

Exploring Structural Complexity in the Discovery and Self-Assembly of a Family of Nanoscale Chalcogenides from {Se₈Mo₃₆} to {Se₂₆Mo₆₈}

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Materials

All reagents and chemicals were purchased from Sigma Aldrich Chemical Company Ltd. and Alfa Aesar. Unless stated otherwise, the materials were used without further purification. Dimeric [Mo₂S₂O₂]²⁺ unit was synthesized according to the modified published procedure by E. Cadot *et.al.*¹ and the obtained [Mo₂O₂S₂(H₂O)₆]²⁺ solution was stored under Ar.

Instrumentation

Fourier-transform infrared (FT-IR) spectroscopy:

The materials were prepared as KBr pellets and FT-IR spectra were collected in transmission mode using a JASCO FT-IR-410 spectrometer or a JASCO FT-IR 4100 spectrometer, Characteristic IR bands are shown above in cm⁻¹; intensities denoted as s = strong, m = medium, w = weak, sh = sharp

UV-Vis spectroscopy:

UV-Vis spectra were collected using a JASCO V-670 spectrometer in the solution in absorption mode and the solid UV spectrum was collected equipped with an ISV723 60mm integrating sphere in diffuse reflectance mode.

Thermogravimetric analysis (TGA):

Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of 5 °C

Microanalysis

Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHN, CE-440 Elemental Analyser.

Flame Atomic Absorption Spectroscopy Analysis:

FAAS analysis was performed at the Environmental Chemistry Section, Department of Chemistry, The University of Glasgow on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer.

Single Crystal X-ray Diffraction

The data for compounds **1-5** were collected at 150(2) K on a Bruker Apex 2 CCD diffractometer (λ (MoK α) = 0.7107 Å) equipped with a graphite monochromator. Suitable single crystals of **1-5** were selected and mounted onto the centre of a thin rubber loop using Fomblin oil. Structure solution and refinement were carried out with SHELXS-97² and SHELXL-97³ using WinGX.⁴ Corrections for incident and diffracted beam absorption effects were applied using analytical methods.⁵ The crystallographic data for compounds **1-5** (CCDC 1540787-1540791) can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; fax:(+44) 1223- 336-033, deposit@ccdc.cam.ac.uk.

Synthesis

Compound **1** {Se₈Mo₃₆}: [N(CH₃)₄]₅K₁₅[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)]₅(Se^{IV}O₃)₈(Mo^{VI}₂O₇)₂(Mo^V₂O₂S₂)(C₄O₄)}·80H₂O \equiv [N(CH₃)₄]₅K₁₅[(Mo^V₂O₂S₂)₁₆(Mo^{VI}₂O₇)₂(OH)₂₀(C₄O₄)₆(Se^{IV}O₃)₈]·80 H₂O

C₄O₄H₂ (0.20 g, 1.75 mmol) was dissolved in 7.4 mL (1.00 mmol) of [Mo^V₂O₂S₂]X₂ (X: Cl⁻, I⁻) (tetramethylammonium cation also exists in this solution which is carried over from the preparation step of [Mo^V₂O₂S₂]²⁺)¹ solution and diluted with 20 mL of deionized water. Then the pH of the solution was adjusted to 3.1 using 1 M K₂CO₃. After that, 10 mL aqueous solution containing Na₂SeO₃ (0.14 g, 0.81 mmol) and Na₂MoO₄·2H₂O (0.10g, 0.41 mmol) was added dropwise into the above solution. The pH of the mixture was adjusted to 5.0 with 1 M K₂CO₃ and stirred at room temperature for two hours. The solution was filtered and kept in an open beaker at 18 °C for 6 weeks. Upon slow evaporation, orange crystals of **1** were obtained. Yield: 280 mg (46.4 % based on Mo^V). Elemental analysis for **1** (C₄₄H₂₄₀K₁₅Mo₃₆N₅O₁₉₄S₃₂Se₈, Fw. 9642.4 g/mol); Cal.: C: 5.48; H: 2.51; N: 0.73; K: 6.08; Mo: 35.82; S: 10.64; Se: 6.55; Found: C: 5.96; H: 2.13; N: 0.69; K: 6.82; Mo: 35.66; S: 10.09; Se: 6.29.

Compound **2** {Se₈Mo₄₀}: [N(CH₃)₄]₂K₁₁H₇[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)₆(Se^{IV}O₃)₈(Mo^{VI}₂O₇)₂·90H₂O] ≡ [N(CH₃)₄]₂K₁₁H₇[(Mo^V₂O₂S₂)₁₈(Mo^{VI}₂O₇)₂(OH)₂₄(C₄O₄)₆(Se^{IV}O₃)₈]·90H₂O

C₄O₄H₂ (0.12 g, 1.1 mmol) was dissolved in 7.6 mL (1.03 mmol) of [Mo^V₂O₂S₂]X₂ (1 M, X: Cl⁻, I⁻) (tetramethylammonium cation also exists in this solution which is carried over from the preparation step of [Mo^V₂O₂S₂]²⁺)¹ solution and diluted with 20 mL deionized water. Then the pH of the solution was adjusted to 2.7 using 1 M K₂CO₃. After that, 10 mL aqueous solution containing Na₂SeO₃ (0.10 g, 0.58 mmol) and Na₂MoO₄·2H₂O (0.05 g, 0.21 mmol) was added dropwise into the above solution. The pH of the mixture was adjusted to 5.0 with 1 M K₂CO₃ and stirred at room temperature for two hours. The solution was filtered and kept in an open 50 mL conical flask at 18 °C for 8 weeks. Upon slow evaporation, orange red block crystals were obtained from the above solution. Yield: 80 mg (13.8% based on Mo^V). Elemental analysis for **2** (C₃₂H₂₃₅K₁₁Mo₄₀N₂O₂₁₂S₃₆Se₈, Fw. 10094.8 g/mol); Cal.: C: 3.81; H: 2.35; N: 0.28; K: 4.26; Mo: 38.01; S: 11.44; Se: 6.26; Found: C: 3.97; H: 2.11; N: 0.30; K: 4.15; Mo: 35.87; S: 11.28; Se: 5.95.

Compound **3** {Se₈Mo₅₆}: [N(CH₃)₄]₄K₁₆H₈{[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)]₃(Mo^{VI}₂O₇)₂(Se^{IV}O₃)₄]₂[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)]₂l₄·100H₂O ≡ [N(CH₃)₄]₄K₁₆H₈[(Mo^V₂O₂S₂)₂₄(Mo^{VI}₂O₇)₄(OH)₃₂(C₄O₄)₈(Se^{IV}O₃)₈]₄·100H₂O

C₄O₄H₂ (0.10 g, 0.88 mmol) and Na₂SeO₃ (0.10 g, 0.58 mmol) were dissolved in 10 mL deionized water. Then a second solution was prepared as follows: 8.0 mL (1.08 mmol) of [Mo^V₂O₂S₂]₂X₂ (1 M, X: Cl⁻, I⁻) (tetramethylammonium cation also exists in this solution which is carried over from the preparation step of [Mo^V₂O₂S₂]²⁺)¹ were diluted with 20 mL deionized water and the pH was adjusted to a value of 3.0 using 1M K₂CO₃. The solution was added dropwise into the φιστ solution. Then solid Na₂MoO₄·2H₂O (0.05 g, 0.21 mmol) was added into the reaction mixture. The solution turned orange clear. The pH of the solution was adjusted to 5.0 with 60% HAc and heated at 50 °C for one hour. Then the solution was stirred at room temperature for an additional 1 hour. The solution was filtered and kept in an open beaker at 18 °C for 20 weeks. Upon slow evaporation, orange red block crystals can be isolated from the mother liquor. Yield: 240 mg (39.0 % based on Mo^V). Elemental analysis for **3** (C₄₈H₂₈₈l₄K₁₆Mo₅₆N₄O₂₆₄S₄₈Se₈, Fw. 13823.25 g/mol), Cal.: C: 4.17; H: 2.10; N: 0.41; K: 4.53; Mo: 38.87; S: 11.13; Se: 4.57; Found: C: 3.90; H: 1.76; N: 0.37; K: 4.30; Mo: 39.97; S: 11.03; Se: 4.39.

Compound **4** {Se₂₀Mo₅₆}: [N(CH₃)₄]₄K₂₈[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)]₈[(Mo^V₂O₂S₂)₂(Se^{IV}O₃)₈]₂(Se^{IV}O₃)₄·56H₂O ≡ [N(CH₃)₄]₄K₂₈[(Mo^V₂O₂S₂)₂₈(OH)₃₂(C₄O₄)₈(Se^{IV}O₃)₂₀]₂·56 H₂O

Solid C₄O₄H₂ (0.12 g, 1.05 mmol) was added to 7.0 mL (0.94 mmol) of [Mo^V₂O₂S₂]₂X₂ (1 M, X: Cl⁻, I⁻) (tetramethylammonium cation also exists in this solution which is carried over from the preparation step of [Mo^V₂O₂S₂]²⁺)¹ were diluted with 20 mL deionized water before adjusting the pH value of the mixture to 2.6 with 1 M K₂CO₃. The solution was stirred at room temperature for 10 min. Then a 5 mL aqueous solution containing Na₂SeO₃ (0.12 g, 0.69 mmol) was added into the above solution and the pH increased to 3.5. The pH of the reaction mixture was adjusted carefully to 5.4 using 1 M K₂CO₃ followed by addition of 60% HAc solution which re-adjusted the pH to a value of 4.9. The solution was heated at 50°C for 1 hour cooled down and

filtered. The final pH of the filtrate was 5.2. The clear orange solution was kept in an open flask at 18 °C for 6 months during which period of time yellow block crystals obtained from the mother liquor. Yield: 200 mg (41.0 % based on Mo^V). Elemental analysis for **4** (C₄₈H₁₉₃K₂₈Mo₅₆N₄O₂₃₆S₅₆Se₂₀, Fw. 14444.7 g/mol), Cal.(%): C: 3.99; H: 1.35; N: 0.39; K: 7.58; Mo: 37.19; S: 12.43; Se: 10.93; Found(%): C: 3.29; H: 1.78; N: 0.40; K: 6.90; S: 12.39; Se: 12.30; Mo: 36.08.

Compound **5** {Se₂₆Mo₆₈}: [N(CH₃)₄]₄K₃₀Na₂[(Mo^V₂O₂S₂)₃(OH)₄(C₄O₄)]₈[(Mo^V₂O₂S₂)₃(OH)₂(Se^{IV}O₃)₅]₂[(Mo^V₂O₂S₂)₂(Se^{IV}O₃)₈]₂·96H₂O ≡ [N(CH₃)₄]₄K₃₀Na₂[(Mo^V₂O₂S₂)₃₄(OH)₃₆(C₄O₄)₈(Se^{IV}O₃)₂₆]·96 H₂O

Solid C₄O₄H₂ (0.10 g, 0.88 mmol) was added to 5.0 mL (0.67 mmol) of [Mo^V₂O₂S₂]_X₂ (1 M, X: Cl⁻, I⁻) (tetramethylammonium cation also exists in this solution which is carried over from the preparation step of [Mo^V₂O₂S₂]²⁺)¹ were diluted with 10 mL deionized water before adjusting the pH value of the mixture to 2.6 with 1 M K₂CO₃. The solution was stirred at room temperature for 10 min. Then a 10 mL aqueous solution containing Na₂SeO₃ (0.14 g, 0.81 mmol) was added into the above solution. The pH value of the reaction mixture was adjusted to 4.6 with 1 M solution of K₂CO₃. The clear orange solution was stirred for 1 hour at room temperature. The orange solution was kept in an open flask at 18 °C for 20 weeks. Upon slow evaporation, orange block crystals were obtained from the mother liquor. Yield: 60 mg, 17.0 % based on Mo^V. Elemental analysis for **5** C₄₈H₂₇₆K₃₀Mo₆₈N₄Na₂O₃₁₀S₆₈Se₂₆, Fw.: 17846.8 g/mol. Cal.(%): C: 3.23; H: 1.56; N: 0.32; K: 6.57; Na: 0.26; S:12.22; Se: 11.50; Mo: 36.55; Found(%): C: 3.39; H: 1.66; N: 0.40; K: 6.80; Na: 0.30; S: 12.39; Se: 11.38; Mo: 35.89 %

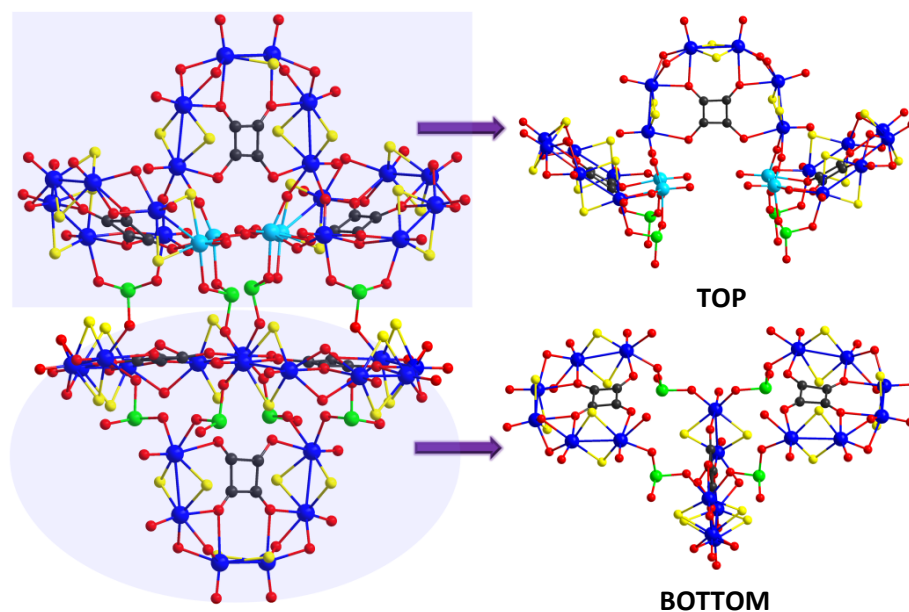


Fig. S1 Ball-and-stick representation of cluster **2**, $\{\text{Se}_8\text{Mo}_{40}\}$, (left). To clarify the structure, the parts were presented respectively (right) (Mo^{VI} : light blue; Mo^{V} : blue; S: yellow; O: red).

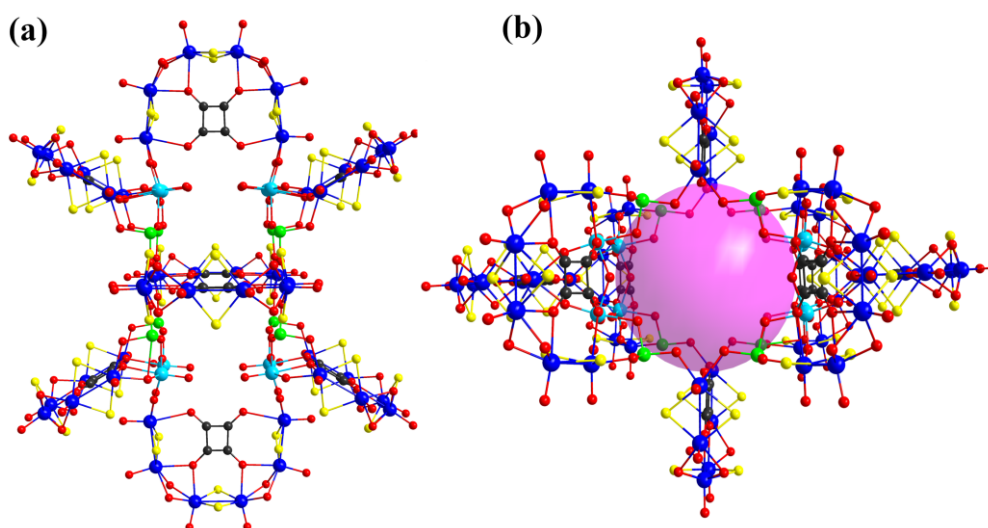


Fig. S2 (a) Projection view of **3**, $\{\text{Se}_8\text{Mo}_{56}\}$, along a axis. (b) Representation of the formed cavity with the diameter 1.2 nm.

FT-IR Spectroscopy

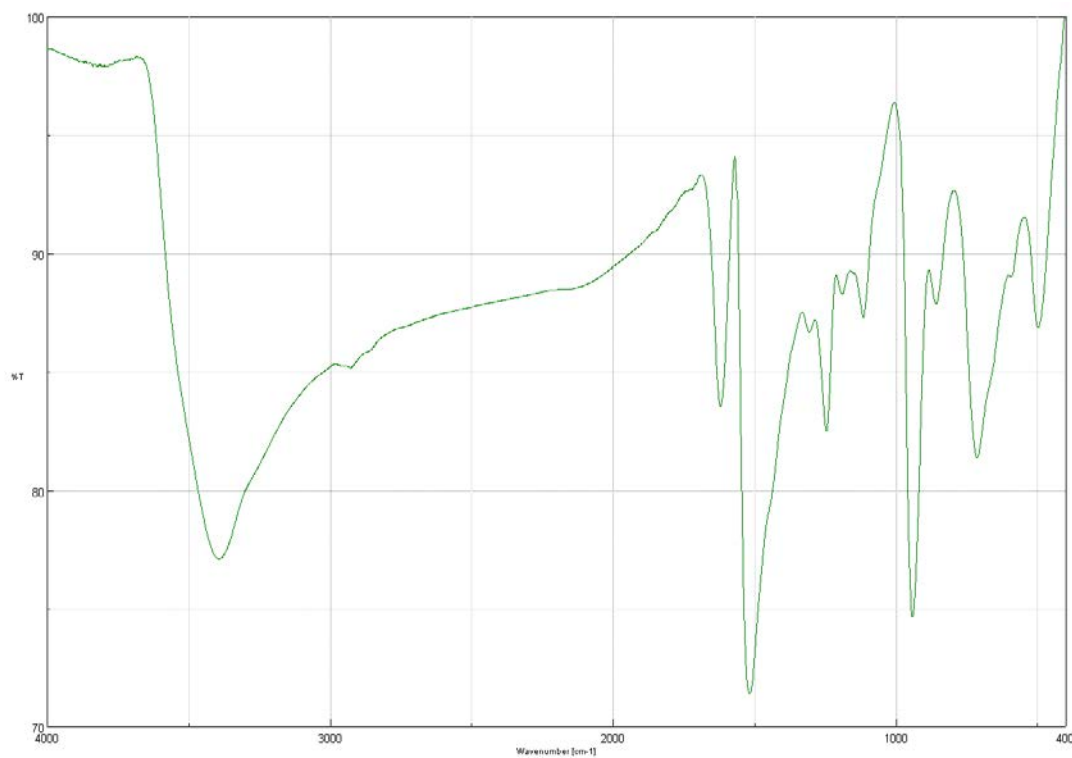


Fig. S3. FT-IR (KBr pellet) spectrum for compound **1** { $\text{Se}_8\text{Mo}_{36}$ }. 3393.1 (s, broad) [-OH]; 1621.8 (m) [H_2O]; 1518.7 (sh) [C-O]; 1116.6 (w); 942.1 (m) [$\text{Mo}=\text{O}$]; 859.1 (m) [Se-O]; 714.5 (sh) [Mo-OH-Mo]; 498.5 [Mo-S-Mo].

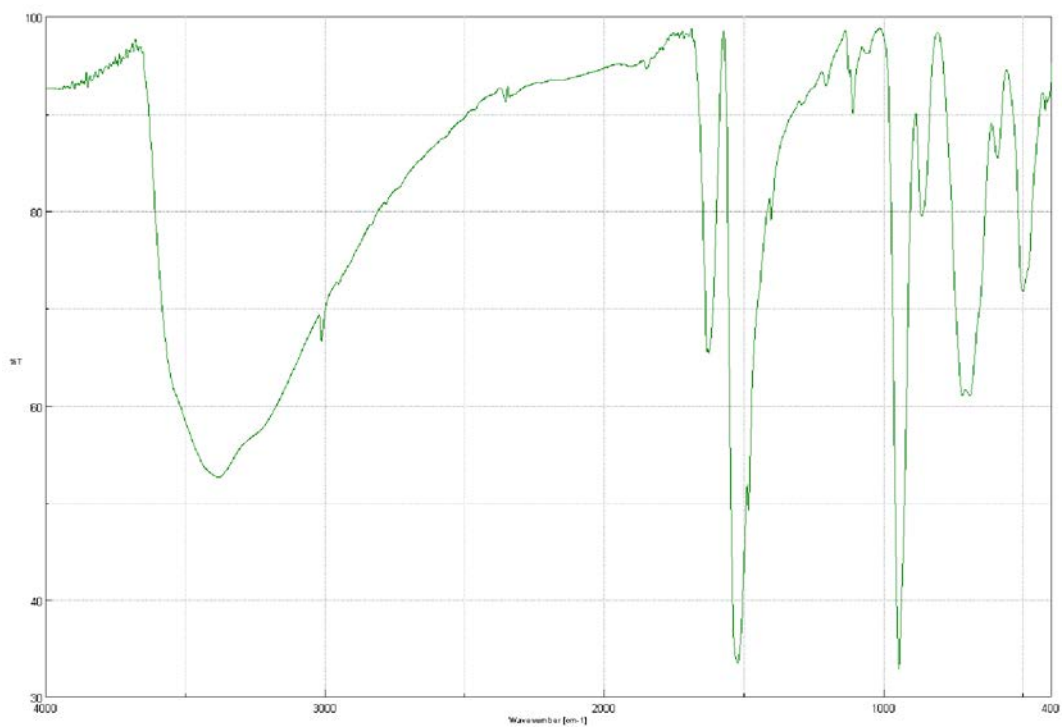


Fig. S4. FT-IR (KBr pellet) spectrum for compound **2** {Se₈Mo₄₀}. 3387.4(s) [-OH]; 1625.7 (s) [H₂O]; 1523.5 (sh) [C-O]; 1482.9 (s), 1402.96 (w) [N-R]; 1109.8 (w), 944.9 (sh) [Mo=O]; 863.9 (m), 869.4 (m) [Se-O]; 720.5 (sh) [Mo-OH-Mo]; 592.0 (w), 499.5 (m) [Mo-S-Mo].

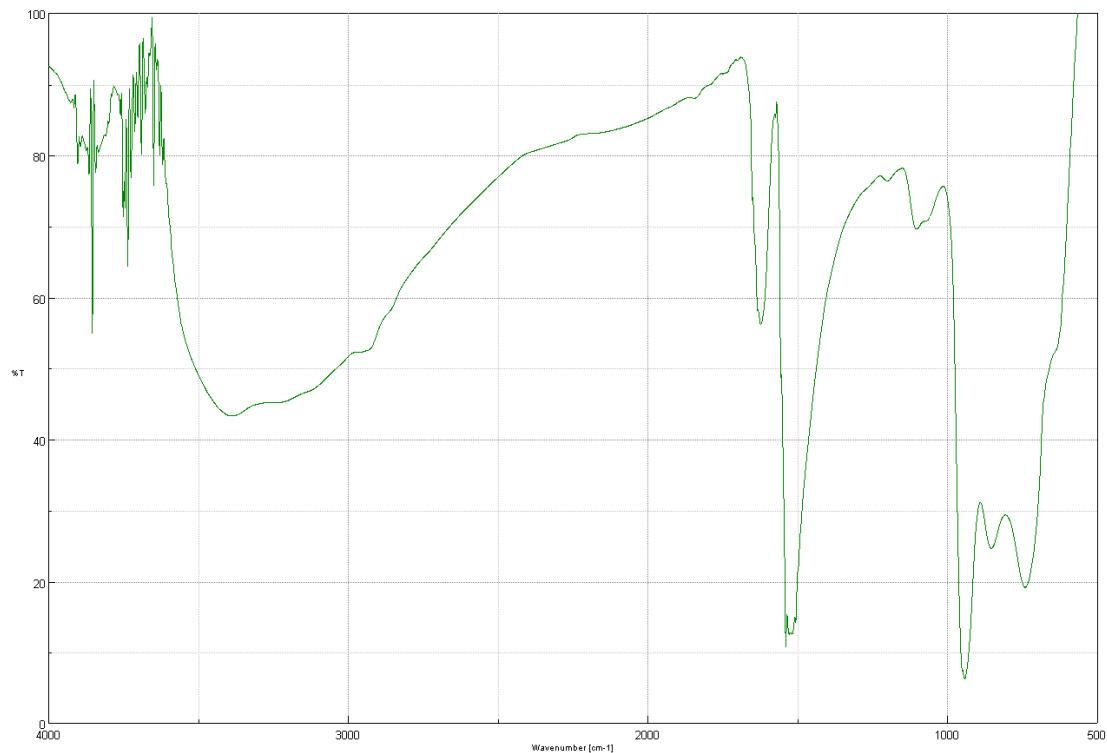


Fig. S5. FT-IR (KBr pellet) spectrum for compound **3** {Se₈Mo₅₆}. 3391.2 (m) [-OH]; 1623.8 (m) [H₂O]; 1539.9 (sh) [C-O]; 1118.8 (w), 943.0 (sh) [Mo=O]; 852.4 (m), [Se-O]; 741.5 (m) [Mo-OH-Mo]; 587.0 (w) [Mo-S-Mo].

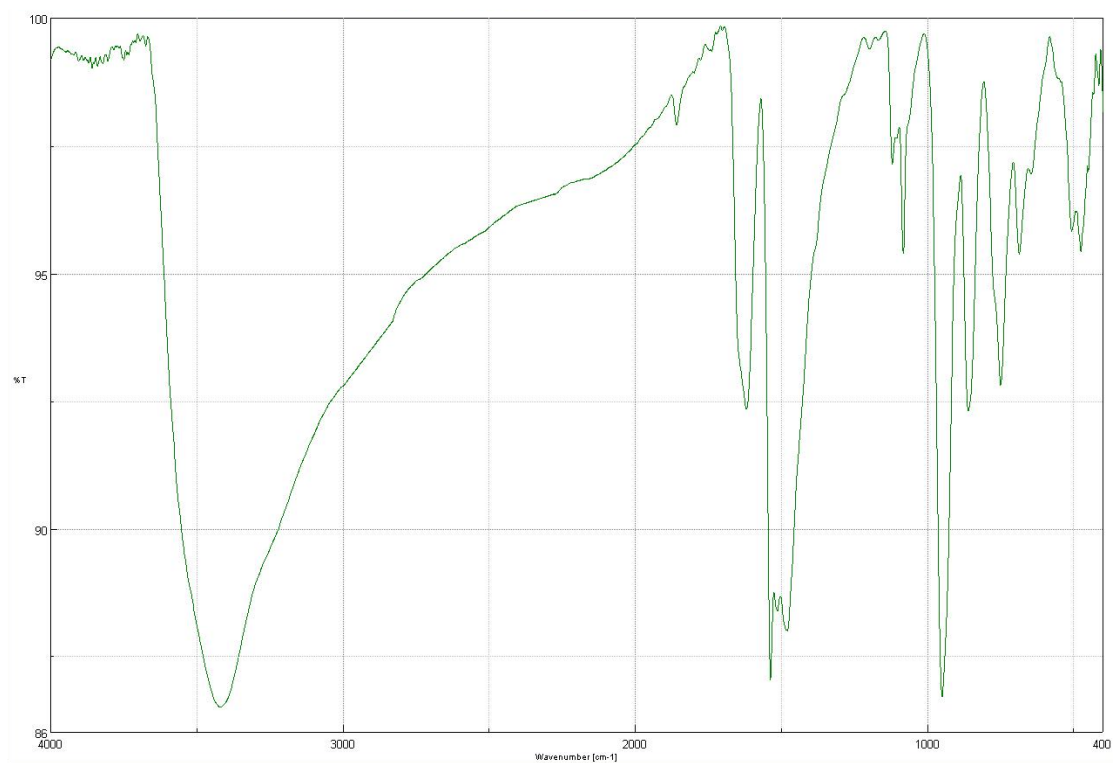


Fig. S6. FT-IR (KBr pellet) spectrum for compound **4** {Se₂₀Mo₅₆}. 3388.2 (m) [-OH]; 1627.4 (m) [H₂O]; 1519.7 (sh) [C-O]; 1108.7 (w), 948.2 (sh) [Mo=O]; 848.1 (m), [Se-O]; 742.3 (m) [Mo-OH-Mo]; 470.8 (w) [Mo-S-Mo].

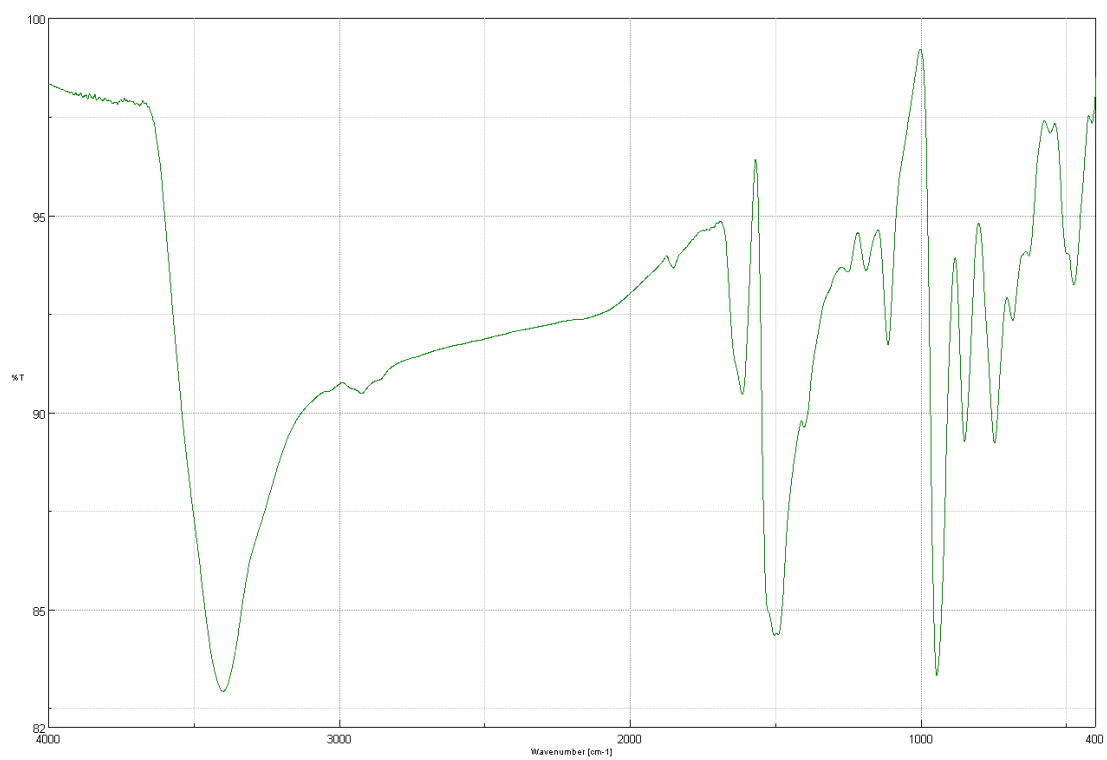


Fig. S7. FT-IR (KBr pellet) spectrum for compound **5** $\{\text{Se}_{26}\text{Mo}_{68}\}$.3390.2 (m) [-OH]; 1627.4 (m) [H_2O]; 1526.7 (sh) [C-O]; 1115.7 (w), 953.4 (sh) [Mo=O]; 859.1 (m), [Se-O]; 752.1 (m) [Mo-OH-Mo]; 481.5 (w) [Mo-S-Mo].

UV-vis spectroscopy

According to the UV-vis studies, compounds **1** - **5** retain their structural integrity in aqueous medium at pH values higher than 4. The recorded UV-vis spectra as a function of the time are shown in Figures S8 – S12 for compounds **1** - **5** respectively, where it's clear that $\alpha\lambda\ \text{c}\lambda\theta\sigma\tau\epsilon\text{p}\varsigma$ are stable for at least 24 hours.

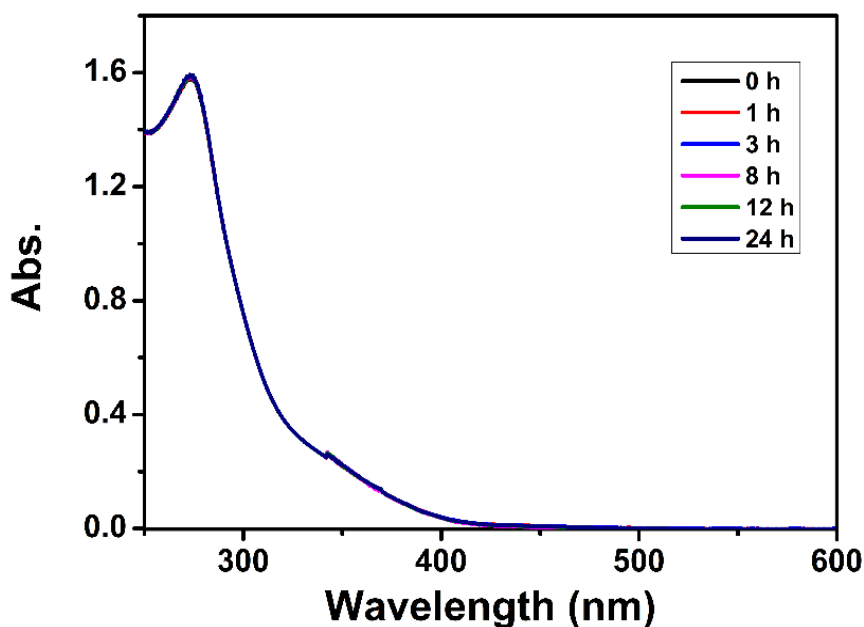


Fig. S8. UV spectrum for compound **1** $\{\text{Se}_8\text{Mo}_{36}\}$ in water.

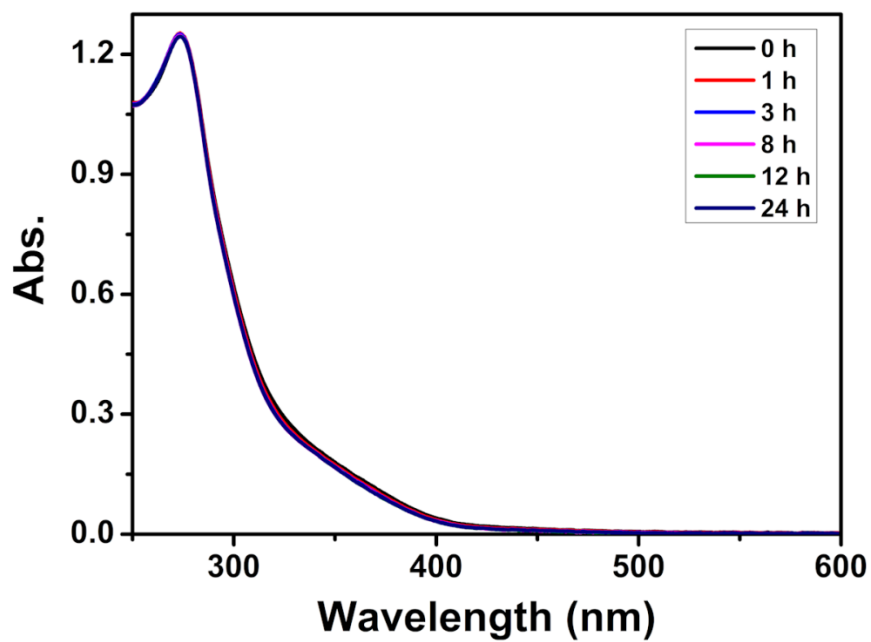


Fig. S9. UV spectrum for compound 2 $\{Se_8Mo_{40}\}$ in water.

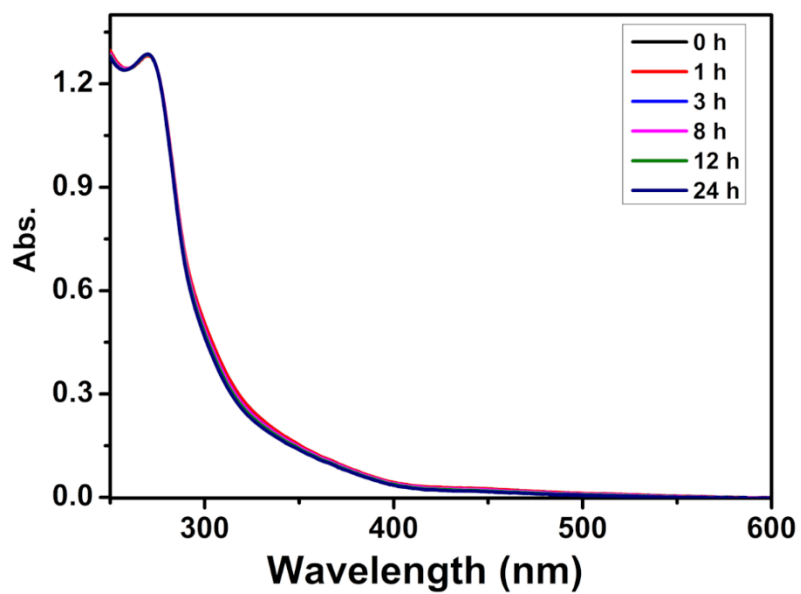


Fig. S10. UV spectrum for compound 3 $\{Se_8Mo_{56}\}$ in water.

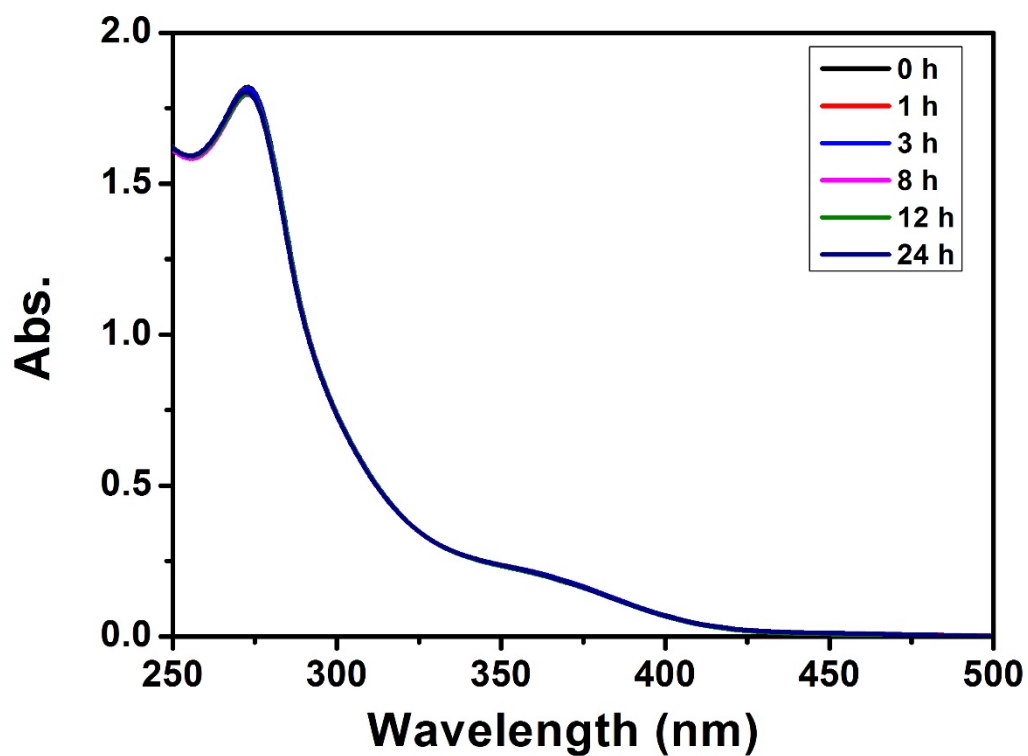


Fig. S11. UV spectrum for compound 4 {Se₂₀Mo₅₆} in water.

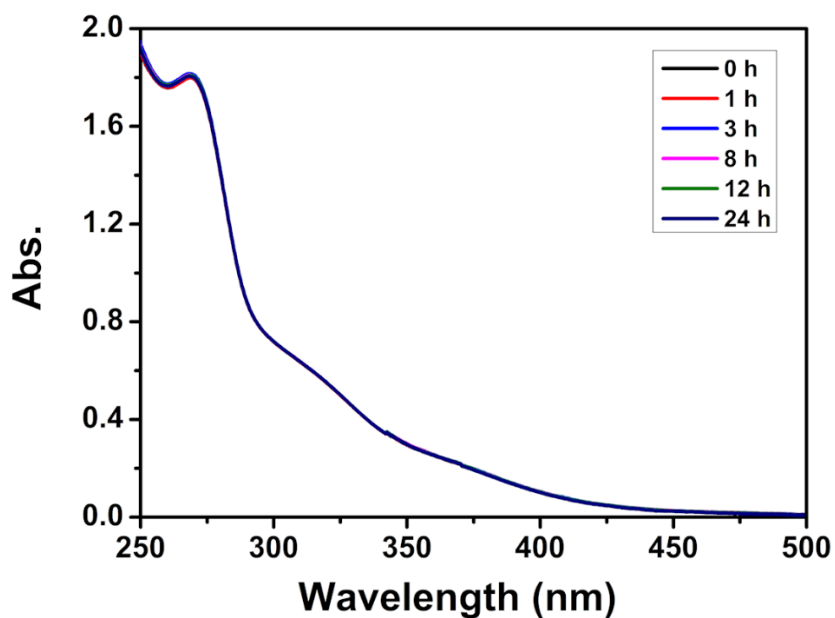


Fig. S12. UV spectrum for compound 5 {Se₂₆Mo₆₈} in CH₃COOH - CH₃COONa (pH=4.5). The UV-vis recorded in a buffered aqueous medium due to compound's poor solubility in water.

TGA analyses

All the compounds, Figures S13 – S17, showed a similar behaviour over the temperature regime of 25 – 800 °C. Initially, it is shown the loss of solvent content (RT – 170 °C) followed by the three overlapping steps (300 – 800 °C) during which C and N content is eliminated as CO₂ and/or hydrocarbons and NH₃ and finally the sulphur content in the form of SO₂ with subsequent decomposition of the framework.

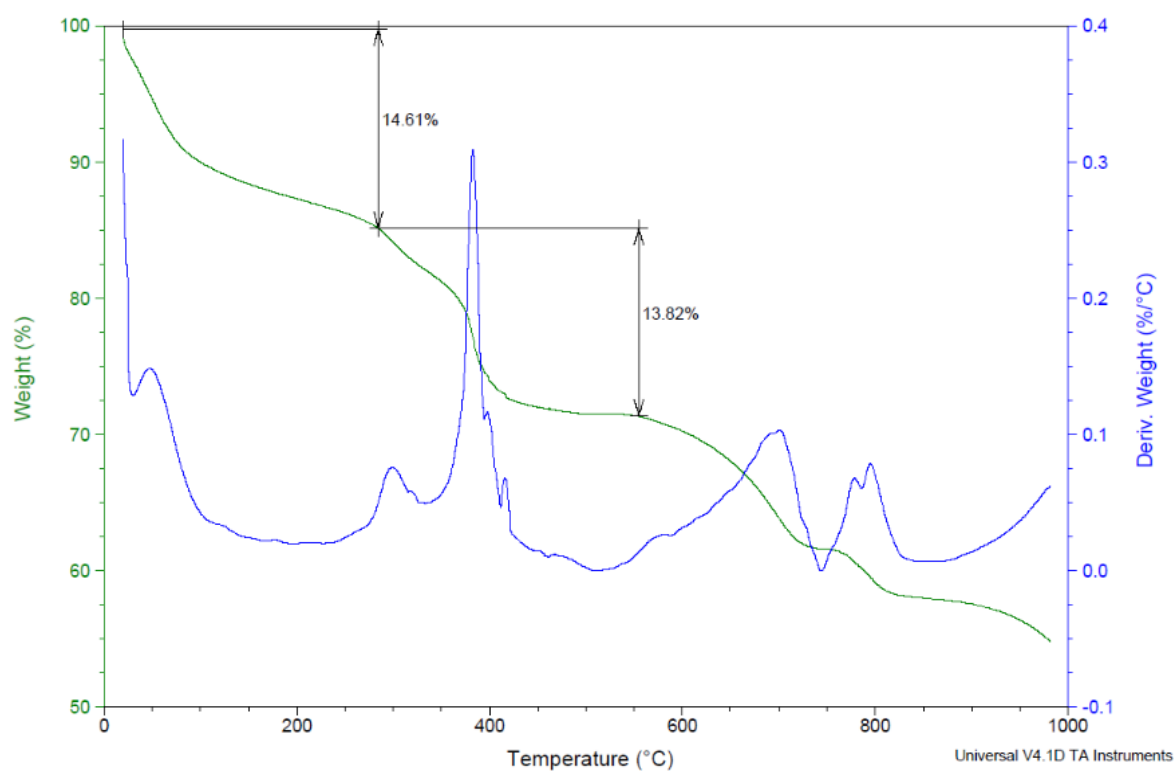


Fig. S13. Thermogravimetric analysis for compound **1** {Se₈Mo₃₆}.

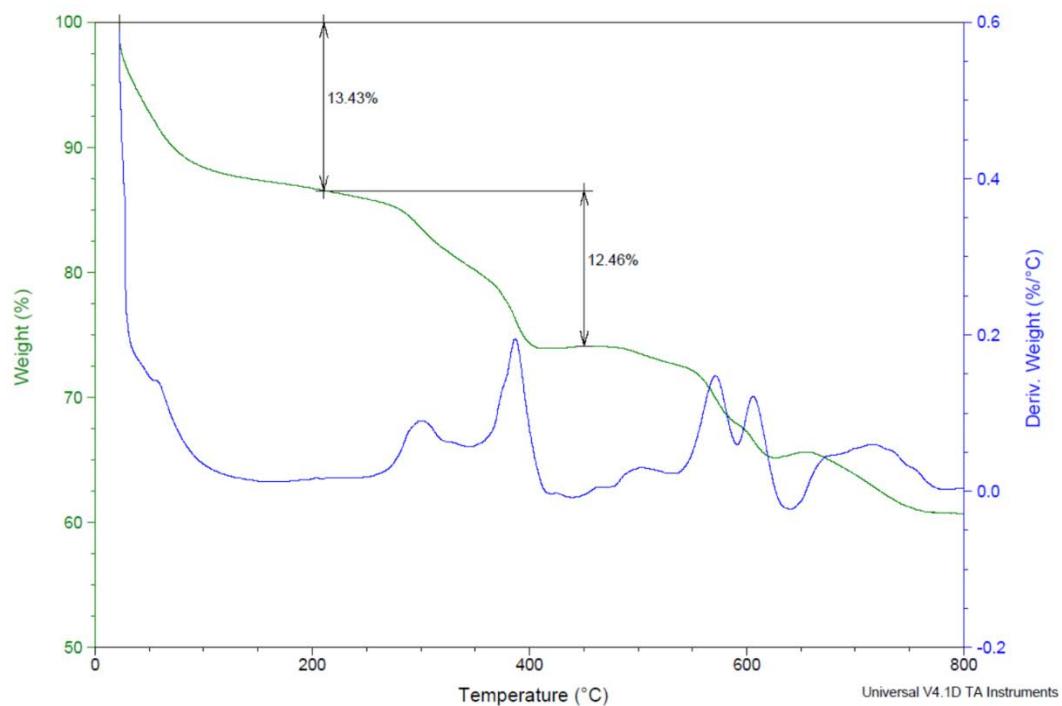


Fig. S14. Thermogravimetric analysis for compound **2** {Se₈Mo₄₀}.

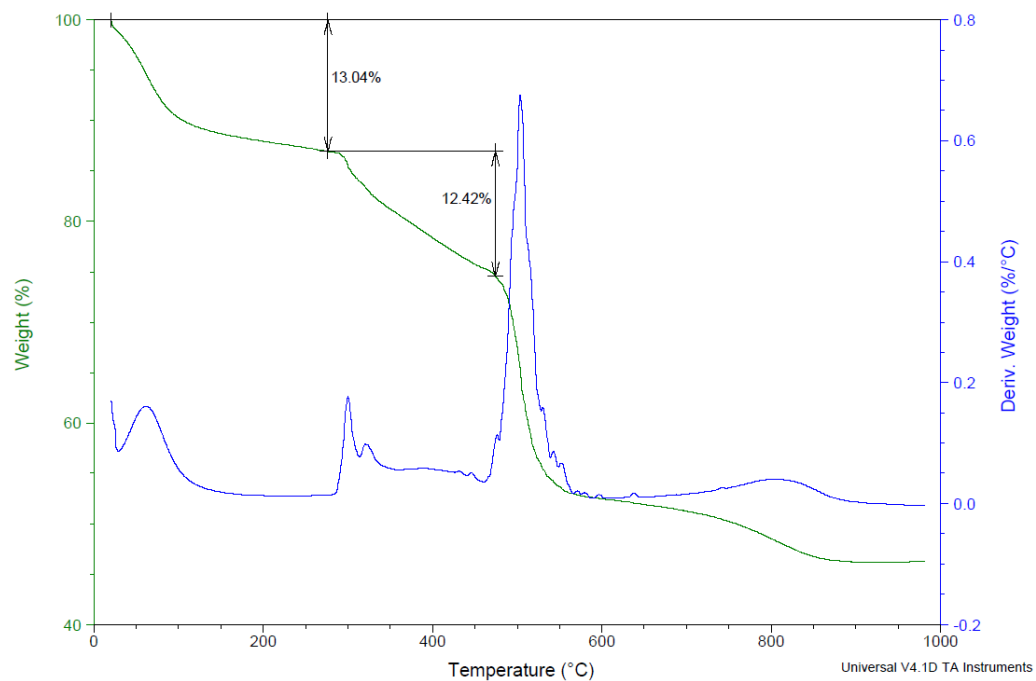


Fig. S15. Thermogravimetric analysis for compound **3** {Se₈Mo₅₆}.

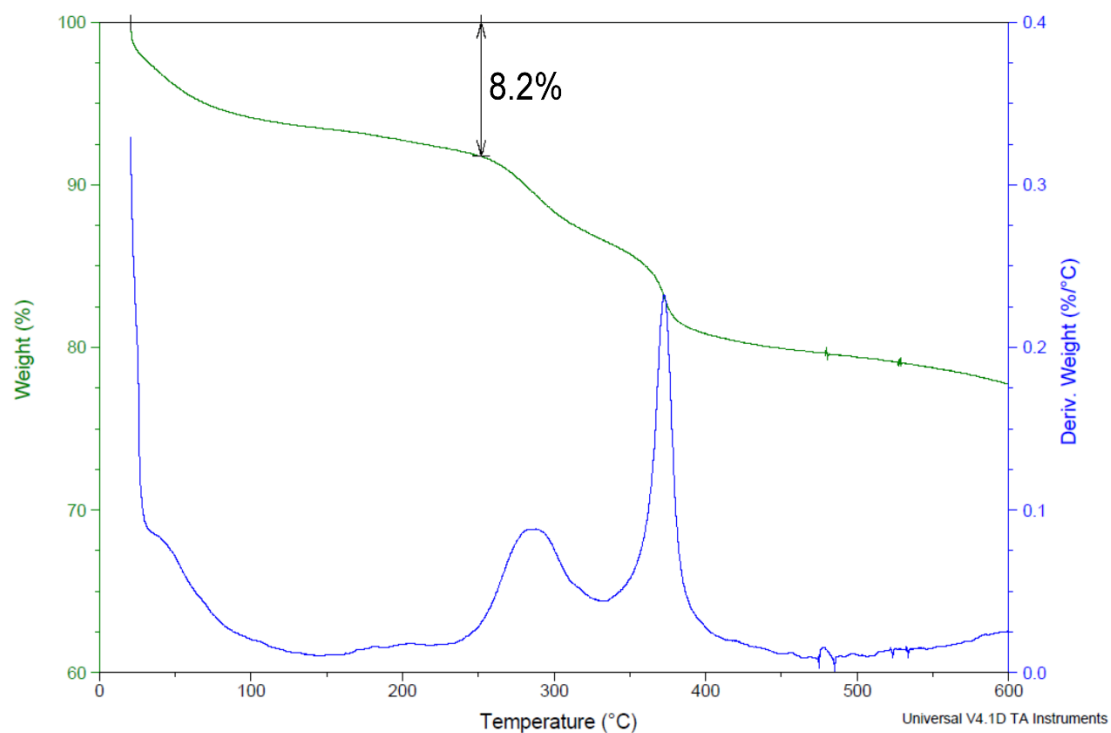


Fig. S16. Thermogravimetric analysis for compound **4** { $\text{Se}_{20}\text{Mo}_{56}$ }.

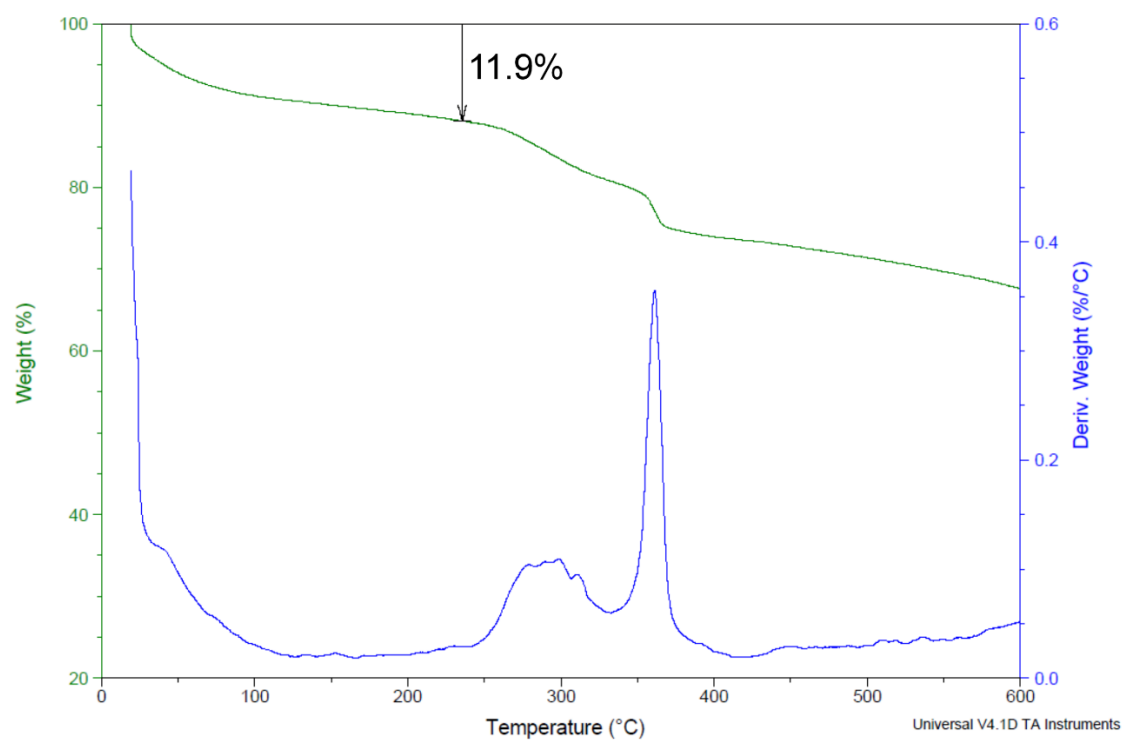


Fig. S17. Thermogravimetric analysis for compound **5** { $\text{Se}_{26}\text{Mo}_{68}$ }.

Table S1 X-ray crystallographic data and structure refinement for compounds **1-5**.

Value	1	2	3	4	5
Formula	C ₄₄ H ₂₄₀ K ₁₅ Mo ₃₆ N ₅ O ₁₉₄ S ₃₂ Se ₈	C ₃₂ H ₂₃₅ K ₁₁ Mo ₄₀ N ₂ O ₂₁₂ S ₃₆ Se ₈	C ₄₈ H ₂₈₈ I ₄ K ₁₆ Mo ₅₆ N ₄ O ₂₆₄ S ₄₈ Se ₈	C ₄₈ H ₁₉₃ K ₂₈ Mo ₅₆ N ₄ O ₂₃₆ S ₅₆ Se ₂₀	C ₄₈ H ₂₇₆ K ₃₀ Mo ₆₈ N ₄ Na ₂ O ₃₁₀ S ₆₈ Se ₂₆
<i>M_r</i> g mol ⁻¹	9642.33	10094.76	13823.21	14444.04	17846.65
crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	28.4084(10)	23.8487(9)	31.8220(13)	20.5753(11)	20.3775(7)
<i>b</i> [Å]	28.8017(10)	37.2576(13)	31.7269(13)	21.4339(13)	21.0899(7)
<i>c</i> [Å]	33.5254(12)	37.8116(15)	24.9385(11)	27.9022(16)	30.3195(12)
α [°]	90	71.584(2)	90	107.720(3)	102.220(2)
β [°]	90.683(2)	87.821(2)	109.253(3)	101.595(3)	100.029(2)
γ [°]	90	77.766(2)	90	105.798(3)	95.818(2)
ρ_{cald} [g cm ⁻³]	2.335	2.153	1.931	2.237	2.388
<i>V</i> [Å ³]	27428.9(17)	31138(2)	23770.1(18)	10724.1(11)	12410.2(8)
<i>Z</i>	4	4	2	1	1
$\mu(\text{MoK}\alpha)$ mm ⁻¹	3.219	2.968	2.722	3.896	4.187
<i>T</i> [K]	150	150	150	150	150
no. rflns (measd)	217052	326300	140692	108850	129811
no. rflns (unique)	53780	111436	18555	15593	19372
no. params	2853	5714	1079	1960	2536
Goodness-of-fit on <i>F</i> ²	1.053	1.024	1.070	1.032	1.029
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.0516	0.0926	0.0778	0.0976	0.0660
<i>wR</i> 2 (all data)	0.1646	0.3021	0.2741	0.3280	0.2122

Additional References

- S1 E. Cadôt, B. Salignac, S. Halut and F. Sécheresse, *Angew. Chem. Int. Ed.*, **1998**, *37*, 611-613
 S2 G. Sheldrick, *Acta. Cryst. A*, **1990**, *46*, 467-473
 S3 G. Sheldrick, *Acta. Cryst. A*, **2008**, *64*, 112-122
 S4 L. Farrugia, *J. Appl. Crystallogr.*, **1999**, *32*, 837-838
 S5 R. C. Clark and J. S. Reid, *Acta. Cryst. A*, **1995**, *51*, 887-897