting that the reaction of 1\textsubscript{a} with divalent metal cations binds them to one terminal oxo position of a formal Mo\textsuperscript{v} centre and one terminal oxo position of an adjacent Mo\textsuperscript{v} centre (O–O = 2.99 Å), although these positions, out of all terminal oxo pairs with O–O distances < 3.3 Å that allow a chelating coordination mode to the Mo\textsuperscript{v} centres, show relatively low negative net charges of −0.41 (Mo\textsuperscript{v}O, the least negatively charged oxo positions) and −0.57 (Mo\textsuperscript{v}O\textsuperscript{2-}). The four Mo(4d) electrons in 1\textsubscript{a} and 2a–7a are mostly localized over the two central \{Mo\textsubscript{2}\} dimers, and correspondingly the orbital overlap between these positions is significant, indicating a single metal–metal bond. Moreover, the net atomic charges of the oxygen centres in 2a–7a, especially of the terminal oxo positions, are distributed in a more uniform way compared to 1\textsubscript{a}. This greater uniformity of net charges is reflected by the maximum deviations from the average values: 16% from the average value of −0.487 for the 22 terminal oxo positions, 20% from the average of −0.469 for the 12 μ\textsubscript{2}-oxo positions (excluding the oxo positions to which the Zn centres are bound), and 12% from the average of −0.506 for all of the 14 μ\textsubscript{2}-oxo positions, see also Fig. 9.

Thus, possible reasons for the apparent absence of species of the...
type \( \{ \text{Mo}^n \text{Mo}_m \} \) with \( n > 2 \) are either the reduced total charge of the anion or the lack of additional reactive “hot spots”, i.e., surface charge maxima.

**Fig. 8** Magnetic susceptibility data (temperature dependence of \( \chi_{Mo} T \) at 0.5 Tesla) for compounds 2, 3, 4, 6, and 7.

**Conclusions**

We have demonstrated the production and complexation of an unusual mixed-valence polymolybdate, which contains sixteen molybdenum centres and displays a non-spherical structure, but is sufficiently reactive to form complexes with other divalent transition metals. This \( \{ \text{Mo}_{16} \} \) cluster appears to be assisted in its formation by the use of bulky organo cations and we have shown that it can react with a number of electrophiles to form the corresponding \( \{ \text{Mo}_{16} \text{M}_2 \} \) adducts. Investigation of the structures using DFT demonstrates the existence of nucleophilic ‘hot-spots’ but do not predict the sites for electrophile coordination, and the magnetic investigation of the paramagnetic \( \{ \text{Mo}_{16} \text{M}_2 \} \) adducts illustrates the efficiency of polyoxomolybdates in mediating magnetic superexchange. Furthermore we discovered that the \( \{ \text{Mo}_{16} \} \) and \( \{ \text{Mo}_{16} \text{M}_2 \} \) adducts are unstable in solution for long periods and decompose to smaller \( \{ \text{Mo}_7 \} \) and \( \{ \text{Mo}_7 \text{M}_2 \} \) units. The potential to utilise the unstable \( \{ \text{Mo}_{16} \} \) and \( \{ \text{Mo}_{16} \text{M}_2 \} \) as precursors to other cluster types and building blocks is now under investigation.

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