Small Polyoxomolybdates

Restraining Symmetry in the Formation of Small Polyoxomolybdates: Building Blocks of Unprecedented Topology Resulting From “Shrink-Wrapping” \([\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}\)-Type Clusters

A mixed-valence polyoxomolybdate cluster \([\text{H}_2\text{Mo}^{VI}_{12}\text{Mo}^{V}_{4}\text{O}_{52}]^{10-}\) was isolated by a new “shrink-wrapping” approach to trap clusters that display low symmetry and nonspherical topology (see scheme; HMTAH = protonated hexamethylenetetraamine). The unprecedented cluster topology results from the restriction of the reorganization of the cluster framework to more symmetrical clusters, yet it reacts with electrophiles, such as \(\text{Fe}^{II}\).


Keywords: cluster compounds · molybdenum · polyoxometalates · self-assembly · supramolecular chemistry

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Trapped polyoxometalate clusters can be isolated in a novel and simple synthetic approach which “shrink-wraps” unstable, unsymmetrical polyoxometalate clusters with large organic cations. This prevents their rearrangement and aggregation to more symmetrical, well known structures. Initial results and reactivities of clusters trapped in this way are presented by L. Cronin et al. on the following pages.
Communications

Restraining Symmetry in the Formation of Small Polyoxomolybdates: Building Blocks of Unprecedented Topology Resulting From “Shrink-Wrapping” \([\text{H}_2\text{Mo}_{16}\text{O}_{42}]^{16-}\) -Type Clusters**

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Dedicated to Professor Achim Müller on the occasion of his 65th Birthday

The structural diversity and potential for the formation of nanoscopic molecules in the field of polyoxomolybdate (POMo) cluster chemistry has been recently demonstrated in dramatic fashion. Sparked by these discoveries and the many applications found and proposed for POMo-based clusters, interest in their rational synthesis has been increasing rapidly. For example, the concept of generating a set of linkable nucleophilic building blocks that can be condensed together according to their intrinsic geometric and electronic properties has been stimulating research on the design of POMos with both high and low nuclearities. A range of smaller polyanions have themselves been incorporated as building blocks into hybrid and network solids, however, there has been little advance in the generation of fundamentally new types of pure Mo–O cluster frameworks in the small-to-medium nuclearity range (Mo10–Mo18). There-eto expand this building-block concept further, the construction of structurally diverse cluster and cluster-based network geometries calls for the generation and isolation of low-nuclearity polyoxometalates that substantially deviate from the well-known “classical” polyoxometalate prototypes. These prototypes include clusters with spherical structures and high symmetry, such as the Lindqvist, Keggin, or Dawson anions. Access to new types of nonspherical, low-symmetry clusters that can be used as building blocks (i.e., that display high negative charge and nucleophilicity) will be significant as their low symmetries are a crucial prerequisite for the emergence of structural complexity when tiling or linking these building blocks to larger aggregates. To accomplish this, we have adopted a simple strategy to prevent the rapid aggregation of metal-oxide-based polyhedra to clusters with a stable uniform spherical topology. This approach relies on trapping and stabilizing nonspherical polyanions of low nuclearity and symmetry before their aggregation and rearrangement to more uniform and stable structures.

By adopting this approach we have synthesized a mixed-valence cluster anion which results when the formation of symmetrical aggregates appears to be restrained by “shrink-wrapping” the anionic POMo cluster. As such the cluster comprises a type of polyoxometalate cluster framework that displays an unprecedented topology, low symmetry, and high negative charge, and is isolated as:

\[
(\text{C}_6\text{H}_4\text{N}_3)_8[\text{H}_2\text{Mo}_{16}\text{O}_{42}]_{10}^{16-}\cdot 34\text{H}_2\text{O} 1
\]

The anion in compound 1 demonstrates a high nucleophilicity and can bind two divalent transition-metal ions (FeII, MnII, CoII, NiII, or ZnII) to its framework. This yields a family of isostructural complexes, as confirmed by powder diffraction studies, and we have been able to determine the structure of an iron-adduct cluster 2, which shows that the basic topology found for the anion in compound 1 is maintained. Hence, 2 can be formulated as:

\[
(\text{C}_6\text{H}_4\text{N}_3)_8[\text{Fe}_2(\text{H}_2\text{O})_6\text{H}_2\text{Mo}_{16}\text{O}_{42}]_{10}^{16-}\cdot 8\text{H}_2\text{O} 2
\]

By using protonated hexamethylenetetraamine (HMTAH+ or C6H12N4+) as counterions, the cluster compounds 1 and 2 were isolated as crystalline precipitates from an acidified molybdate solution in the presence of a reducing agent in around 20–30% yield. Compounds 1 and 2 were characterized by single-crystal X-ray structure analyses bond valence sum (BVS) calculations, redox titrations, and elemental analyses, to aid in the determination of the (formal) number of MoV centers and protonation sites and also using IR and UV/Vis spectroscopy, and magnetic susceptibility measurements. In addition, the purity of the bulk phase of compounds 1 and 2 has also been confirmed by X-ray powder diffraction.

X-ray crystallographic analysis of 1 reveals that the anions present consist of a highly negatively charged framework of the composition \([\text{H}_2\text{Mo}_{16}\text{O}_{42}]^{16-}\) (Figure 1). The cluster framework displays an unusual flat shape and despite its high charge and nonspherical structure, this mixed-valence cluster compound is stable in the solid state as the salt 1. Redox titrations, bond valence sum calculations, and elemental analysis reveal the formal oxidation numbers of the Mo centers to be MoVMoVI. The four Mo centers comprise two centrosymmetrically related MoV2 groups (located in the central part of the \([\text{H}_2\text{Mo}_{16}\text{O}_{42}]^{16-}\) cluster core) which display a short Mo(2)-Mo(3) contact of 2.6427(4) Å, which is characteristic of Mo–Mo single bonds, and also explains the brown color that is associated with clusters containing these groups. The shape of the cluster resembles that of a “bat” and its main “body” consists of a central unit with twelve molybdenum atoms and two “wings” each with two molybdenum centers (according to the formulation \([\text{Mo}_{12}] + 2[\text{Mo}_3]\)). In contrast to known polyoxomolybdates, 1 has a...
The coordination of the FeII centers to these particular sites is provided by water molecules. The polyoxomolybdate anion present in Figure 2 is derived from the cluster \([\text{H}_2\text{MoV}_4\text{O}_{12}]^{4-}\) to \([\text{H}_2\text{MoV}_4\text{O}_{12}]^{6-}\) 42-oxo, ten 4-oxo groups are shown by the large red spheres, the \(\mu_5\)-oxo groups by smaller red spheres, and the \(\mu_2\)-oxo bridging and terminal oxo ligands as red sticks. Finally, the two \([\text{Mo}_2]\) “wings” are shown in yellow and the hydrogen bonds are indicated by red dotted lines. The bond lengths for all terminal Mo–O bonds range from 1.687(3) to 1.730(3) Å, while the bridging O–Mo bonds range from 1.752(2) to 2.394(2) Å.

A flat structure with approximate dimensions of 13 × 11 × 6 Å. Of the twelve molybdenum centers which form the main body of the “bat”, eight molybdenum centers are arranged in two lines of four to form two \([\text{Mo}_4]\) “backbones”, which are highly condensed. This is illustrated by the large number of bridging oxo ligands in this central fragment, which comprises 18 (four \(\mu_2\)-oxo, ten \(\mu_5\)-oxo, and four \(\mu_3\)-oxo ligands) of the 52 oxo ligands in total. The two protons in the \([\text{H}_2\text{MoV}_4\text{MoVI}_{12}\text{O}_{52}]^{4-}\) anion are involved in hydrogen-bonding interactions between the backbone and the wings, highlighted in Figure 1 as red dotted lines (O···O: 2.732(5) Å).

Complex 2 can be isolated as the salt \((\text{C}_6\text{H}_{13}\text{N}_4)_6[\text{Fe}_2(\text{H}_2\text{O})_8\text{H}_2\text{MoV}_{12}\text{O}_{52}]8\text{H}_2\text{O}\) and consists of \([\text{Fe}_2(\text{H}_2\text{O})_8\text{H}_2\text{MoV}_{12}\text{O}_{52}]^{n-}\) cluster anions, HMTAH⁺ cations, and solvent water molecules. The polyoxomolybdate anion present in 2 (Figure 2) is derived from the cluster \([\text{H}_2\text{MoV}_4\text{MoVI}_{12}\text{O}_{52}]^{4-}\) anion in 1 with its structural features retained, and in the two \([\text{Fe}_2(\text{H}_2\text{O})_8\text{H}_2\text{MoV}_{12}\text{O}_{52}]^{n-}\) units are each coordinated to two terminal oxo ligands attached to MoVI(4) and MoV(3) (as labeled in the parent anion shown in Figure 1) at the opposite ends of the central \([\text{Mo}_2]\) body of the polyoxomolybdate anion. The coordination of the FeII centers to these particular sites is unexpected as semiempirical and preliminary DFT calculations of the cluster anion suggest that, among all terminal neighbored oxygen positions in the cluster anion in 1 that allow both steric access and a bidentate chelating coordination to a M⁺ ion, the particular O(Mo3) and O(Mo4) positions actually display the lowest negative partial charges.

While compound 1 is diamagnetic because of strong antiferromagnetic exchange within each of the two pairs of MoV units (with \(\gamma_{\text{adiabatic}} = -1.1 \times 10^{-3}\) emu·mol⁻¹; \(\gamma_{\text{adiabatic}} = -9.0 \times 10^{-4}\) emu·mol⁻¹) is best fitted to a Heisenberg model, employing the spin Hamiltonian \(\mathcal{H} = -J \mathbf{S}_i \cdot \mathbf{S}_j + D \mathbf{S}_i^2 + E \mathbf{S}_i \cdot \mathbf{S}_j\) with an exchange constant \(J = -0.8\) K and a single-ion anisotropy \(D = 8\) K (reflecting the zero-field splitting of the \(3^2T_2\) term of the high-spin 3d⁶ FeII centers in an octahedral field). This exemplifies the efficiency of reduced polyoxomolybdates to act as superexchange ligands, where in the present case the superexchange pathways involve at least six centers and both MoV(4) dimers of the \([\text{Mo}_2]\) framework. The encapsulation of the cluster anion also effectively prevents any significant intercluster exchange interactions. Antiferromagnetic (yet weaker) coupling is also observed for the other magnetic derivatives \([\text{MnII}_{12}\text{MoVI}_{12}]^n\) and \([\text{NiII}_{12}\text{MoVI}_{12}]^n\) in the isostructural series of 2.

An interesting aspect of the encapsulation is that it appears to also cause a high degree of condensation; the relative content of \(\mu_5\) and \(\mu_2\)-oxo ligands is around twice that found for \([\text{Mo}_6\text{V}_4]\)-type Dawson or \([\text{Mo}_6\text{V}_4]\)-type Keggin anions. The significance of the encapsulation for the solid state is furthermore reflected by the very close interaction between surface oxo ligands of the anions present in 1 and 2 and the HMTAH⁺ cations; there are 18 short hydrogen-bonded cluster surface oxygen-to-cation interactions for the anion.
present in 1 and 14 for the anion in 2. These interactions are in the range 2.581(7) ≤ d[E-H]−O(Mo) ≤ 3.140(5) Å, where E = N, C; there are an additional 18 longer contacts for 1 and 10 for 2 in the range 3.157(5) ≤ d[E-H]−O(Mo) ≤ 3.296(3) Å. Furthermore, while the anion layers in 1 are effectively separated from each other by two cation layers, the separation in 2 involves only one cation layer, which permits limited cluster A-cation-cluster B contacts: In 2 the HMTAH+ cations are associated via strong (NH)−O(Mo) hydrogen bonds to cluster A and via weak (CH)−O(Mo) contacts to a neighboring cluster B. This analysis shows that both of the clusters are extensively linked to the HTMAH+ cations via hydrogen bonds; Figure 3 illustrates that the cluster anions are effectively covered, or “shrink-wrapped” by the HTMAH+ cations in the solid state.

Although cation−anion association will be present in solution, encouraged by both electrostatic and hydrogen-bonding effects, the extent of the interactions seen in the solid state also appears to play a crucial role in solution. This is because experiments attempting to synthesize the [Mo16]− cluster under similar reaction conditions (e.g., pH value, concentrations, ionic strength, and temperature), but with different large cations (e.g., [HN(CH2CH2OH)3]2+, [CH3CH2ONa]+, [CH3CH2ONa]2+) result in the formation of well-known spherical-type POM clusters of the Dawson type.[15] Furthermore, the isolation of compounds 1 and 2 is only possible in a narrow pH range (4.0–4.5) at room temperature in the presence of a large excess of HMTAH+ (HTMAH+:[Mo16]− = 60:1). Dissolving compounds 1 and 2 in the presence of different cations appears to result in the decomposition of the cluster anions.[19]

The importance of the encapsulation event in the “shrink-wrapping” synthesis of these clusters is also supported by the fact that there is only one other structural type comprising an [Mo16]− nuclear framework reported previously,[18] [X,Mo16(OH)3]4−(18–20) (where X is Na or H2) but, in contrast to the fundamentally new topology presented here, this [Mo16]− framework is based upon the well-known spherical topology and adopts the high Td symmetry of the inner e-Keggin motif.[21] In this case the highly charged central, compact, and fully reduced [Mo1−] e-Keggin unit is stabilized by the condensation of four corner-sharing Mo6V1O14 units. Although the cluster types in 1 and 2 bear no geometrical resemblance to the e-Keggin-type [Mo16]− ion,[17] in analogy their two [Mo16]− wing fragments are also linked to their backbone fragments exclusively in a corner-sharing mode. Therefore it is interesting to note that the removal of those [Mo16V1O14]− wings would produce an [Mo12]− cluster, yet to be isolated, with the same nuclearity of a classical Keggin ion, but with a new topology for an [Mo12]− fragment (shown in blue in Figures 1 and 2).

In summary, this work demonstrates that it is possible to redefine the structures of lower-nuclearity POMos away from the symmetrical spherical structures. In further work we will attempt to incorporate other types of electrophiles, for example EuIII, in addition to studies that aim to exploit our new cluster topology in the formation of large clusters based on this interesting building block, that utilize the nonspherical nature of this new class of POMo clusters. There are certainly many other interesting structural types to be trapped and characterized using the approach outlined here, and we expect that this will provide access to a fundamentally more diverse set of POMo-based building blocks.

**Experimental Section**

1: Hexamethylenetetraamine (2.2 g, 15.7 mmol) was dissolved in water (20 mL) at room temperature and the resulting solution was acidified with 1.2 mL hydrochloric acid (37%). To the resulting solution Na2MoO4·2H2O (0.96 g, 4.0 mmol) and Na2S2O4 (0.07 g, 0.44 mmol) were added simultaneously while stirring. After addition the color of the solution changed firstly to green, then to yellowish green, and finally to brown (the pH of the solution was 4.0–4.5). The solution mixture was filtered and scaled in a small vial, from which brown crystals of 1 formed over a period of two days in a yield of 0.20 g (18%); all yields calculated based on Mo[10]. IR (KBr disk): υ = 3443, 1631, 1461, 1400, 1378, 1308, 1289, 1253, 1203, 1018, 1009, 978, 926, 817, 794, 658 cm−1; elemental analysis calcd for C36H112Fe2Mo16N24O68: C 11.96, H 3.12, N 9.30; found: C 11.90, H 3.00, N 8.96%. Dissolving compounds 1 and 2 formed overnight. Yield: 0.25 g (28%). IR (KBr disk): υ = 3426, 1637, 1462, 1401, 1384, 1259, 1017, 980, 925, 887, 639 cm−1; elemental analysis calcd for C36H112Fe2Mo16N24O68: C 11.96, H 3.12, N 9.30; found: C 11.90, H 3.00, N 8.96%.

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a) The work presented here is the first example of the isolation of MoV atoms are the only positions that could support a proton. CCDC-205853 (1) and CCDC-205854 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).


[14] The partial charges on O(Mo3) and O(Mo4) were deduced by extended Huckel–MO and preliminary DFT studies and further computational and synthetic work, which examines the nature of the addition of electronegative bond to O(Mo3) and O(Mo4), is ongoing and the results will be reported in due course.
