

Observation and Theoretical Analysis of the “Sensitive Coordination Sites” in the Isopolyoxomolybdate Cluster $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}]^{8-}$

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Two isopolyoxomolybdate $\{\text{Mo}_{36}\}$ cluster compounds are presented, where one incorporates two sodium ions into the $\{\text{Mo}_{36}\}$ cluster cavity and the other does not, showing different “sensitive coordination sites” to organic cation ligands TEAH^+ (protonated triethanolamine) as identified by X-ray crystallography, and rationalized by DFT calculations. The compound $(\text{TEAH})_6\{\text{Na}_2[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}]\} \cdot 28\text{H}_2\text{O}$ (**1**) crystallizes in the triclinic space group $P-1$, $a = 15.8931(2) \text{ \AA}$, $b = 17.3089(2) \text{ \AA}$, $c = 18.1880(3) \text{ \AA}$, $\alpha = 101.210(1)^\circ$, $\beta = 95.481(1)^\circ$, $\gamma = 116.585(1)^\circ$, $V = 4292.95(10) \text{ \AA}^3$, $D_c = 2.688 \text{ g cm}^{-3}$. 16838 unique reflections and 1213 refined parameters were used in structure refinement. $R1 = 0.032$, $R2 = 0.071$. When sodium is eliminated from the reaction system, the new compound $(\text{TEAH})_8[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}] \cdot 10 \text{ H}_2\text{O}$ (**2**) was also isolated and crystallographically characterized. Compound **2** crystallizes in the monoclinic space group $P-1$, $a = 16.3351(3) \text{ \AA}$, $b = 16.5709(4) \text{ \AA}$, $c = 18.5803(5) \text{ \AA}$, $\alpha = 83.330(1)^\circ$, $\beta = 65.010(2)^\circ$, $\gamma = 85.107(2)^\circ$, $V = 4524.08(18) \text{ \AA}^3$, $D_c = 2.525 \text{ g cm}^{-3}$. 17591 unique reflections and 1016 refined parameters were used in structure refinement. $R1 = 0.044$, $R2 = 0.128$.

KEY WORDS: Isopolymolybdate; sensitive coordination sites; self assembly; theoretical studies.

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INTRODUCTION

The formation of clusters based on polyoxometalates (POM) at low pH continues to be of great interest [1]. This is because understanding of the initial mechanism for self-assembly may give rise to routes that can be used to systematically control the overall cluster architecture and properties. Furthermore the 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 clusters and multi-functional materials, which take advantage of the unique physical properties associated with this extraordinary class of molecules [1]. The true enormity of this challenge can be further clarified when one realizes that the main route to synthesize POM clusters (large or small) often employs 'one-pot' reactions [1–4]. One possible route to the goal of designing new clusters is to utilize bulky organic cations to isolate new cluster structure types by virtue of the cations used to 'encapsulate' the new building blocks, thereby limiting their reorganization to simpler structural types, and this approach has recently been adopted by us [5–9].

Herein, we present the synthesis, isolation, crystallographic characterization and theoretical analysis of two new $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}]^{8-}$ clusters decorated with the organic cation, protonated triethanolamine (TEAH), where compound **1** = $(\text{TEAH})_4\{\text{Na}_2[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}](\text{TEAH})_2\} \cdot 28\text{H}_2\text{O} = (\text{TEAH})_4\mathbf{1a} \cdot 28\text{H}_2\text{O}$, and compound **2** = $(\text{TEAH})_6\{[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{14}](\text{TEAH})_2\} \cdot 10\text{H}_2\text{O} = (\text{TEAH})_6\mathbf{2a} \cdot 10\text{H}_2\text{O}$. Here the organic cation does not give rise to a fundamentally new structure type, but ligates to the $\{\text{Mo}_{36}\}$ cluster anion in two possible sites which appear to be manipulated by the complexation of sodium ions within the cluster cavity. Normally, the acidification of an aqueous solution of molybdate under ambient conditions has been shown to yield the $\{\text{Mo}_{36}\}$ type cluster, e.g. $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$, with two $\{\text{Mo}_{17}\}$ groups linked by two $\{\text{Mo}_1\}$ units [10]. It appears that this is the dominant species in solution and the cluster crystallizes readily from solution, see Fig. 1.

EXPERIMENTAL

Preparation of Compounds

Compound **1**: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.8 g, 7.4 mmol) and TEA (1.8 g, 12.0 mmol) were dissolved in H_2O (30 ml). HCl (4 M) was dropped into the solution until the pH decreased to ~ 1.2 and then the mixture was refluxed for 1.5 hrs whereby cooling to room temperature yielded colourless crystals within one hour. Yield 0.42 g (29%, based on Mo). Chemical analysis, Calcd. (found) for $\text{C}_{36}\text{H}_{180}\text{Mo}_{36}\text{N}_6\text{Na}_2\text{O}_{172}$: C 6.22 (6.51), H 2.61 (1.80), N 1.21 (1.08), Na 0.66 (0.93)%. IR (KBr disk) ν/cm^{-1} : 3428 (s, b), 2963 (w),

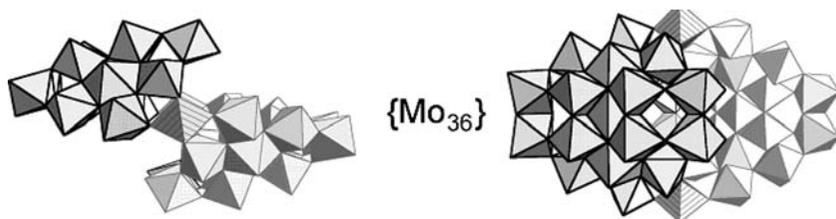


Fig. 1. Polyhedral representation of the classical cluster anion $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$. The MoO_6 octahedra which are connecting the two $\{\text{Mo}_{17}\}$ units shown as hatched polyhedra.

2925 (w), 2874 (w), 1625 (m), 1448 (w), 1385 (w), 1261 (m), 1209 (w), 1095 (m), 1028 (w), 956 (m), 878 (s), 799 (s), 696 (w), 620 (m), 573 (s). Thermal analysis showed 7.6% mass lose up to 110 °C, corresponding to 7.3% calculated for losing the 28 solvated water molecules in **1**. Overall mass lose 24.2% up to 420 °C corresponds to 23.8% calculated for 6 TEAH plus 42 water molecules. Compound **2**: 0.2 g of $(\text{TEAH})_6[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$ [7] was dissolved in 40 ml water in a plastic flask and the blue solution gradually changed to colourless over a period of few weeks. Slow evaporation of the solution to near dryness over several months yielded colourless needle crystals. Yields 0.11 g (59%). $(\text{TEAH})_6[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]$ was chosen as sodium free Mo and TEAH sources (also plastic reaction and crystallization vessels were used). Under these conditions the reduced cluster was oxidized by air gradually and decomposed to form $\{\text{Mo}_{36}(\text{TEAH}^+)_2\}^{6-}$. This strategy to produce **2** takes a long time, especially when crystals good enough for x-ray determination are desired. We are trying to use other sodium free Mo and TEAH+ sources to synthesis **2** quantitatively without waiting for the cluster $[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{6-}$ to oxidize and decompose. Chemical analysis, Calcd. (found) for $\text{C}_{48}\text{H}_{176}\text{Mo}_{36}\text{N}_8\text{O}_{160}$: C 8.38 (7.72), H 2.58 (2.44), N 1.63 (1.50)%. IR (KBr disk) ν/cm^{-1} : 3412 (s, b), 1617 (m), 1447 (m), 1397 (m), 1261 (w), 1207 (w), 1091 (m), 1066 (m), 979 (m), 957 (s), 877 (vs), 788 (s), 689 (s), 625 (s), 574 (s). Thermal analysis showed 3.0% mass lose up to 100 °C, corresponding to 2.6% calculated for losing the 10 solvated water molecules in **2**. Overall mass lose 24.4% up to 430 °C corresponds to 23.7% calculated for 8 TEAH plus 24 water molecules.

X-ray Crystallography

Intensity data collections were carried out on a Nonius Kappa CCD diffractometer equipped with an area detector using Mo-K α monochromatized radiation ($\lambda = 0.71073 \text{ \AA}$), omega scans. The absorption correction

Table I. Crystallographic data collection, intensity measurements and structure refinement parameters for **1** and **2**

Chemical Formula	C ₃₆ H ₁₈₀ Mo ₃₆ N ₆ Na ₂ O ₁₇₂	C ₄₈ H ₁₇₆ Mo ₃₆ N ₈ O ₁₆₀
M (gmol ⁻¹)	6949.68	6879.81
Symmetry	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	15.8931(2)	16.3351(3)
<i>b</i> /Å	17.3089(2)	16.5709(4)
<i>c</i> /Å	18.1880(3)	18.5803(5)
α /°	101.210(1)	83.330(1)
β /°	95.481(1)	65.010(2)
γ /°	116.585(1)	85.107(2)
<i>V</i> /Å ³	4292.95(10)	4524.08(18)
<i>Z</i>	1	1
<i>D</i> _c /g cm ⁻³	2.688	2.525
μ /mm ⁻¹	2.666	2.520
<i>F</i> (000)	3348	3312
crystal size/mm	0.25 × 0.20 × 0.18	0.20 × 0.20 × 0.16
Data collection ranges	1.54 ≤ θ ≤ 26.0	1.66 ≤ θ ≤ 26.0
Number of data measured	55854	63978
Number of unique data	16838	17591
Number of observed data	13997	14511
Number of variables	1213	1016
<i>R</i> 1	0.032	0.044
<i>R</i> 2 (all data)	0.071	0.123
Goodness of fit, <i>S</i>	1.043	1.066
Maximum shift/error	0.001	0.001

was applied using empirical methods [11]. The structures were solved by direct methods and refined by full matrix least-squares using the SHELXTL 97 package. Crystallographic data are given in Table I. Although only few TEAH⁺ units could be unambiguously located, both the elemental analysis, and the bond valence sum analysis of the cluster strongly suggest the presence of six TEAH⁺ cations per cluster in compound **1** and eight in **2**.

RESULTS AND DISCUSSION

In the synthesis presented here the incorporation of TEAH⁺ cations yields the isolation of a {Mo₃₆} cluster anion, **1a**, with two confined sodium ions inside the cluster and two decorating TEAH⁺ ligands outside the cluster, so that **1a** can be represented as {Na₂ ⊂ {Mo₃₆}(TEAH)₂}⁴⁻ and is charge balanced by another four further TEAH⁺ cations. The main body of the {Mo₃₆} cluster consists of two {Mo₁₈} (a {Mo₁₇} and a bridging {Mo₁}

subunit) moieties, which are related by a crystallographic inversion centre with the asymmetric unit comprising only one $\{\text{Mo}_{18}\}$ moiety. The $\{\text{Mo}_{17}\}$ subunit is constructed from the combination of sixteen $\{\text{MoO}_6\}$ pseudo-octahedra and two $\{\text{MoO}_7\}$ distorted pentagonal bipyramids. The $\{\text{Mo}_{17}\}$ subunit can also be described by a $\{\text{Mo}_7\}$ heptamolybdate framework extended along its two ends (each having three further Mo centres attached) and its two sides (each having an edge-sharing dimer), see Fig. 1. The heptamolybdate framework's two ends are exactly the positions of the $\{\text{MoO}_7\}$ distorted pentagonal bipyramid centres. This $\{\text{Mo}_{17}\}$ framework has interestingly a C_{2v} symmetry and is a basic building blocks in forming high nuclearity molybdate clusters like $\{\text{Mo}_{142}\}$, $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{176}\}$ [1–4].

In contrast to the archetypal $\{\text{Mo}_{36}\}$ reported previously, cluster anion **1a** supports 14 rather than 16 water ligands. This was confirmed by bond valence sum analysis and the difference is due to the fact that two of the 16 possible sites are coordinated by the one of the hydroxyl groups on the TEAH^+ ligand in **1a**, see Fig. 2.

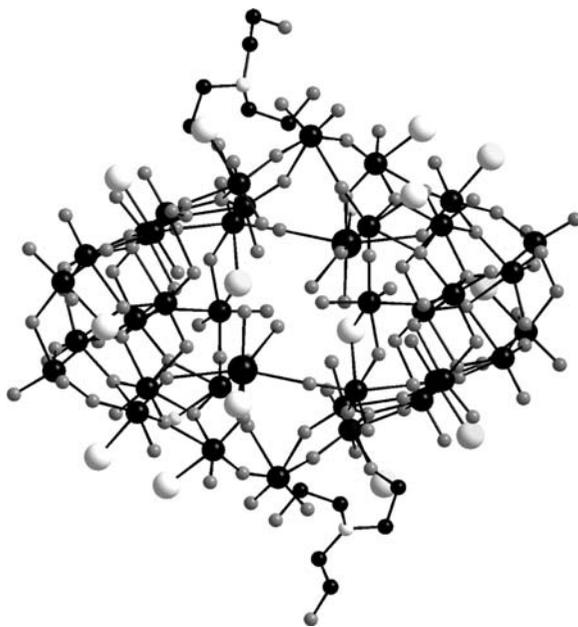


Fig. 2. Ball and stick representation of the cluster anion, **1a**, found in compound **1**. The Na ions are shown as large black spheres, the Mo ions as medium black spheres, the oxo ligands as grey spheres, C atoms as small black spheres, N atoms as small white spheres and the water ligands as large white spheres and this colour scheme will be used throughout.

The sodium ions are coordinated to the inner wall of the cluster cavity in a seven-coordinate environment with 4 oxo ligands being donated from the cluster (Na \cdots O range: 2.41–3.02 Å), and the coordination sphere is completed by the coordination of three water molecules (Na \cdots O range: 2.38–2.70 Å), see Fig. 3. Each sodium cation is ligated by the terminal oxo ligands associated with the bottom part of two of the four $\{\text{Mo}_6\}$ pentagonal building blocks present in the $\{\text{Mo}_{36}\}$ cluster type.

The cluster anion, **2a**, found in compound **2** in contrast is not formed by the a self-assembly process from sodium molybdate in the presence of TEAH^+ , but from the oxidation and decomposition of the TEAH^+ salt of the sulfite-based Dawson-like cluster, $(\text{TEAH})_6[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]$, [7] which was chosen as a sodium free Mo and TEAH sources (also plastic reaction and crystallization vessels were used). Under these conditions the reduced cluster was oxidized by air gradually and decomposed to form $\{\text{Mo}_{36}(\text{TEAH}^+)_2\}^{6-}$ (**2a**), which is then charge balanced by six further TEAH^+ cations, see Fig. 4, and the 5 Å wide central cavity is occupied by solvent water molecules. Indeed we found that the Dawson-like cluster, $\{\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2\}$, can only be obtained as its reduced form in the presence of TEAH^+ cations. Non-reduced systems all produce Mo36 clusters regardless if Na cations exist or not [7].

Careful examination shows that the coordination sites occupied by the TEAH^+ cations are both located on one edge of the pentagon in the $\{\text{Mo}_{17}\}$ subunits in **1a** and **2a** (Fig. 5). In order to explore whether the positioning of the two TEAH^+ ligands on the $\{\text{Mo}_{36}\}$ anions is effectively controlled by the coordination of Na^+ cations or whether the coordination sites result from crystal lattice packing effects, Density Functional Theory (DFT)

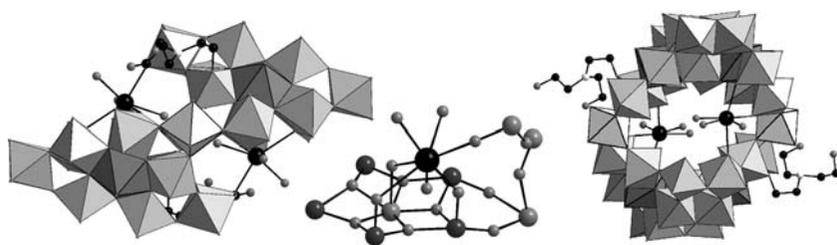


Fig. 3. LHS / RHS show a polyhedral representation of the cluster anion, **1a**, found in compound **1** with the two coordinated sodium cations and two ligated TEAH^+ ligands shown in ball and stick. The middle representation shows the immediate coordination environment around the sodium cation with the four oxo ligands coming from the cluster anion and three water ligands. The coordination environment is characterized by five shorter contacts and two longer ones: Na-O71 = 2.337(5), Na-O85 = 2.378(9), Na-O52 = 2.409(4), Na-O86 = 2.445(16), Na-O34 = 2.479(4), Na-O74 = 2.698(5), Na-O32 = 2.748(4).

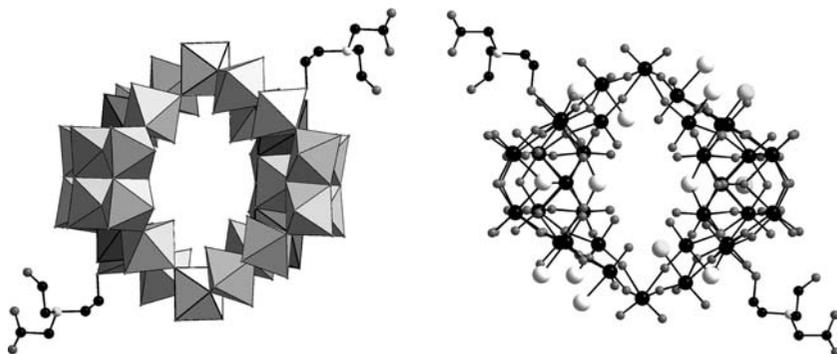


Fig. 4. LHS shows a polyhedral representation of the cluster anion, **2a**, found in compound **2** with the two ligated TEAH⁺ ligands shown in ball and stick. Right middle representation shows the whole structure in ball and stick with the water ligands highlighted as large white spheres.

calculations[12] on both {Mo₃₆} cluster anions were performed to establish charge densities – as the role of the sodium cation is limited mostly to charge polarization, a set of arguments was established from simple charge distribution effects.

First, one has to explore if the actual coordination site of the sodium cation in **1a** is determined by the coordination site of the TEAH⁺ ligand. However, calculations on **2a** and on **1a** with the [Na(OH₂)₃]⁺ group removed clearly indicate that, while small charge differences are observed for the three terminal oxo groups to which the Na⁺ cation eventually binds (only taking Na–O contacts <2.75 Å into account; see Fig. 5b) in **1a**, their values add to the same total charge (Σ: –0.44) regardless of the site of the TEAH⁺ coordination. Although the Na⁺ cation could also occupy other positions in the interior “pockets” of the two convex halves of the {Mo₃₆} framework that allow coordination to a different set of three terminal oxo groups, all of these sets yield a decreased total charge (with charge sums of up to –0.40) and thus a decreased electrostatic binding energy, rendering the Na⁺ position observed in **1a** the energetically most optimal.

Calculations on **1a** and **2a** with the TEAH⁺ ligands replaced by water molecules then yield charge distributions for the molybdenum centres which indicate that the coordination sites of the TEAH⁺ ligands are indeed subject to these charge variations: Out of all Mo positions to which water ligands can coordinate, the Mo position A (and its symmetry equivalent, see Fig. 5b), i.e. the position to which TEAH⁺ coordinates in **1a**, is found to be most electrophilic with a charge of +0.465 in {**1a**+2H₂O}, compared to charges in the range of +0.338 to +0.391 for the other Mo(OH₂) positions.

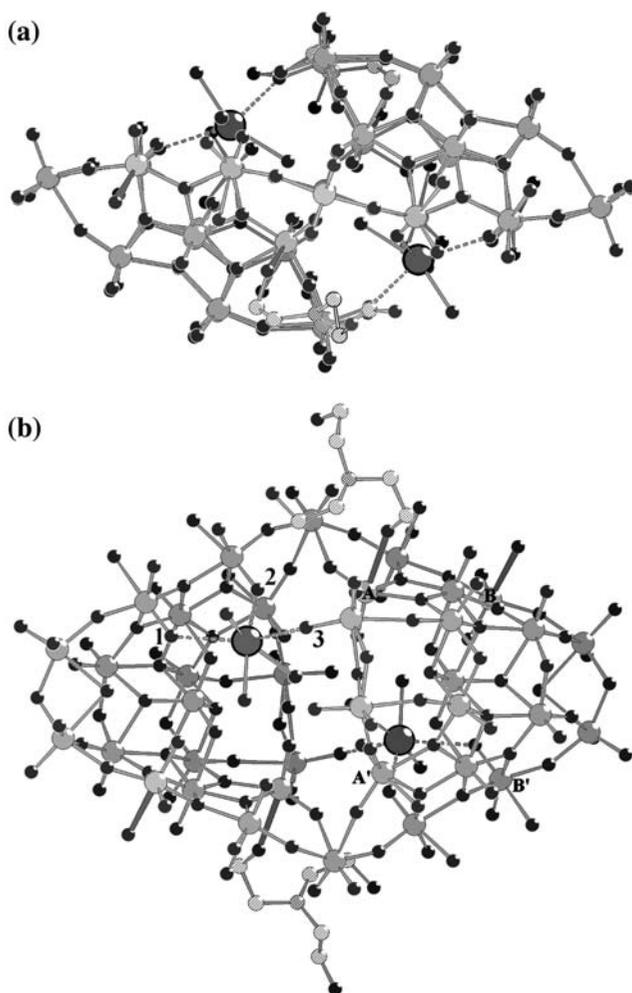


Fig. 5. Perpendicular ball-and-stick representations of the structure of the cluster anion **1a**. (Mo: grey spheres, O: dark grey small spheres, C: white hatched spheres, N: white cross-hatched spheres, Na: black-bordered large spheres). (a) Illustration of the binding modes of the two $[\text{Na}(\text{OH}_2)_3]^+$ groups that are embedded into the “pockets” of the $\{\text{Mo}_{36}\}$ structure. Each Na^+ cation binds to three terminal oxo positions of the polyoxomolybdate (dashed bonding lines). (b) Illustration of the binding sites of the TEAH^+ ligands in clusters **1a** and **2a** respectively (Mo position A, hatched with white lines, for **1a**, Mo position B, cross-hatched with white lines, for **2a**). Positions A and B (and their symmetry equivalents A' and B') correspondingly represent the most electropositive Mo centres in **1a** and **2a**, respectively, that can ligate H_2O molecules. The three terminal oxo positions to which one of the two Na^+ cations binds are designated as 1, 2, and 3. This coordination mode results in the maximum electrostatic binding interaction, independent of TEAH^+ coordination.

For $\{2\mathbf{a} + 2\text{H}_2\text{O}\}$, the spread of Mo charges is less pronounced but Mo position B (Fig. 5b) results as most electrophilic, with a charge of +0.402 compared to charges ranging from +0.339 to +0.369 for the remaining Mo positions that are available for an $\text{H}_2\text{O} - \text{TEAH}^+$ exchange.

In summary, the coordination modes of the TEAH^+ ligands in $\mathbf{1a}$ and $\mathbf{2a}$ can be understood and predicted on basis of the electronic structure and charge distribution of the cluster anions that themselves are modified by the coordination of Na^+ cations, i.e. by the associated charge-polarizing effects and the resulting small geometry distortions. Therefore, the addition of sodium cations can be seen to “switch” the coordination sites of the TEAH^+ ligand. In further work we will attempt to use and extend this theoretical approach to help direct new synthetic strategies towards new POM and ligand-POM architectures.

SUPPLEMENTARY MATERIALS AVAILABLE

Crystallographic data for the structural analysis of compounds $\mathbf{1}$ and $\mathbf{2}$ has been deposited with the Cambridge Crystallographic Data Centre, CCDC refs 292391 and 292392. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (int. code) +44(1223) 336-033 or email: deposit@ccdc.cam.ac.uk or [www.http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)].

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12. Computational details: DFT calculations were performed on isolated cluster anions using the TURBOMOLE 5.7 program package (O. Treutler, R. Ahlrichs (1995). *J. Chem. Phys.* **102**, 346) employing TZVP basis sets and hybrid B3-LYP exchange/correlation functionals. In a first step, hydrogen positions of H₂O ligand groups were modelled onto the crystallographic coordinates of the {Mo₃₆} anions **1a** and **2a** whereby molecular C_i symmetry was maintained. These coordinates were then allowed to relax until the total DFT energies converged, this resulted in maximum deviations smaller than 0.04 Å from the initial crystallographic coordinates. Atomic point charges were derived from the such-obtained final geometries using the Löwdin formalism. The use of the COSMO solvation model to account for continuum polarization effects in aqueous solution significantly and evenly decreased the energies of the frontier orbitals but did not significantly affect the charge distributions.