A three-dimensional adamantane-like nanoscopic cage built from four iodide-bridged triangular \( \text{Mo}_3\text{S}_7 \) cluster units

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Chemical oxidation of a \( \text{Mo}_3\text{S}_7 \) cluster featuring catecholate ligands, namely \([\text{Mo}_3\text{S}_7(\text{Cl}4\text{cat})_3]_2^2\) (\(\text{Cl}4\text{cat} = \text{tetrachlorocatecholate} \)), allows the isolation of a unique nanoscopic molecular cage made of four iodide-bridged \( \text{Mo}_3\text{S}_7 \) clusters as the kinetically favoured product.

Metal-directed self-assembly is a versatile synthetic approach to produce discrete three dimensional polyhedral or cage compounds. Metal centers bring a variety of coordination sites and bond angles to a supramolecular framework, and in combination with different bridging ligands provide great versatility for chemical and structural modification of the inner cavity. Recently, the use of multi-nuclear systems with labile positions (for example dimeric \( \text{M}_2 \), where \( \text{M} = \text{Mo, Rh} \)) to build 3D supramolecular cages has also been explored, and new perspectives have been obtained on the facility for fine tuning the net charge, the magnetic properties and the electronic communication between the metal units.

In this context, the family of triangular \([\text{Mo}_2(\mu_3\text{S})-(\mu_2\text{S}_2)X_3]_2^2 \) (\(X = \text{halide} \)) clusters are promising candidates as building blocks for multi-nuclear aggregates. This is due to the presence of two labile binding sites in a \textit{cis} configuration (an \(X-\text{Mo-X} \) angle of ca. 90°, see Scheme 1a), which can be easily occupied by a wide spectrum of ligands. In addition, ligand substitution in the \([\text{Mo}_3\text{S}_7X_6]_2^2\) dianion can be carried out selectively, affecting all six halide ligands or only the three halides \textit{cis} to the \( \mu_2\text{S} \) sulfur atom, demonstrating the geometry-guiding versatility of the metal centers (see Scheme 1b and c). Therefore, the \( \text{Mo}_3\text{S}_7 \) cluster can be regarded as a tritopic building block to construct convex corners in tetrahedral symmetry-like supramolecular capsules or cages that enclose an isolated nanospace. To date, all molecular architectures based on \( \text{Mo}_3\text{S}_7 \) cluster entities possess 1 or 2D character (open structures), including the well known polymeric \([\text{M}_3\text{S}_7X_2X_4]n\) solid phases (\( \text{M} = \text{Mo, W} \)), where each \( \text{Mo}_3\text{S}_7 \) unit is covalently linked to its neighbors through four halide bridges forming zigzag chains. Herein, we report the synthesis of a novel 3D cage based on a dodecanuclear \( \text{Mo}_{12} \) complex adopting an adamantanoid structure built from four trinuclear \( \text{Mo}_3\text{S}_7 \) entities bridged by six \( \mu_1\text{S} \) atoms and encapsulating one iodide anion. This discrete cluster was first obtained as an unexpected product, but a detailed study has since revealed the experimental factors leading to its efficient self-assembly.

In recent years, our research interests have focused on the coordination of redox-active ligands such as 1,2-dithiolenes to the trinuclear \( \text{Mo}_3\text{S}_7 \) cluster, to afford diionic \([\text{Mo}_2(1,2-\text{dithiolene})\text{S}_7]_2^2 \) complexes, which after chemical or electrochemical oxidation afford single-component conductors. During the course of this work we have explored the coordination chemistry of 1,2-dioxolenes. The compound \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7(\text{Cl}4\text{cat})_3]_2 \) (\(\text{Cl}4\text{cat} = \text{tetrachlorocatecholate} \)) is prepared in high yield by treatment of \((\text{PPh}_4)_3[\text{Mo}_3\text{S}_7\text{I}_3]_4\) with an excess of \( \text{Cl}4\text{catH}_2 \) in the presence of triethylamine. Unexpectedly, the slow diffusion of an excess of iodine into \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\) solutions produces \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4(\mu_1\text{I})_1\text{I}(\text{PPh}_4)_2\) (Scheme 1). Optimal conditions for its preparation were found using a 3 : 1 iodine to \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\) (ca. 40%). The use of low iodine to \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\) ratios (typically below 3 : 1) reduced the yield of \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\), while the use of higher ratios did not improve the yield. On the basis of the ratios of \( \text{Mo}_3\text{S}_7 : I_2 \) used for optimal preparation of \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\), the proposed stoichiometry is shown in eqn (1).

\[
4(\text{PPh}_4)_2[\text{Mo}_3\text{S}_7(\text{Cl}4\text{cat})_3]_2 + 12\text{I}_2
\rightarrow (\text{PPh}_4)_3[[\text{Mo}_3\text{S}_7(\text{I}_3)_4(\mu_1\text{I})_1]\text{I} + 5\text{PPh}_4\text{I} + 3\text{Cl}4\text{cat}
\]

The molecular structure of \((\text{PPh}_4)_2[\text{Mo}_3\text{S}_7\text{I}_3]_4\) has been determined by X-ray crystallographic methods. The compound crystallizes in the acentric cubic space group \(P43\) and is comprised of dodecanuclear triion units built from four \( \text{Mo}_3\text{S}_7 \) trinuclear clusters (Fig. 1). The repeating metal core can be written as \( \text{Mo}_3\text{S}_7\text{I}_3\text{I}_3\), where three bridging iodines connect the trinuclear \( \text{Mo}_3\text{S}_7 \) units. Each trinuclear unit consists of an equilateral \( \text{Mo}_3 \) triangle capped by a \( \mu_1\text{S}^2 \) atom that lies above the \( \text{Mo}_3 \) plane.
and axial positions (S_{ax}, labeled S(1)) located out of the metal plane, highlighting the fact that Cl\textsuperscript{4cat} to iodide replacement is this behaviour. From this, the Mo\textsubscript{3Q7} cores derive the ability simple procedures and gives high yields, which is ascribed to pointed out that metal-directed self-assembly typically involves sulfur atoms\textsuperscript{interstitial} iodide–anion close to the “electrophilic” axial positions (S_{ax}, those labeled S(2)), essentially in the Mo\textsubscript{3} plane, and axial positions (S_{ax}, labeled S(1)) located out of the metal plane. Two iodide ligands fill the remaining two positions of the seven-coordinate molybdenum atoms and are oriented almost perpendicular to the Mo\textsubscript{3} plane. The bridging iodides define the octahedral assembly of a discrete molecular cage that closely resembles an adamantane-like structure. This octahedron circumscribes two different cuboctahedrons defined by the 12 S_{ax} or S_{eq} atoms (see Fig. S2\textsuperscript{w}) and also the tetrahedron defined by the centroids of the four Mo\textsubscript{3} units.\textsuperscript{8}

The formation of the discrete dodecanuclear cluster ([PPh\textsubscript{4}]\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} is unprecedented despite the rich structural chemistry of Mo\textsubscript{3}Q\textsubscript{7} complexes (Q = S, Se). Mo\textsubscript{3}Q\textsubscript{7} (Q = S, Se) based supramolecular aggregates are ubiquitous in the solid state owing to the prominent electrophilic character of the three axial sulfur atoms. In the present work, the presence of PPh\textsubscript{4}X (X = Cl, Br) salts and we observed that the tetrahedral configuration of the Mo\textsubscript{3}S\textsubscript{7} clusters around the iodide-templating atom. To evaluate this possibility we have carried out the reaction of the starting (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} complex; the trinuclear (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} compound being obtained instead in an almost quantitative yield.\textsuperscript{†} This distinctive reactivity represents a unique example where two different products, (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} and (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2}, can be isolated under a set of experimental conditions that differs in the rate of Cl\textsuperscript{4cat} oxidation. We thus suggest that slow iodine oxidation of (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} yields, after a relatively short reaction time, the adamantane-like cage ([PPh\textsubscript{4}]\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2}, which can be trapped from the reaction mixture as the PPh\textsubscript{4}I\textsuperscript{−} salt. Conversely, the trinuclear (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} is obtained after prolonged heating and therefore represents the thermodynamically favoured product (see Scheme 2).

We have also investigated the effect of the counter-cation as the structural template for the formation of the (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} complex. Oxidation of other salts of the I\textsuperscript{−} cluster, such as the n-But\textsubscript{4}N\textsuperscript{+}, Et\textsubscript{4}N\textsuperscript{+} or PPN\textsuperscript{+} (PPN = bis(triphenyl-phosphine)-iminium) salts did not lead to the characteristic crystallization of the 2\textsuperscript{−} cage complex. Only substitution of PPh\textsubscript{4} by the topologically related AsPh\textsubscript{4} cation afforded, upon reaction with iodine, the isostructural (AsPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} cage species, as confirmed by their solid state UV-vis spectra and XPD patterns.\textsuperscript{†} This result is a good indication that the solubility of the cage is affected by the presence of PPh\textsubscript{4} or AsPh\textsubscript{4} cations, which do “intercept” (and precipitate) the 3D cage complex. Finally, it is also reasonable to hypothesize that the S_{ax}⋅⋅⋅I_{interstitial} interaction observed in the solid state structure of 2\textsuperscript{−} might play a significant role at pre-organizing the tetrahedral configuration of the Mo\textsubscript{3}S\textsubscript{7} clusters around the iodide-templating atom. To evaluate this possibility we have carried out the reaction of the starting (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} with I\textsubscript{2} in the presence of PPh\textsubscript{4}X (X = Cl, Br) salts and we observed that the characteristic appearance of single-crypts of (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} was dramatically reduced. This suggests that the non-covalent S_{ax}⋅⋅⋅I_{interstitial} interaction plays an important role in promoting the self-assembly of the 3D (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} cage. A closely related example that emphasizes the importance of this S_{ax}⋅⋅⋅I_{interstitial} interaction has been recently reported, namely [Mo\textsubscript{3}S\textsubscript{7}(dtp)\textsubscript{3}]\textsubscript{4}−{I(HgI\textsubscript{3})\textsubscript{3}} in which four Mo\textsubscript{3}S\textsubscript{7} clusters with dithiophosphate ligands are arranged around an interstitial iodide atom.\textsuperscript{10}

The thermal stability of compounds (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} and (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} upon heating are very similar, with basically flat TG-DTA curves up to ca. 300 °C and hence a remarkable thermal stability. At higher temperatures, between 300 and 600 °C, exothermic processes occur with mass losses of ca. 65% (for (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} and 60% (for (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2}). Furthermore, XPD experiments at different temperatures for compound (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} showed a gradual loss of crystallinity starting from 250 °C to yield an amorphous solid above 300 °C. Both TG-DTA and XPD measurements rule out a plausible interconversion from (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} to (PPh\textsubscript{4})\textsubscript{2}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} in the solid state.

Compound (PPh\textsubscript{4})\textsubscript{3}[Mo\textsubscript{3}S\textsubscript{7}I\textsubscript{6}])\textsubscript{2} is not soluble in common organic solvents (toluene, CHCl\textsubscript{3}, tetrahydrofuran, CH\textsubscript{3}CN, CH\textsubscript{3}OH).
It slowly dissolves in dimethylformamide under stirring to give an orange solution whose UV-Vis spectrum is identical to that of complex (PPh₄)₃[Mo₃S₇I₅] (PPh₄)₃[Mo₃S₇I₆] in dimethylformamide recorded at different time intervals are shown in Fig. 2.

Initially, the presence of the hexanuclear [Mo₆S₁₄I₉]⁻ species is observed (Fig. 2a, top) to finally disappear after ca. 20 min. It is reasonable to hypothesize that aggregate [Mo₆S₁₄I₉]⁻ is an intermediate species resulting from the disruption of the cage 2⁻. ESI mass spectra also show additional trimuclear [Mo₅S₇I₆]⁻ (m/z = 1145.9), [Mo₄S₇I₇]⁻ (m/z = 1021.1) and [Mo₃S₇I₃]⁻ (m/z = 892.2) anions, as well as [Mo₅S₇I₆]²⁻ (m/z = 637.5) dianions, which are also observed upon ESI of (PPh₄)₃[Mo₃S₇I₉] under identical conditions.

In summary, we report the first example of polyhedral molecules assembled from trimuclear corner pieces and iodide linkers which were obtained via spontaneous self-assembly. It is clear that in the self-assembly of complex architectures, a number of kinetic products may appear before formation of the thermodynamic product(s). In the present system, both the kinetic and thermodynamic products have been successfully isolated and characterized, mainly because of their distinctive solubility. It is shown that iodine oxidation of the dioxolene [Mo₅S₇(Cldcat)]³⁻ complex forms the thermodynamically stable [Mo₅S₇I₆]²⁻ (3⁻) dianion by way of a metastable adamantine-like cage trianion, namely 2⁻, which can be intercepted flightingly as a PPh₄⁻ and AsPPh₄⁻ salt. Besides the importance of the counter-cation, our results also reveal that the presence of iodide either as bridging-ligands or interstitials play a crucial role in the self-assembly of the 3D (PPh₄)₂[Mo₃S₇I₉] cage.

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Notes and references

† Crystal data. For (PPh₄)₂[Mo₃S₇I₉]: C₇₇H₸₂Cl₄Mo₃O₄P₃S₁₉, M = 2013.49, monoclinic, space group P2₁/c, a = 20.565(4) Å, b = 25.840(5) Å, c = 14.510(3) Å, β = 99.27(3)°, V = 7610(3) Å³, Z = 4, T = 293(2) K, 42,587 reflections measured, 13,370 unique (Rint = 0.1044). Final R = 0.0633 (I > 2σ(I)) and wR = 0.1857 (all data). For (PPh₄)₃[Mo₆S₁₄I₉]·2MeCN−: C₅₇H₴₄Cl₄Mo₉O₆P₃S₁₉, M = 5594.33, cubic, space group P4₃n, a = 19.086(4) Å, V = 6953(3) Å³, Z = 2, T = 100(2) K. 51,071 reflections measured, 2278 unique (Rint = 0.0808). Final R1 = 0.0532 (I > 2σ(I)) and wR = 0.1275 (all data). For (PPh₄)₃[Mo₃S₇I₅]: C₄₈₈H₴₂Cl₅I₉Mo₃P₃S₁₉, M = 1994.84, monoclinic, space group P2₁/c, a = 18.519(1) Å, b = 20.911(1) Å, c = 17.268(9) Å, β = 106.822(1)°, V = 6401.06 Å³, Z = 4, T = 293(2) K. 42,209 reflections measured, 14,670 unique (Rint = 0.0454). Final R = 0.0391 (I > 2σ(I)) and wR = 0.1294 (all data). CCDC 713962 for (PPh₄)₃[Mo₃S₇I₉] and 713963 for (PPh₄)₃[Mo₃S₇I₅].