

Electronic Supporting information

A Three Dimensional Adamantane-like Nanoscopic Cage Built from Four Iodide-Bridged Triangular Mo₃S₇ Cluster Units

Larry R. Falvello,^a Rosa Llusar,^{*b} Sonia Triguero^b and Cristian Vicent^{*c}

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Experimental Section

Elemental analyses were performed on an EA 1108 CHNS microanalyzer. Uv-vis spectra were recorded in the 300-800 cm^{-1} range using a VARIAN UV/vis spectrophotometer (model CARY 500 SCAN) using dimethylformamide as solvent or dispersed on KBr. IR spectra were recorded on a Perkin- Elmer System 2000 FT-IR using KBr pellets. TGA/SDTA analysis were measured on a Mettler Toledo 851e instrument in the 25–600 $^{\circ}\text{C}$ range in air or N_2 at 10 $^{\circ}\text{C}/\text{min}$. Powder X-ray (PXR) diffraction measurements were carried out on samples heated at 25, 100, 200 and 300 $^{\circ}\text{C}$ on a SIEMENS D5000 diffractometer using $\text{Cu-K}\alpha$ radiation. Electrospray ionization mass spectra were recorded on a Q-TOF Premier mass spectrometer with an orthogonal Z-spray electrospray interface (waters, Manchester, UK) operating in the W mode at a resolution of ca. 17000 (FWHM). The cone voltage (U_c) was set at 30 V unless otherwise stated, using ca. 5×10^{-5} M dimethylformamide: CH_3CN (50:50) sample solutions. For the ESI-MS analysis of compound $(\text{PPh}_4)_3[\mathbf{2}]$, it was stirred in dimethylformamide, a portion of the slurry was extracted, filtered, diluted with CH_3CN and a negative-ion mass spectrum collected. The reaction solution was reexamined at 5 min intervals until no change in solution speciation was observed. The chemical composition of each peak was determined by comparison of experimental and calculated isotopic patterns with the theoretical using the MassLynx 4.1 program.

Synthesis

Compounds $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ was prepared as described in the literature.¹ The reactants were obtained from commercial sources and used as received.

Preparation of $(\text{PPh}_4)_2[\text{Mo}_3\text{S}_7(\text{tcc})_3]$ ($(\text{PPh}_4)_2[\mathbf{1}]$): A solution of Et_3N (150 μL , 1 mmol) and tetrachlorocatechol (Cl_4catH_2) (0.12 g, 0.5 mmol) in acetonitrile (15 mL) was allowed to react for 15 min. After that, $(n\text{-Bu}_4\text{N})_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ (0.23 g, 0.15 mmol) was added to the reacting solution and stirred during 12 hours. The resulting solution was evaporated to dryness,

redissolved in MeOH and filtrated. PPh₄Br was added to the filtered solution and the desired compound (PPh₄)₂[1] precipitated as a dark powder. The precipitate was separated from the solution by filtration, washed thoroughly with MeOH and diethylether and recrystallized from CH₂Cl₂/MeOH mixtures (0.29 g, 83 %). (Found: C, 39.59; H, 2.26, S 10.73, N 1.96. Mo₃S₇O₆Cl₁₂C₆₆H₄₀P₂ requires C, 41.10; H 2.09, S 11.64, N 1.98). IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 1434 (s, C-O_{catechol}), 1253(s), 1108 (s), 974 (s), 808 (s, C-Cl), 528 (m, S_{eq}-S_{ax}), 334 (w); ESI-MS(-) *m/z*: 624.2 [M]²⁻.

Compounds of general formula (Cat)₂[1] (Cat = n-Bu₄N⁺, Et₄N⁺, AsPh₄⁺ and PPN⁺) were prepared following a similar procedure to that described for (PPh₄)₂[1] except that precipitation was carried out by adding CatBr instead of PPh₄Br.

Preparation of (PPh₄)₃{[Mo₃S₇I₃]₄(μ -I)₆I} ((PPh₄)₃[2]): Slow diffusion of a 0.1 M solution of I₂ in acetone (1.5 mL, 0.15 mmol) to a red-dark solution of (PPh₄)₂[Mo₃S₇(Cl₄cat)₃] ((PPh₄)₂[1]) (0.1 g, 0.05 mmol) in dichloromethane (10 mL) gave needle brown crystals that were washed thoroughly with dichloromethane and acetone and characterized as (PPh₄)₃[2] (0.025 g, 37 %). (Found: C, 17.30; H, 1.47; Mo₁₂S₂₈I₁₉C₇₈H₇₂P₃O₂ requires C, 16.74; H 1.30). IR (KBr) cm^{-1} : 548 (m, S_{eq}-S_{ax}), 344 (w).

Compound (AsPh₄)₃{[Mo₃S₇I₃]₄(μ -I)₆I} ((AsPh₄)₃[2]) was prepared in a similar way by slow diffusion of a solution of I₂ to a solution of (AsPh₄)₂[Mo₃S₇(Cl₄cat)₃] ((PPh₄)₂[1]) in dichloromethane to give needle brown crystals that were washed thoroughly with dichloromethane and acetone and characterized as (AsPh₄)₃[2]. Elemental analysis, absorption spectra as well as PXR diffractogram (see figures S3 and S6 below) suggest that both (PPh₄)₃[2] and (AsPh₄)₃[2] are isostructural.

Preparation of (PPh₄)₂[Mo₃S₇I₆] ((PPh₄)₂[3]): I₂ (0.1 M in acetone 1.5 mL, 0.15 mmol) and a solution of (PPh₄)₂[Mo₃S₇(tcc)₃] ((PPh₄)₂[1]) (0.1 g, 0.05 mmol) in dichloromethane (10 mL) were stirred under reflux conditions. The characteristic precipitation of compound (PPh₄)₃[2]

was not observed. The resulting orange solution was taken to dryness, washed with methanol, diethylether and recrystallized from CH₂Cl₂/ether to yield single crystals of compound (PPh₄)₂[**3**] (0.045 g, 46 %). (Found: C, 29.22; H, 2.27; Mo₃S₇I₆C₄₈H₄₀P₂ requires C 29.53; H 2.07); IR (KBr) cm⁻¹: 538 (m, S_{eq}-S_{ax}), 329 (w). ESI-MS(-) *m/z*: 636.4 [M]²⁻, 892.2 [M - 3I]⁻, 1021.1 [M - 2I]⁻ and 1145.9 [M - I]⁻.

X-ray Crystallography

(PPh₄)₂{Mo₃S₇(Cl₄cat)₃} ((PPh₄)₂[1**]) and (PPh₄)₂[Mo₃S₇I₆] ((PPh₄)₂[**3**]):** The crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxy cement. X-Ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo-Ka radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The data were collected with a frame width of 0.3 in ω at a crystal to detector distance of 4 cm. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.^{2, 3} The structures were solved by direct methods and refined by the fullmatrix method based on F2 using the SHELXTL software package.⁴ The nonhydrogen atoms of the cluster in structures (PPh₄)₂[**1**], (PPh₄)₂[**3**] were refined anisotropically; the positions of all hydrogen atoms of tetraphenylphosphonium cations were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. Bond distances of carbon atoms involving the C(106)-C(111) phenyl ring had to be constrained to a fixed value (typically ca. 1.38 Å) which corresponds to usual C-C_{phenyl} bond distances. The last difference Fourier map showed the presence of one molecule and half a molecule of CH₂Cl₂ in structure (PPh₄)₂[**1**] and (PPh₄)₂[**3**], respectively which were refined isotropically under rigid conditions. Hydrogen atoms from the solvent molecules were also included in the refinement.

(PPh₄)₃{[Mo₃S₇I₃]₄(μ -I)₆I} ((PPh₄)₃[2**]):** Several sets of diffraction data were gathered, each from a different sample. All of the samples were irregularly shaped frond-like masses which,

nevertheless, produced single-crystal diffraction patterns. The diffraction was weak in all cases, and all of the data sets had several features in common. In all cases the average intensity in resolution shells fell rapidly at about 1 Å resolution. All cases presented a pronounced pseudo-absence for I-centering. The refinement that we report here was based on the strongest diffraction data set that we obtained, which was measured using a SMART Apex diffractometer with Mo radiation. Frames of 0.3° depth in ω were measured for 60 sec each. Successful resolution and refinement of the structure were achieved using space group P(-4)3n; but since the path to this result was not straightforward, we will describe the structure solution in detail. After integration of the intensity data, the 61815 reflections in the data set had a mean $I/\sigma(I)$ value of 4.31; and the 30880 reflections with $(h + k + \ell) \neq 2n$ presented an average $I/\sigma(I)$ of 1.0, with a mean intensity of 7.2 as compared to a mean intensity of 84.9 for the entire data set (on an arbitrary scale). Only 1997 of the $(h + k + \ell)$ -odd reflections had $I/\sigma(I) > 3.0$.

With this ambiguity in the systematic absences, we first solved the structure using space group I(-4)3m, a choice reflecting the supposition that the 'majority absences' were real rather than pseudo-extinction conditions, with minor intensity obtained through any of several possible mechanisms -- twinning and disorder among them. It was possible to refine a structural model to values of $R1 = 0.0668$ and $wR2 = 0.2173$, but the chemical results were unusual enough to raise suspicions. The model described a novel cluster of formula $\{[Mo_3(\mu-S_2)_3(\mu_3-S)I_3]_4(\mu_2-I)_6I\}^{3-}$, which turned out to be correct, with charge balanced by a polymer which, from the crystallographic model, appeared to have formed by condensation of $(PPh_4)^+$ to form a 3-D net that encapsulated the anionic cluster. In addition to the highly unusual nature of the polymeric cation, some P-C distances were greater than 2 Å -- another source of suspicion. Accordingly, the symmetry was reduced to I23, a subgroup of I(-4)3m that does not possess any four-fold symmetry. Resolution using this group was straightforward, but produced equally suspect

chemical results with acceptable crystallographic indicators, namely $R1 = 0.0613$ and $wR2 = 0.1653$. The absolute structure parameter refined stably to a reasonable value of $0.06(7)$.

In light of the doubts that persisted about the nature of the result, the symmetry was further reduced, this time removing the body-centering and the three-fold axes -- which gave the orthorhombic subgroup $P222$. Again, the structure was solved without complication using direct methods, revealing the same novel Mo-containing cluster; but this time three units of the more credible cation $(PPh_4)^+$ emerged in the structural model instead of the more exciting, less credible 3-dimensional polymer. This structural model was submitted to Platon for "missed symmetry" analysis, which revealed space group $P(-4)3n$ as the maximal description of the symmetry of the structure. This group, $P(-4)3n$, is the maximal *klassengleiche* subgroup of the first spacegroup used, the pseudosymmetric $I(-4)3m$. The immediate use of this group after the first suspicious solution would have saved one step in the correct resolution of the structure.

The trianionic dodecanuclear cluster $\{[Mo_3(\mu-S_2)_3(\mu_3-S)I_3]_4(\mu_2-I)_6I\}^{3-}$ occupies a special position of symmetry 23 (Wyckoff symbol $2a$), with multiplicity 2, while the cation $(PPh_4)^+$ occupies a site of symmetry (-4) (Wyckoff $6d$), with multiplicity 6. A disordered acetone molecule was located on a 3-fold axis and refined with total residue multiplicity of 4. Thus, the formulation derived from the structural model is $(PPh_4)_3\{[Mo_3(\mu-S_2)_3(\mu_3-S)I_3]_4(\mu_2-I)_6I\}\cdot 2Me_2C=O$, with $Z = 2$.

Refinement of Solvent Acetone Disorder Assembly. Atomic sites describing a disordered, partially occupied acetone molecule were found in voids whose volume was calculated by Platon⁵ to be 138 \AA^3 . Since a molecule of acetone is calculated⁶ to require some 83.5 \AA^3 , this solvent molecule, not surprisingly, was found to be disordered. The solvent space is located astride a crystallographic 3-fold axis, with a multiplicity of eight such volumes per unit cell. The model that we developed for the acetone, to be described presently, was also partially

occupied in such a way that a total of four acetone molecules per unit cell was added to the overall description of the structure.

For the acetone site, atomic positions were found near the corners of a slightly irregular tetrahedron, one of whose vertices sits on the three-fold axis. Each of the four triangular faces of this tetrahedron -- three lateral faces related to each other by the symmetry element and one basal face perpendicular thereto -- was modelled as a plane containing one partially occupied acetone molecule. Three of the vertices of the tetrahedral solid volume were split into two atomic sites each, one carbon and one oxygen; the one singly occupied site was the apex that sits on the 3-fold axis, and this was modeled as an oxygen atom. Each of the three lateral triangular faces of the tetrahedron, which are related to each other by the 3-fold axis, has as its upper vertex the oxygen atom lying on the symmetry element, and as its two lower vertices split oxygen-carbon sites. (*N.b.*, the carbon components belong to both the lateral and basal faces, while the oxygen components of the split sites belong only to the residue in the basal plane.) The three split sites, related to each other by the 3-fold axis, form the vertices of the basal triangular face of the reference tetrahedron, so that the acetone molecule in the basal plane was modeled as having a statistical disorder of mixed O/C occupancies at its termini. The occupancies were derived so as to maintain the 2:1 methyl-to-carbonyl ratio of acetone within each disorder group and in the disorder assembly as a whole (using the IUCr terminology for disorder group and disorder assembly). A central carbon atom was located near the plane of the unique lateral face and another was located on the three-fold axis, in the plane of the basal face. The composite picture is shown in Figure S1, in which C7 is at the center of the basal face and models an acetone molecule with O1Z, C8ⁱ and C8ⁱⁱ (i: *y,z,x*; ii: *z,x,y*). O1Z occupies a split site whose carbon component is C8. C7Z is the central carbon atom on the lateral face and in Fig. S1 is shown modeling an acetone molecule with O1, C8 and C8ⁱ. O1 is the un-split site lying on

the three-fold axis. The central atoms of the other two lateral faces, $C7Z^i$ and $C7Z^{ii}$, are related to $C7Z$ by the three-fold axis.

While arriving at an overall occupancy for this part of the structure was not straightforward, following some calculations and consideration of displacement parameters, we developed a model giving a total of 4 acetone molecules per cell, or 0.5 acetone total per solvent-occupied volume. The breakdown of SHELX occupancy factors is given in Table S1, which also recapitulates the calculation of the total stoichiometry.

Although this zone of the structure seemed sufficiently ill-defined to warrant more severe treatment, such as the Squeeze algorithm,⁷ we refined the atomic model using a fairly complete set of constraints and restraints. All C---C and C=O distances were restrained to average literature values, an approximation that we feel is warranted under the circumstances. The C- and O-components of the split sites were constrained to have identical anisotropic displacement parameters. ADP's of atomic sites located within 1.7 Å of each other were restrained to similarity. The atoms of a given disorder group (*i.e.*, a given acetone moiety) were restrained to planarity. To effect the restraints most efficiently, given the presence of the three-fold axis and the various possibilities offered by SHELXL-97 for this purpose, we used four pseudo-atoms -- symmetry relatives of model atoms, but with zero occupancy -- as geometrical placeholders in the calculations.⁸

The refinement converged with the residuals reported in the manuscript. Despite the organizational complexity of the refinement of the solvent space, the calculations themselves proceeded with no complications.

Table S1. Atomic site description for the acetone disorder assembly in the crystal structure of $(\text{PPh}_4)_3\{\text{[Mo}_3(\mu\text{-S}_2)_3(\mu_3\text{-S})\text{I}_3]_4(\mu_2\text{-I})_6\text{I}\}\cdot 2\text{Me}_2\text{C}=\text{O}$. Symmetry operations i: y,z,x ; ii: z,x,y .		
component atoms	SHELX occupancy	description
<i>Lateral face:</i>		
C7Z O1 C8 C8 ⁱ	0.0833/3	lateral face 1, orientation 1
<i>The second lateral face is related to the first by the crystallographic 3-fold axis.</i>		
C7Z ⁱ O1 C8 ⁱ C8 ⁱⁱ	0.0833/3	lateral face 2, orientation 1
<i>The third lateral face is related to the first and second by the crystallographic 3-fold axis.</i>		
C7Z ⁱⁱ O1 C8 ⁱⁱ C8	0.0833/3	lateral face 3, orientation 1
<i>Basal face, perpendicular to the 3-fold axis:</i>		
C7 O1Z C8 ⁱⁱ C8 ⁱ	0.0833/3	basal face, orientation 1
C7 O1Z ⁱⁱ C8 ⁱ C8	0.0833/3	basal face, orientation 2
C7 O1Z ⁱ C8 C8 ⁱⁱ	0.0833/3	basal face, orientation 3
<i>SHELX occupancies:</i>		
C7Z (1/12) 0.083333		
C7 (1/12) 0.083333		
O1 (1/12) 0.083333		
C8 (1/3) 0.33333 [C8 and O1Z occupy a split position.]		
O1Z (1/12) 0.083333		
<i>Total stoichiometry:</i>		
C(sp ²): (1/12) + (1/12) = 1/6 [C7Z + C7]		
C(Me): 1/3 [C8]		
O: (1/12) + (1/12) = 1/6 [O1 + O1Z]		
Total: (1/6)[Me ₂ C=O]		
Space group multiplicity = 24, so 4 Me ₂ C=O per cell.		

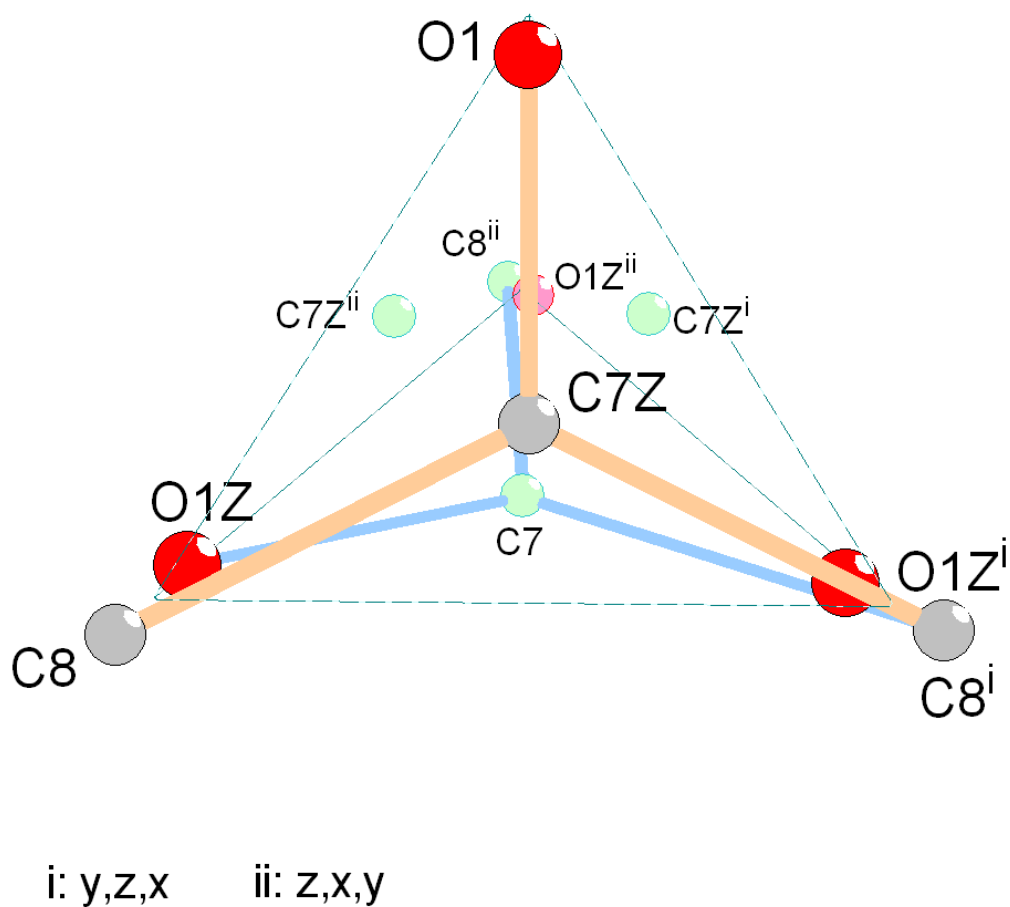


Figure S1. Composite drawing of the atomic sites for the acetone disorder assembly in the crystal structure of $(\text{PPh}_4)_3\{[\text{Mo}_3(\mu\text{-S}_2)_3(\mu_3\text{-S})\text{I}_3]_4(\mu_2\text{-I})_6\text{I}\} \cdot 2\text{Me}_2\text{C}=\text{O}$, $\{(\text{PPh}_4)_3[2] \cdot 2\text{Me}_2\text{C}=\text{O}\}$.

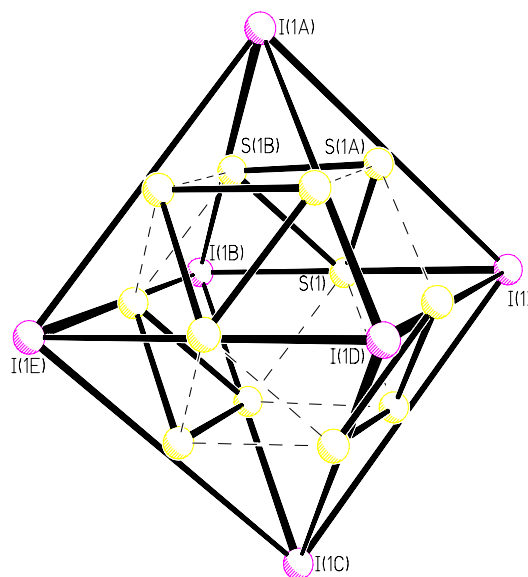


Figure S2a. Schematic view of the cuboctahedron defined by the axial sulfur ligands circumscribed by an octahedron defined by the iodide-bridged ligands. Sulfur ligands linked by solid lines represent S_{ax} belonging to the same Mo_3 cluster.

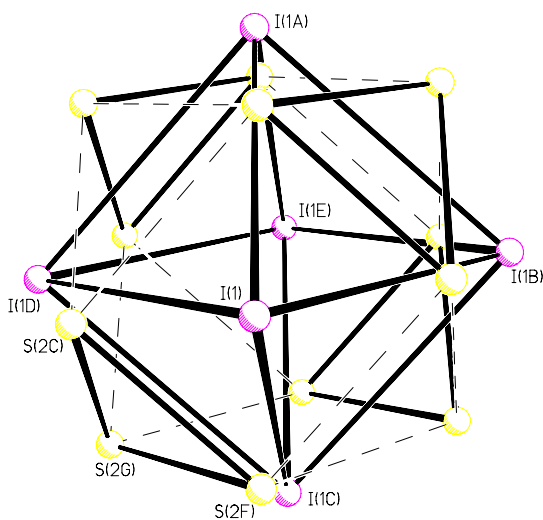


Figure S2b. Schematic view of the cuboctahedron defined by the equatorial sulfur ligands circumscribed by an octahedron defined by the iodide-bridged ligands. Sulfur ligands linked by solid lines represent S_{eq} belonging to the same Mo_3 cluster.

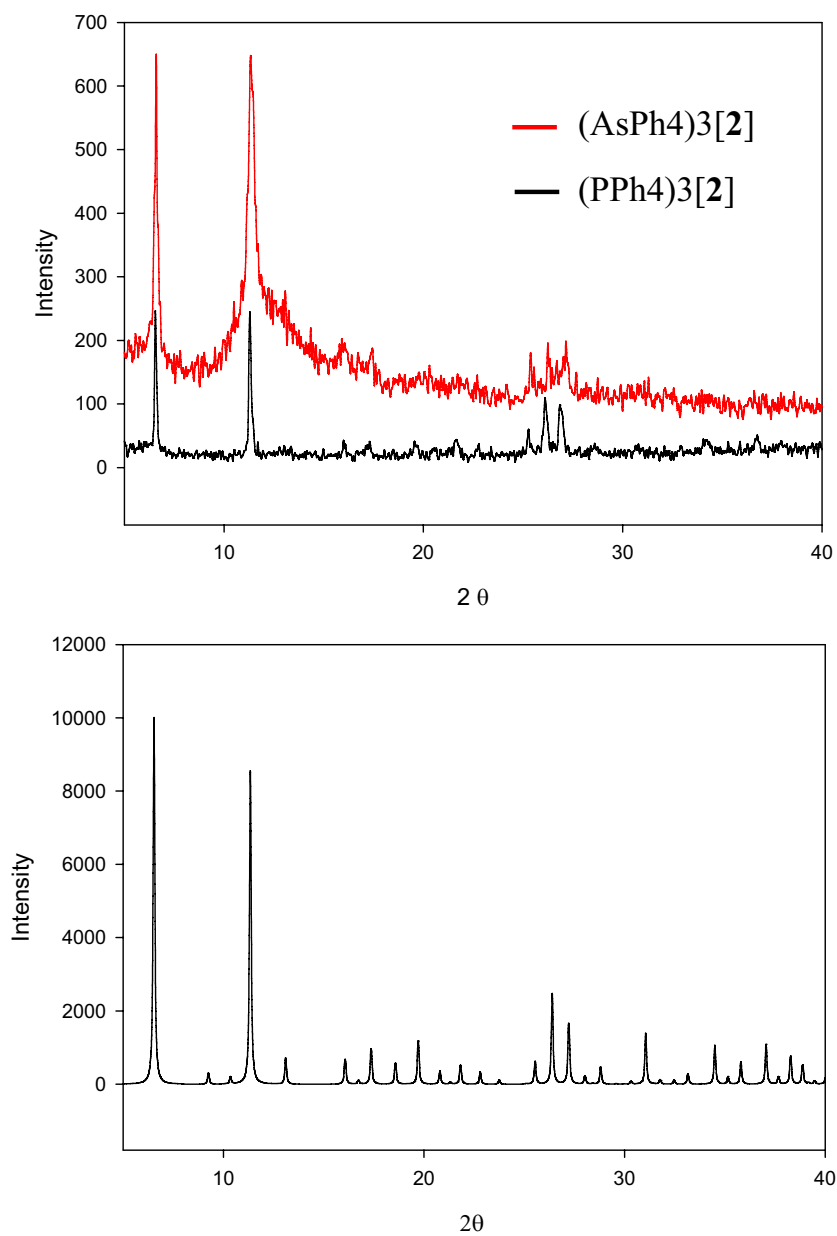


Figure S3. XPD spectra of complexes (PPh₄)₃[2] (AsPh₄)₃[2] (top) together with the simulated XPD from crystal data of (PPh₄)₃[2] (bottom).

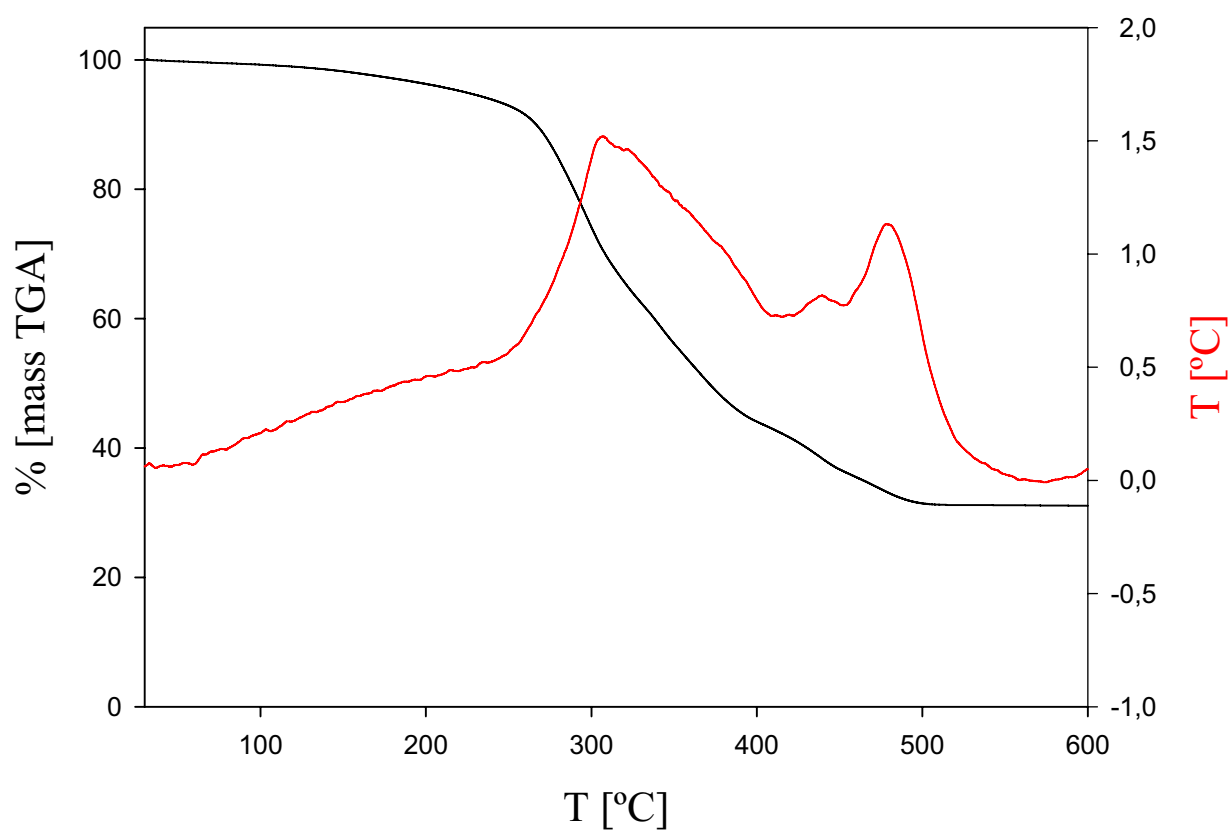


Figure S4. TGA (red line) and DTA (red line) curves of compound $(\text{PPh}_4)_3[\mathbf{2}]$ recorded at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

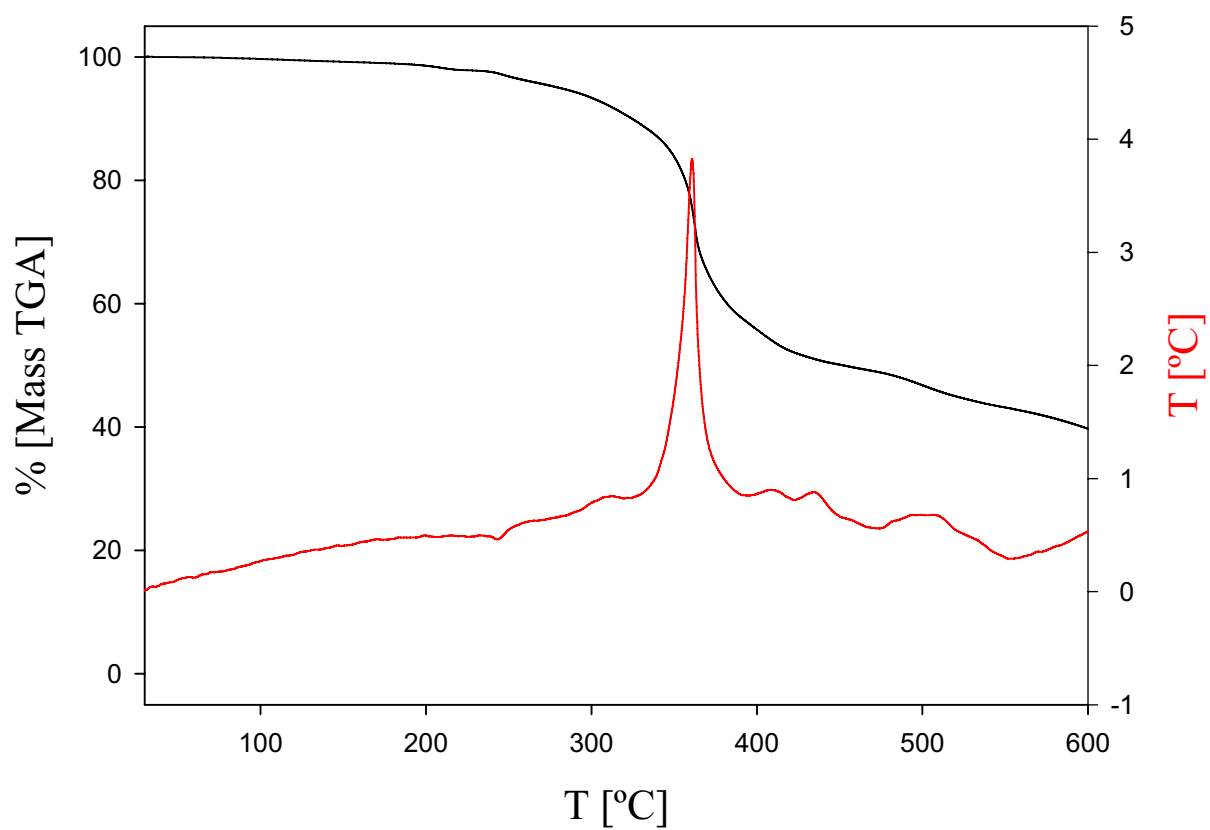


Figure S5. TGA (red line) and DTA (red line) curves of compound $(\text{PPh}_4)_2[\mathbf{3}]$ recorded at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

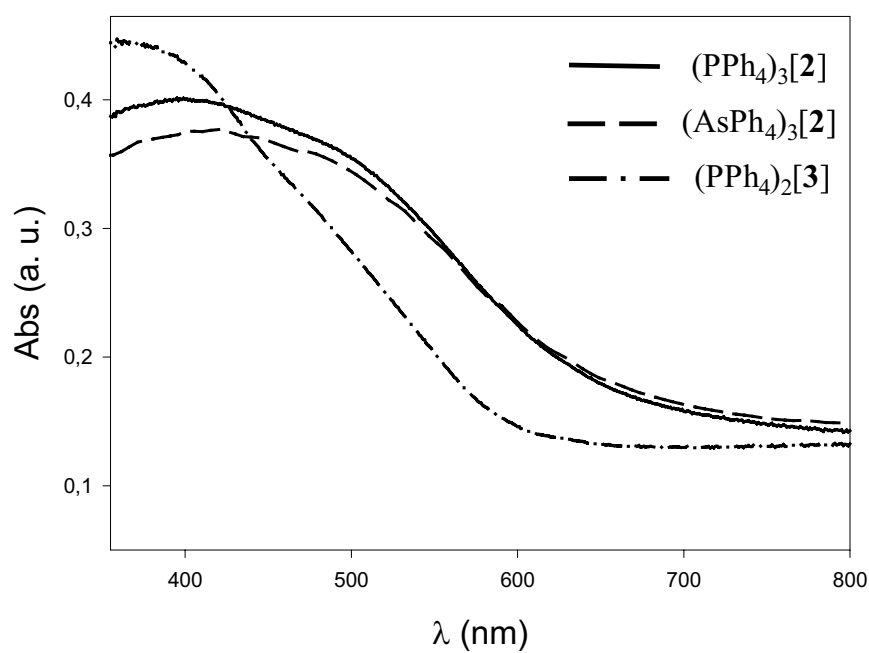


Figure S6. UV-vis absorption spectra of compounds (PPh₄)₃[2], (AsPh₄)₃[2] and (PPh₄)₂[3] dispersed in KBr in the 350- 800 nm range. Bands below 500 nm are characteristic of trinuclear Mo₃S₇ complexes bearing terminal halide ligands.⁹

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