

# Water soluble polyoxometal clusters of molybdenum (V) with pyrazole and triazole: synthesis and study of cytotoxicity and antiviral activity

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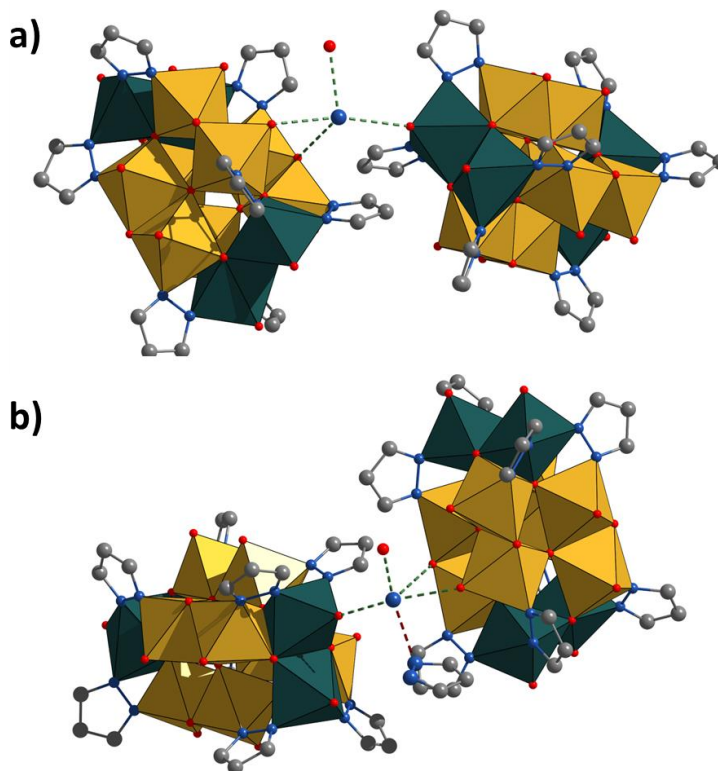
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## Crystal structure data

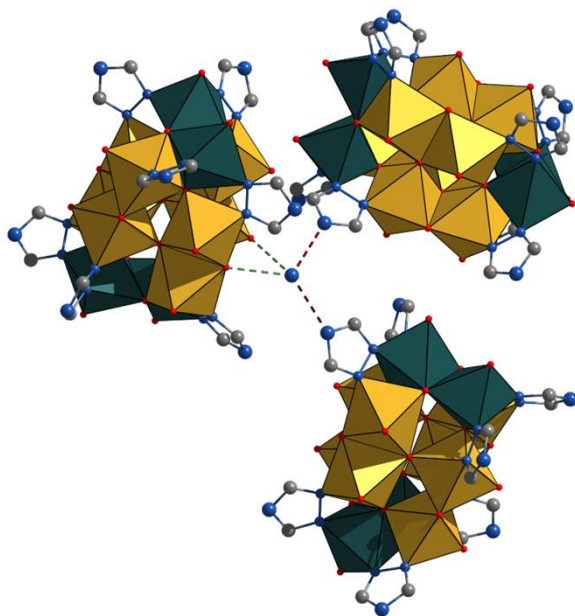
**Table S1.** Main interatomic distances (Å) for **1**, **2** and **3** in comparison with literature data.

Compound	Mo–Mo	Mo–μ–O	Mo–N	Ref
<b>1</b>	2.5773(11)– 2.6225(12)	1.916(7)– 1.990(7)	2.143(8)– 2.197(9)	This study
<b>1</b>	2.5803– 2.6014(9)	1.923(4)– 1.981(4)	2.148(5)– 2.199(5)	This study
<b>3</b>	2.5731(4)– 2.6036(4)	1.913(2)– 1.989(3)	2.157(3)– 2.229(3)	This study
[Mo <sup>V</sup> <sub>6</sub> Mo <sup>VI</sup> <sub>2</sub> (μ-pz) <sub>6</sub> O <sub>18</sub> (pzH) <sub>6</sub> ]	2.5722(5)– 2.5752(4)	1.928(2)– 1.950(2)	μ-pz: 2.195(2)– 2.206(2) pzH: 2.256(2)– 2.240(2)	1
[Mo <sub>8</sub> <sup>V</sup> Mo <sub>2</sub> <sup>VI</sup> O <sub>26</sub> (3-Me-Py) <sub>8</sub> ]	2.5576(8)– 2.6128(8)	1.812(4)– 2.050(5)	2.213(6)– 2.251(6)	2

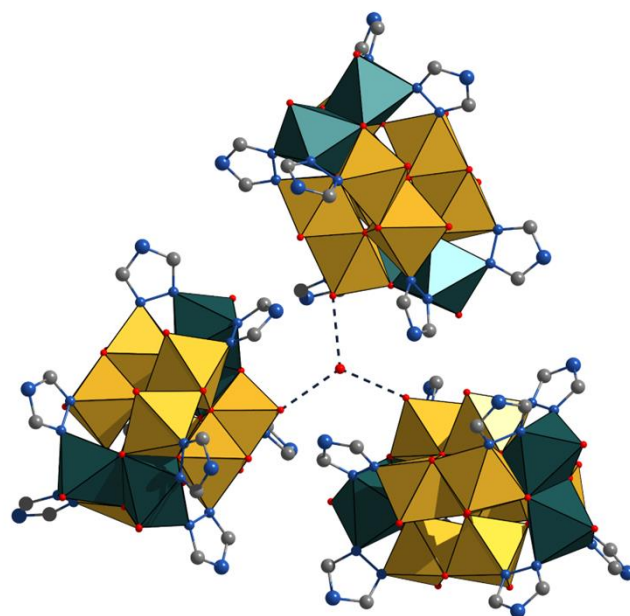


**Figure S1.** Hydrogen bonds observed in the crystal structure of **1**. Color code: O – red, C – gray, N – blue, Mo<sup>V</sup><sub>2</sub>O<sub>6</sub>N<sub>4</sub> – yellow edge-connected octahedrons, Mo<sup>V</sup>O<sub>8</sub>N<sub>2</sub> – blue-green edge-connected octahedrons, N...O – green dashed line, N...N – red dashed line.

a)

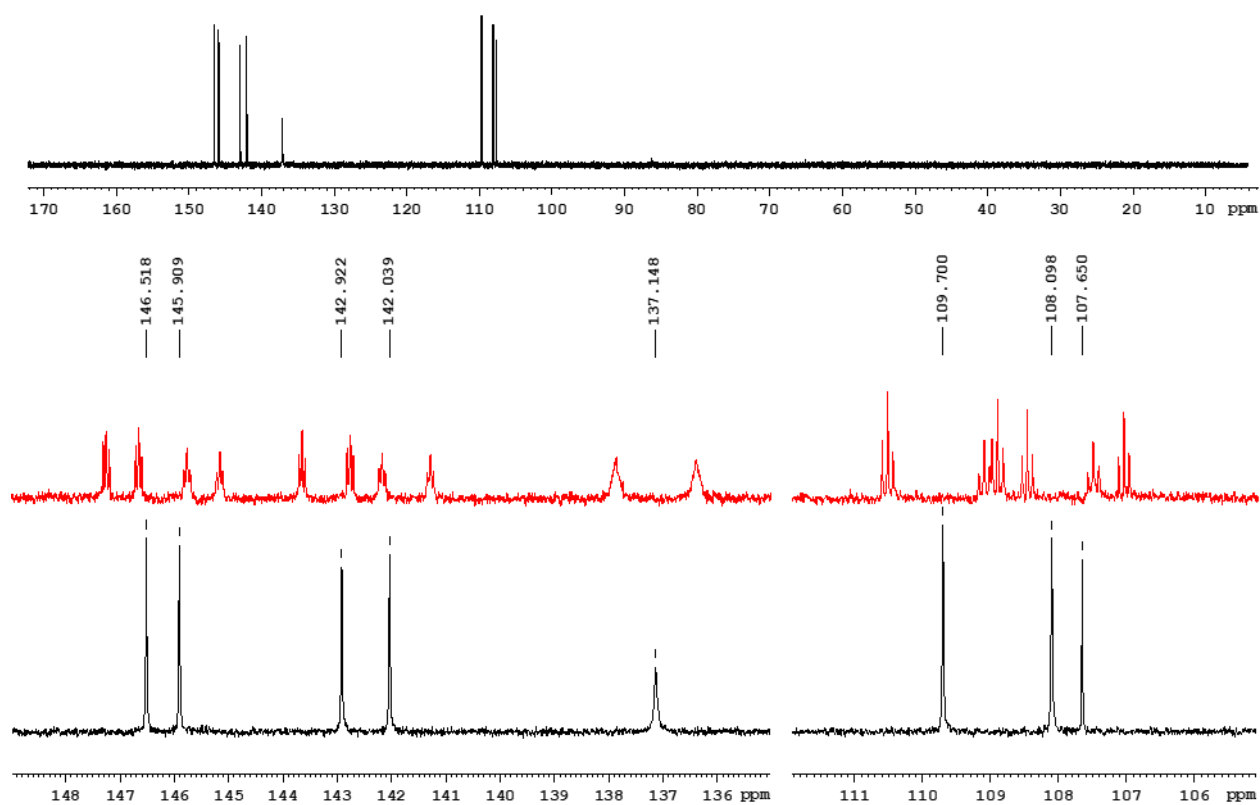


b)

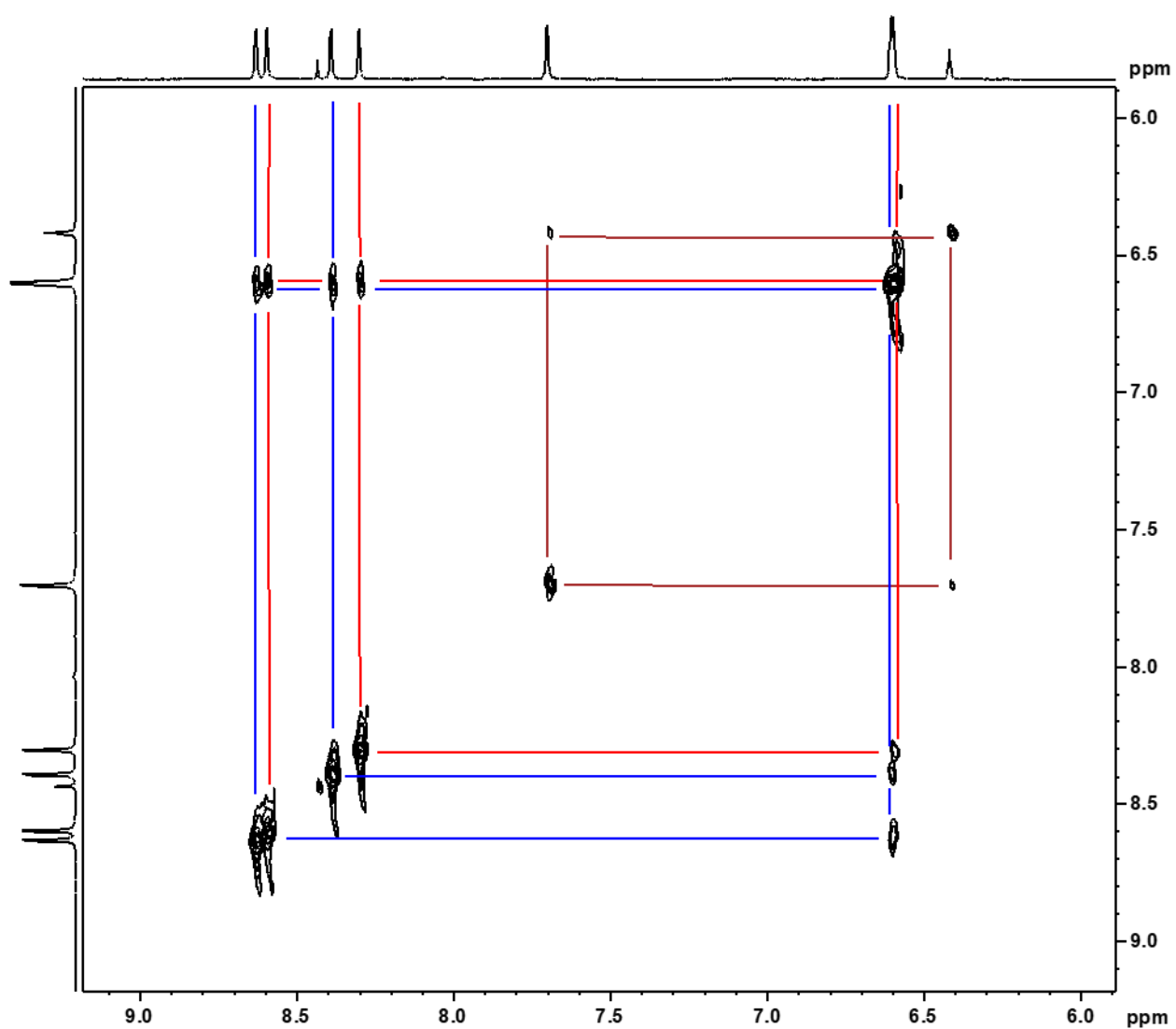


**Figure S2.** Hydrogen bonds observed in the crystal structure of **2**. Color code: O – red, C – gray, N – blue,  $\text{Mo}^{\text{V}}_2\text{O}_6\text{N}_4$  – yellow edge-connected octahedrons,  $\text{Mo}^{\text{V}}\text{O}_8\text{N}_2$  – blue-green edge-connected octahedrons,  $\text{N}\cdots\text{O}$  – green dashed line,  $\text{N}\cdots\text{N}$  – red dashed line,  $\text{O}\cdots\text{O}$  – blue dashed line.

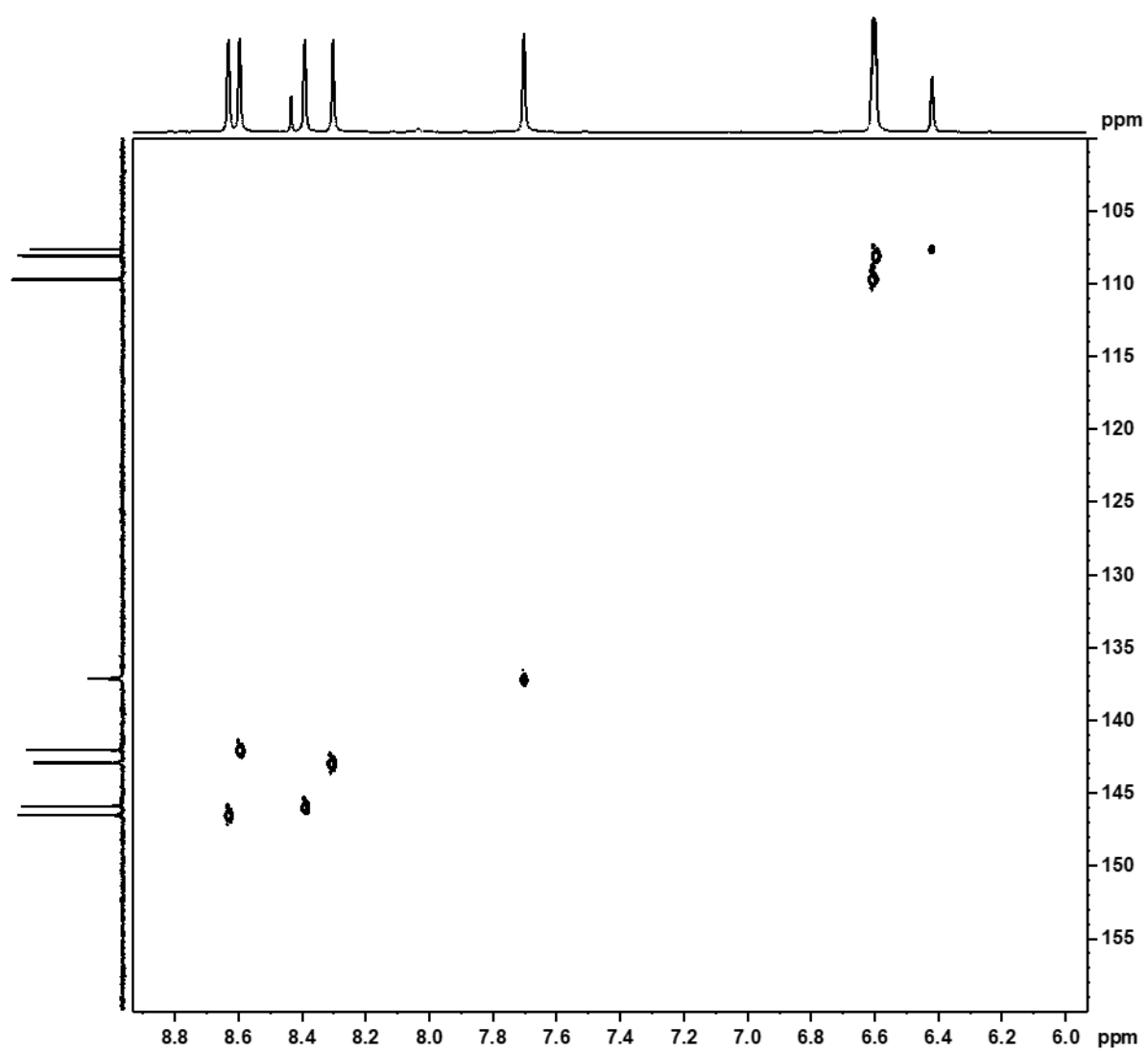
## NMR and mass-spectrometry data for 1



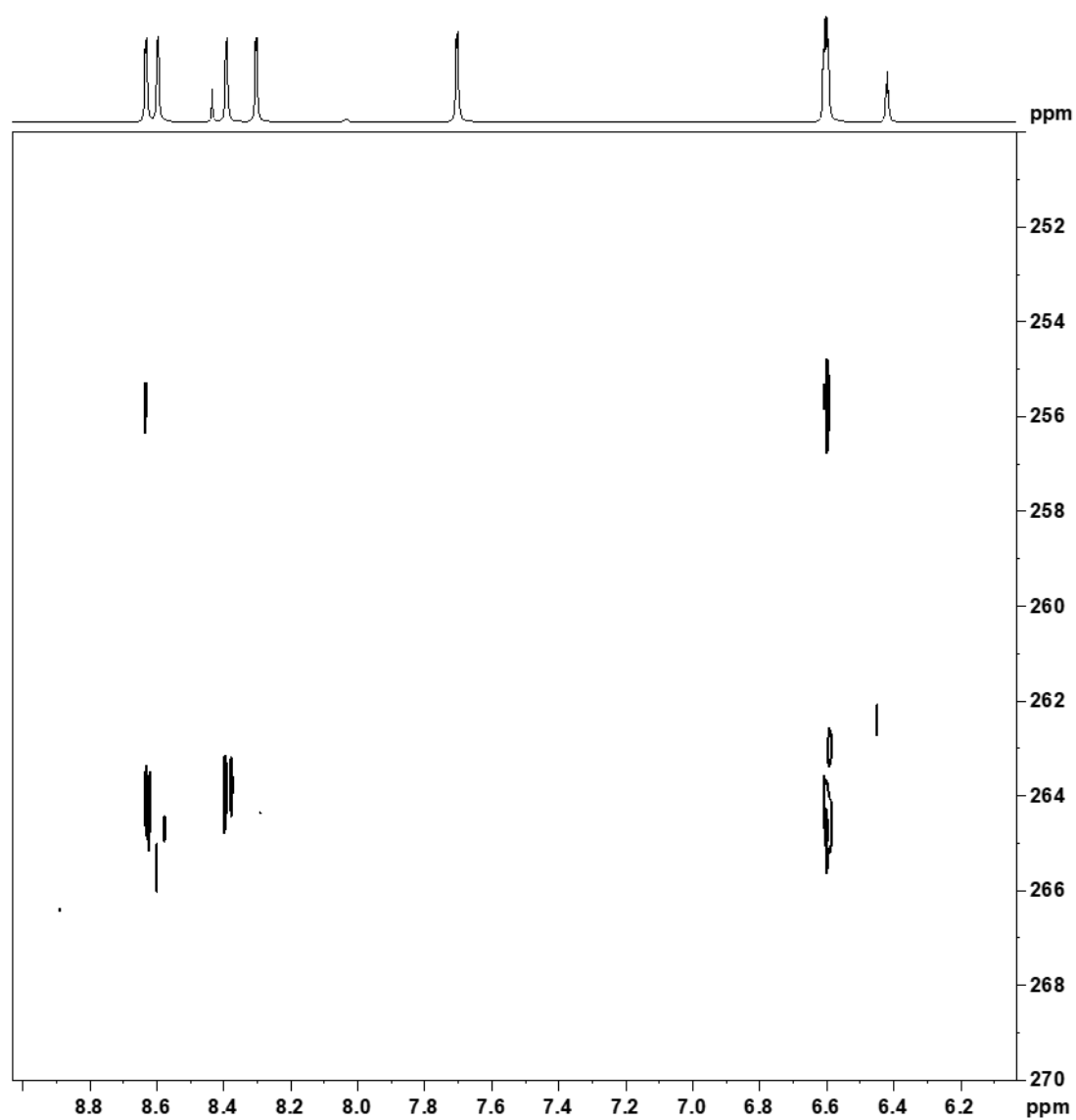
**Figure S3.** <sup>13</sup>C NMR (red) and <sup>13</sup>C{<sup>1</sup>H} (black) spectra of 1 in D<sub>2</sub>O.



**Figure S4.**  $^1\text{H}$ ,  $^1\text{H}$ -NMR correlation spectra of **1** in  $\text{D}_2\text{O}$ .

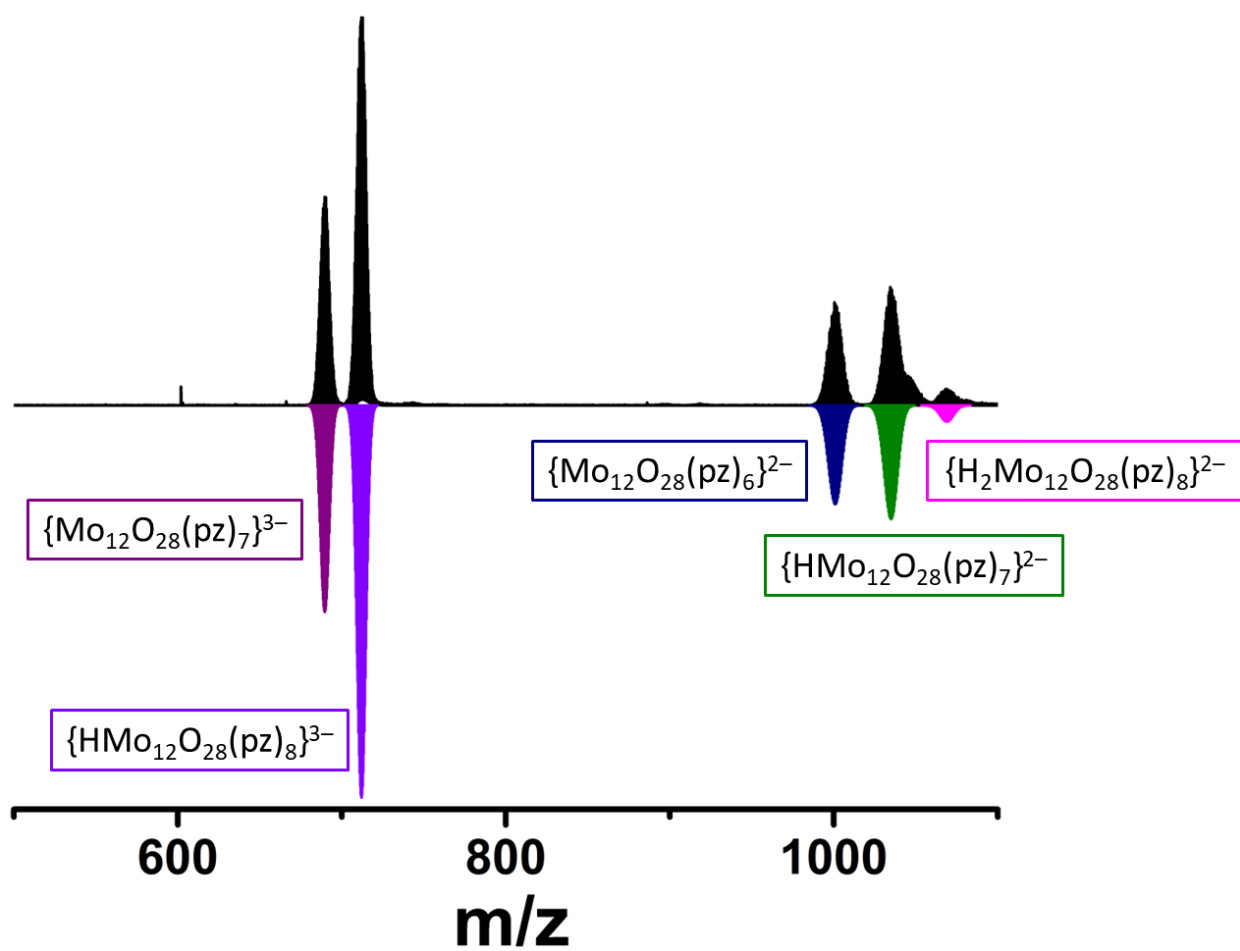


**Figure S5.** <sup>1</sup>H, <sup>13</sup>C-NMR correlation (HSQC) spectra of **1** in D<sub>2</sub>O.



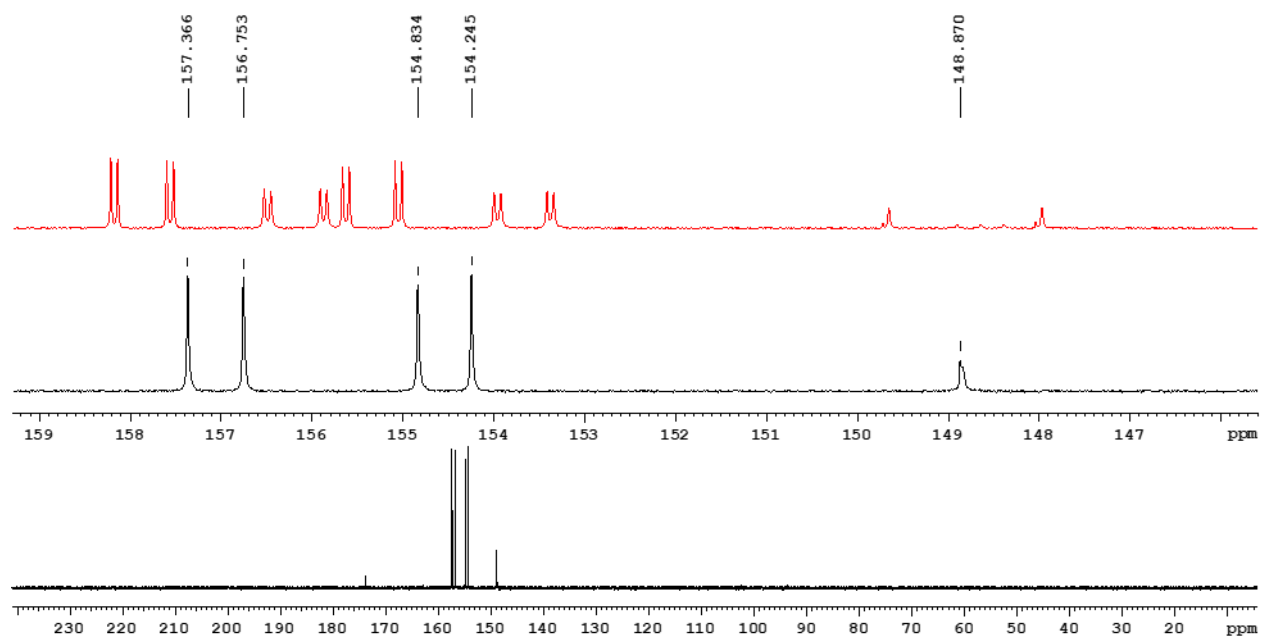
**Figure S6.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectra of **1** in  $\text{D}_2\text{O}$ .



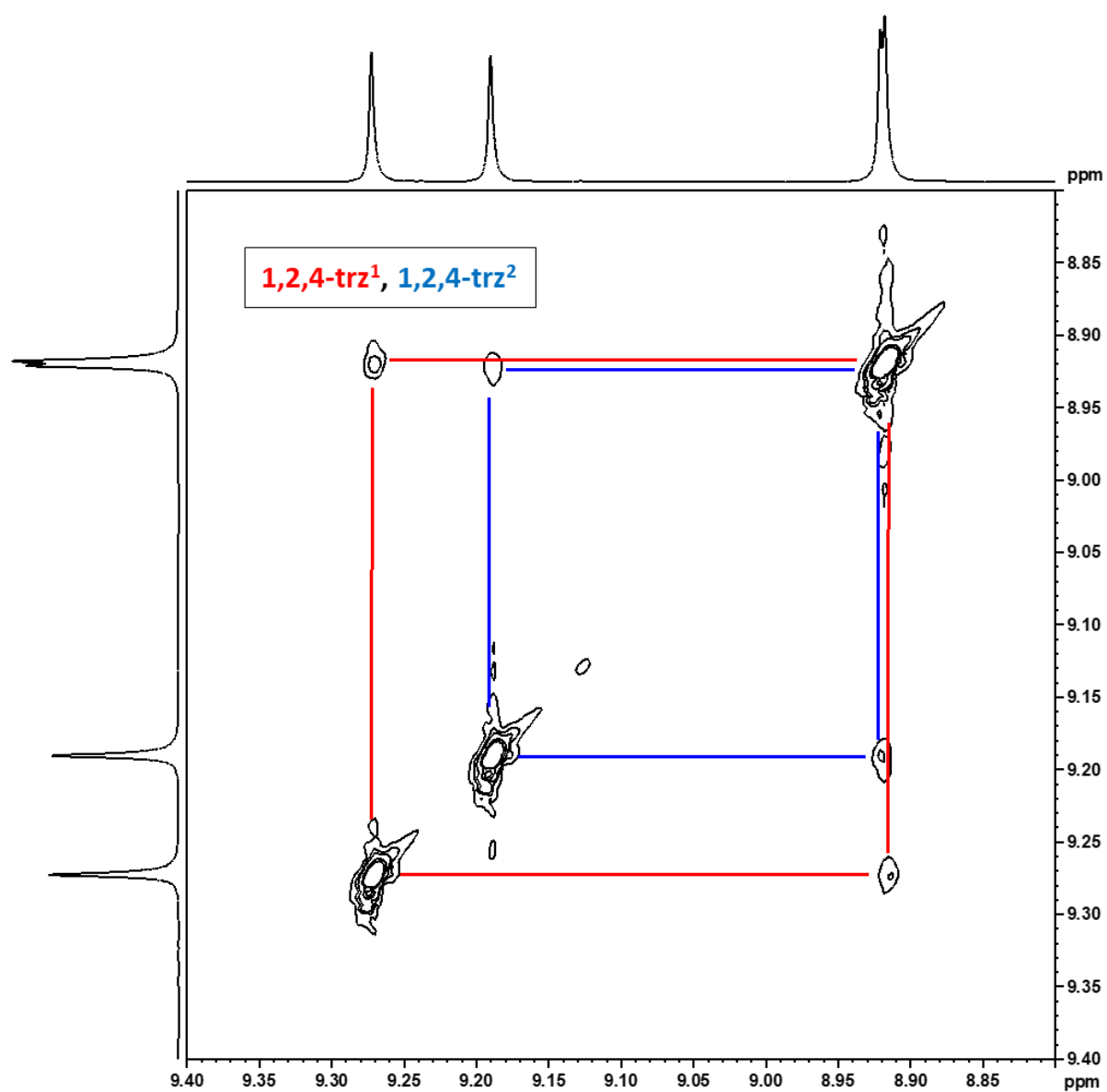


**Figure S7.** HR-ESI-MS spectrum of solution of **1** in water (black) and simulations of cluster forms (colored).

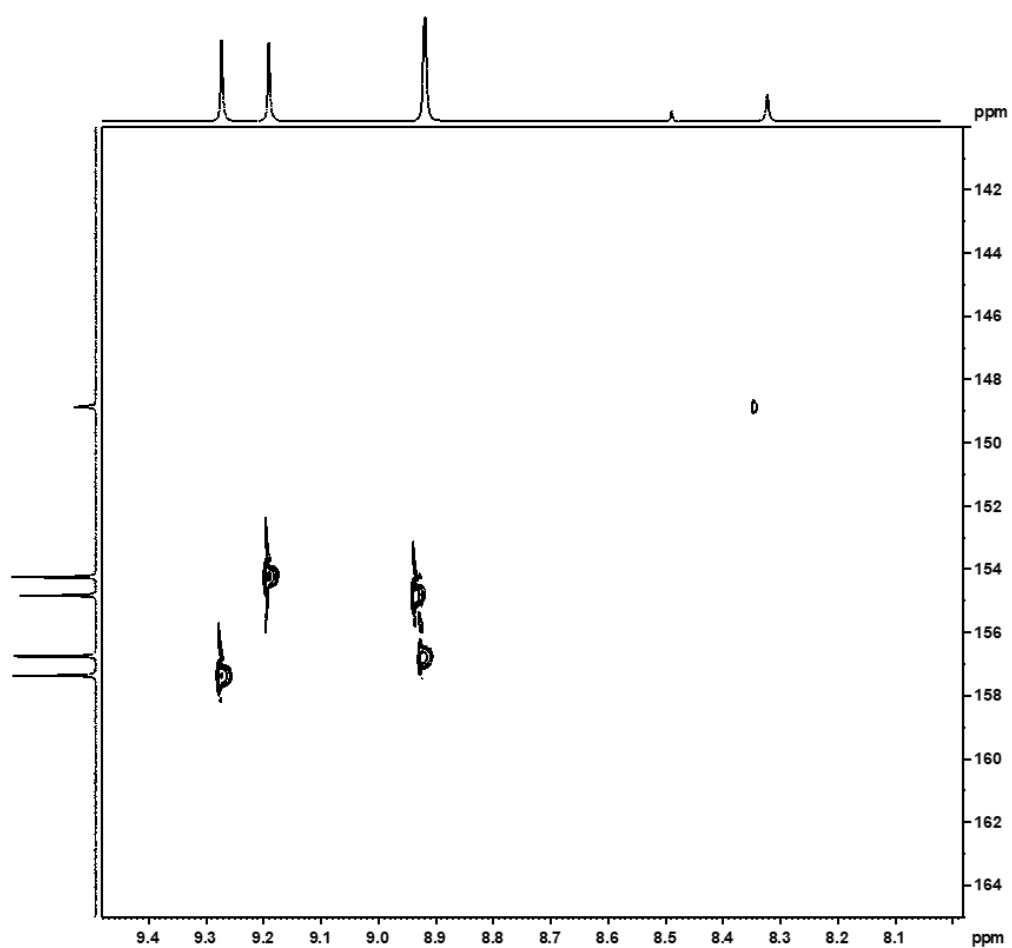
## NMR and mass-spectrometry data for 2



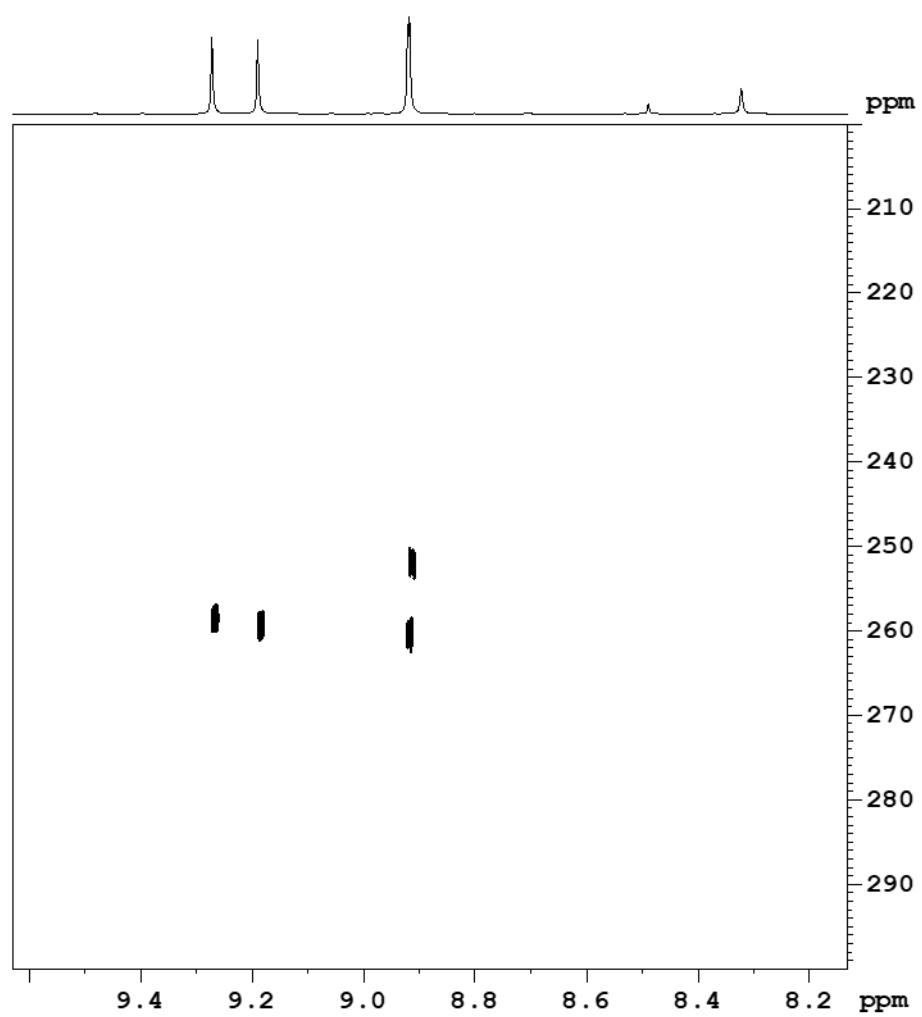
**Figure S8.** <sup>13</sup>C NMR (red) and <sup>13</sup>C{<sup>1</sup>H} (black) spectra of 2 in D<sub>2</sub>O.



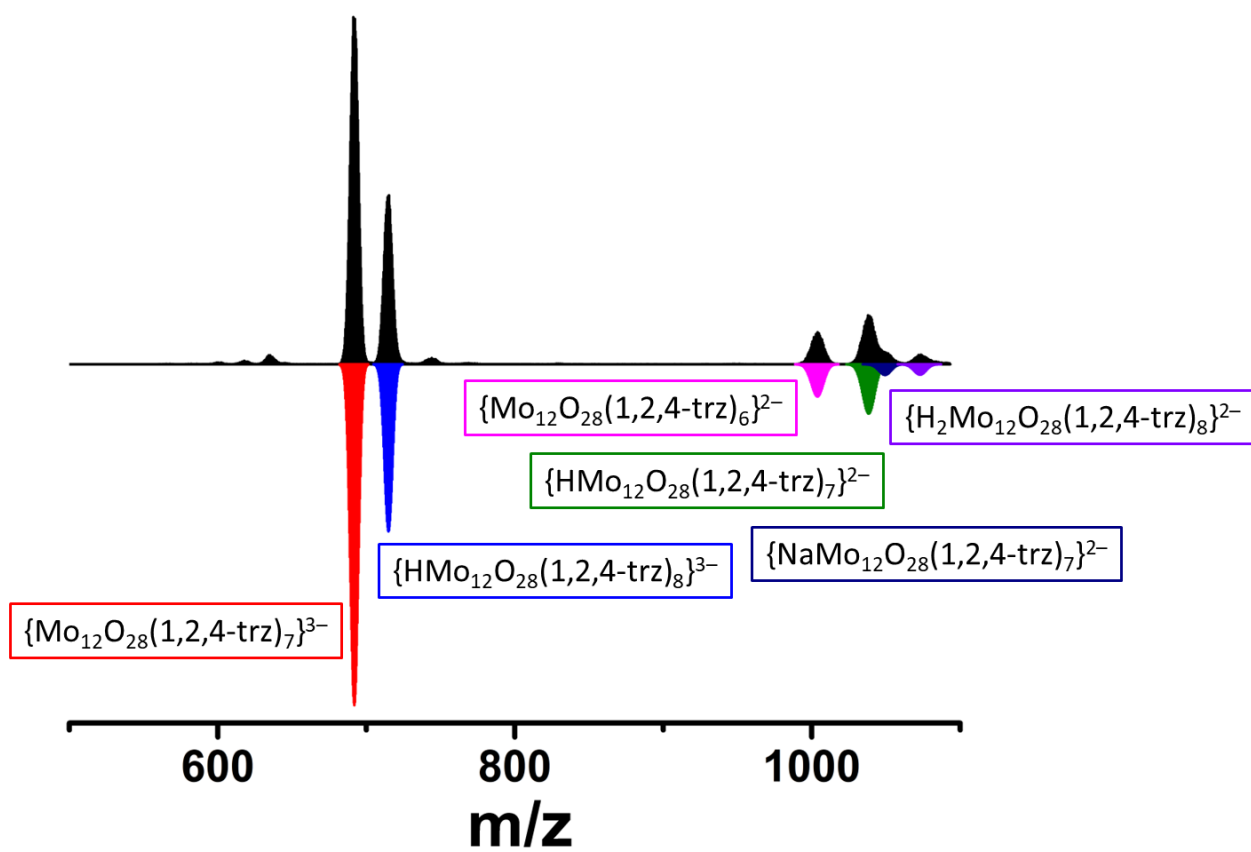
**Figure S9.**  $^1\text{H}$ ,  $^1\text{H}$ -NMR correlation spectra of **2** in  $\text{D}_2\text{O}$ .



**Figure S10.**  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR correlation (HSQC) spectra of **2** in  $\text{D}_2\text{O}$ .

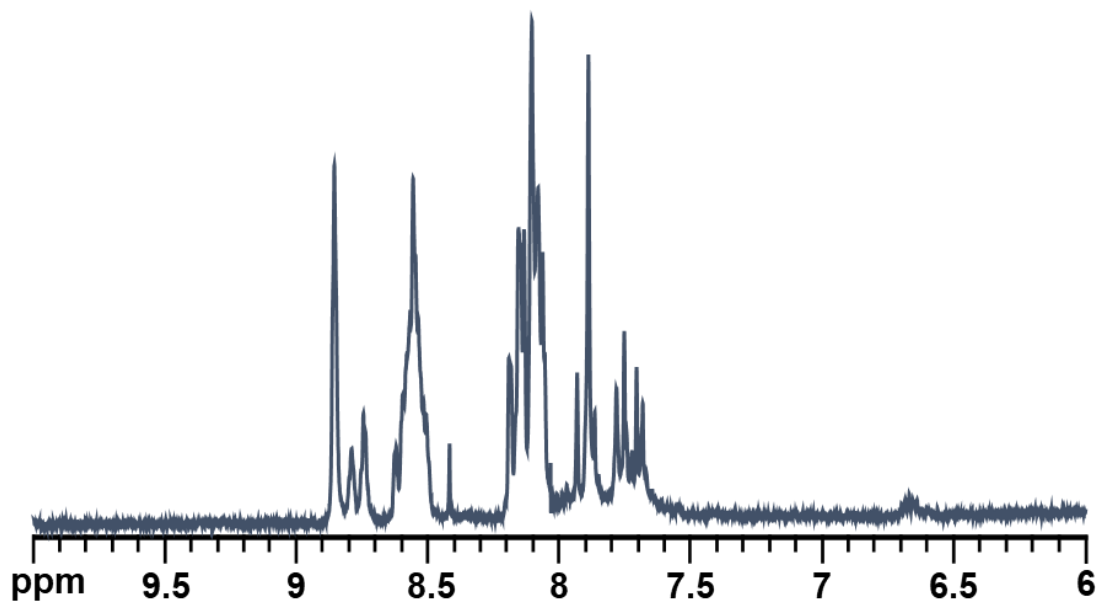


**Figure S11.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC NMR spectra of **2** in  $\text{D}_2\text{O}$ .

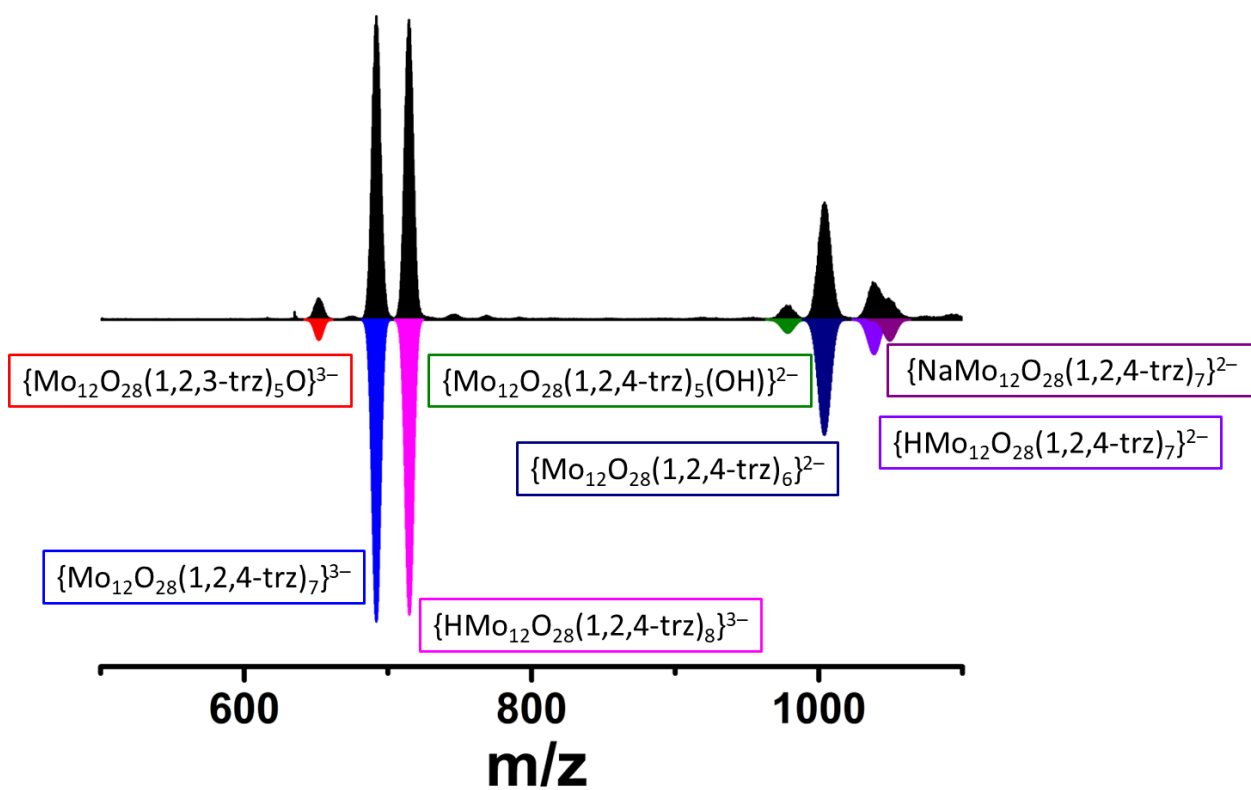


**Figure S12.** HR-ESI-MS spectrum of solution of **2** in water (black) and simulations of cluster forms (colored).

## NMR and mass-spectrometry data for **3**

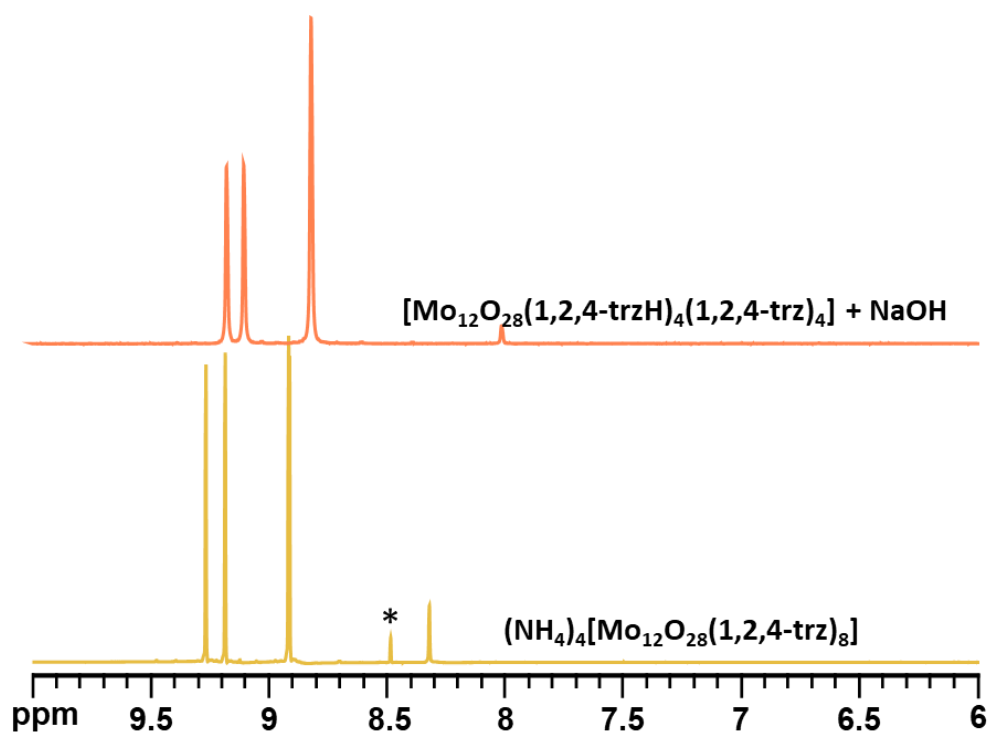


**Figure S13.**  $^1\text{H}$  NMR spectra of **3** in  $\text{D}_2\text{O}$ .



**Figure S14.** HR-ESI-MS spectrum of solution of **3** in water (black) and simulations of cluster forms (colored).

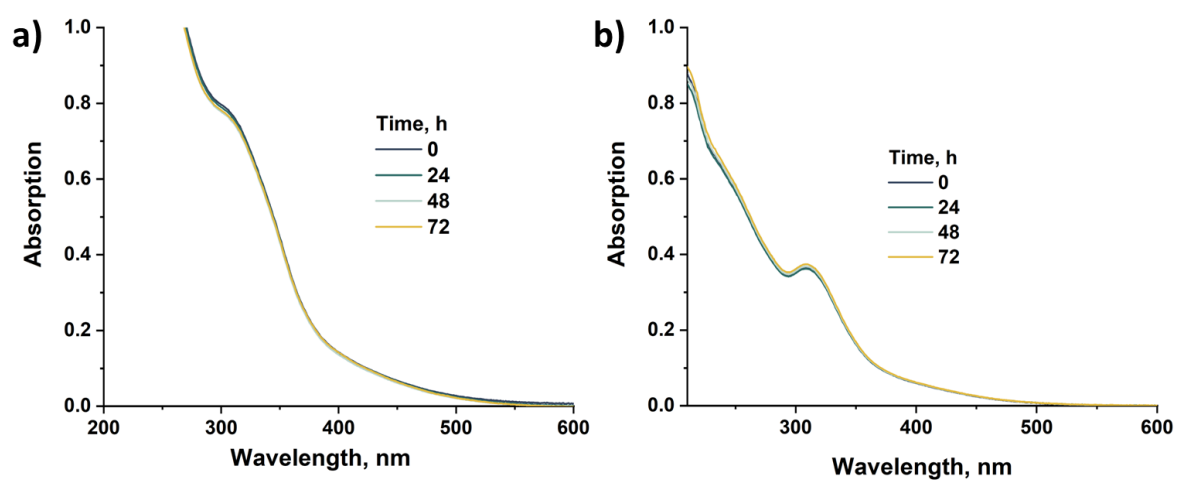
## NMR-spectra of 2 after precipitation with HCl



**Figure S15.**  $^1\text{H}$  NMR spectra of **2** before (bottom) precipitation with HCl and spectra of dissolved precipitate with NaOH (top) in  $\text{D}_2\text{O}$ .



## UV-vis spectra of solutions in culture medium



**Figure S16.** UV-vis spectra of compounds **1** (a) and **2** (b) in culture medium in time.

## ICP-AES data

**Table S2.** Quantities of Mo accumulated by cells (Hep-2 and MRC-5) after incubation in 1 mM ( $\sim 2350 \mu\text{g Mo} / 5 \cdot 10^5 \text{ cells}$ ) of solutions of **1** and **2** for 30 minutes, 2, 6, 24 and 48 h.

Sample type	Time	Hep-2, $\mu\text{g Mo}/5 \cdot 10^5 \text{ cells}$	MRC-5, $\mu\text{g Mo}/5 \cdot 10^5 \text{ cells}$
Control		0.02	0.01
<b>1</b>	30 minutes	0.25	0.22
	2 hours	0.46	0.25
	6 hours	0.47	0.24
	24 hours	0.75	0.77
	48 hours	0.75	0.83
<b>2</b>	30 minutes	0.18	0.23
	2 hours	0.32	0.11
	6 hours	0.33	0.12
	24 hours	0.43	0.34
	48 hours	0.42	0.34

## IR spectra

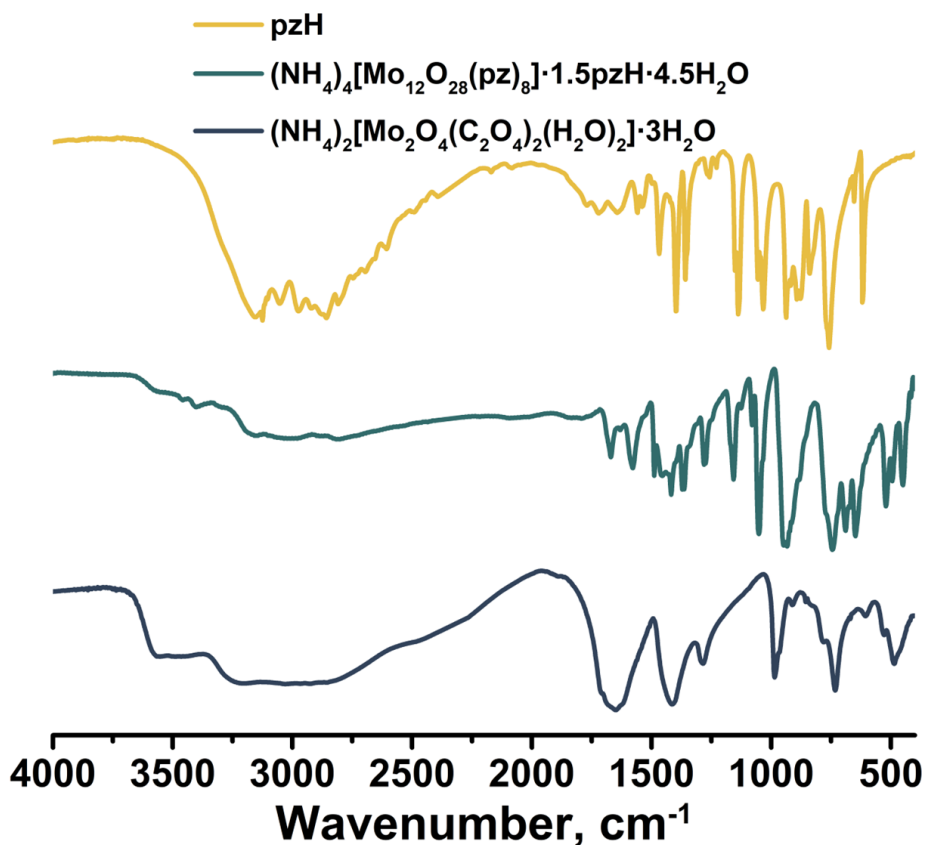


Figure S17. FTIR spectra of **1** in comparison with pyrazole and initial cluster.

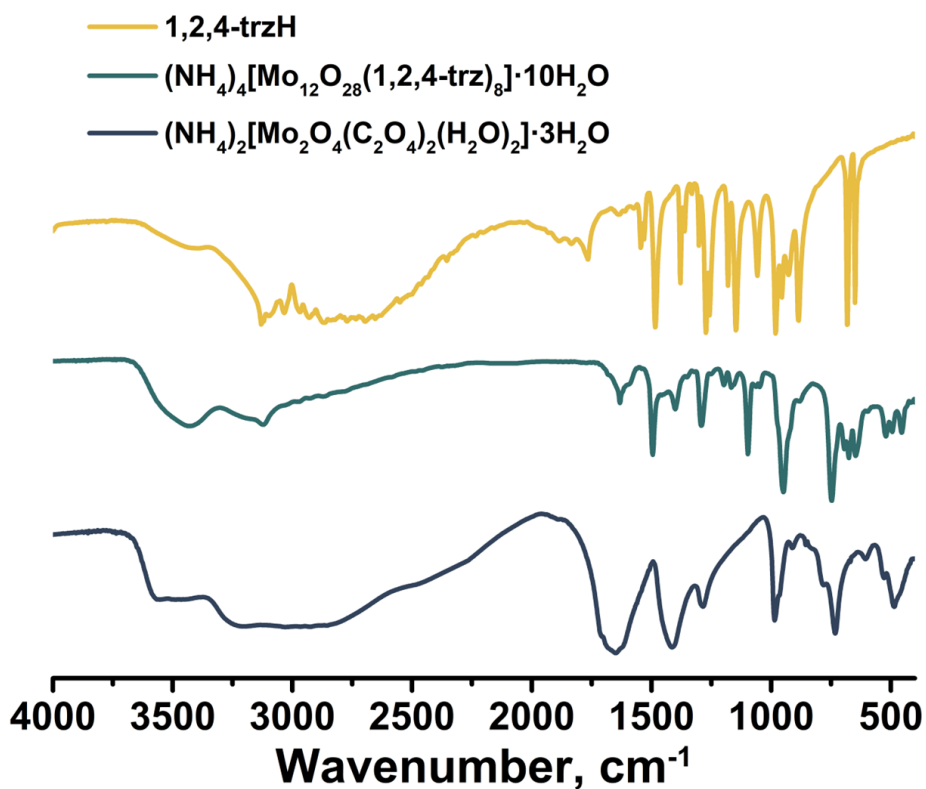
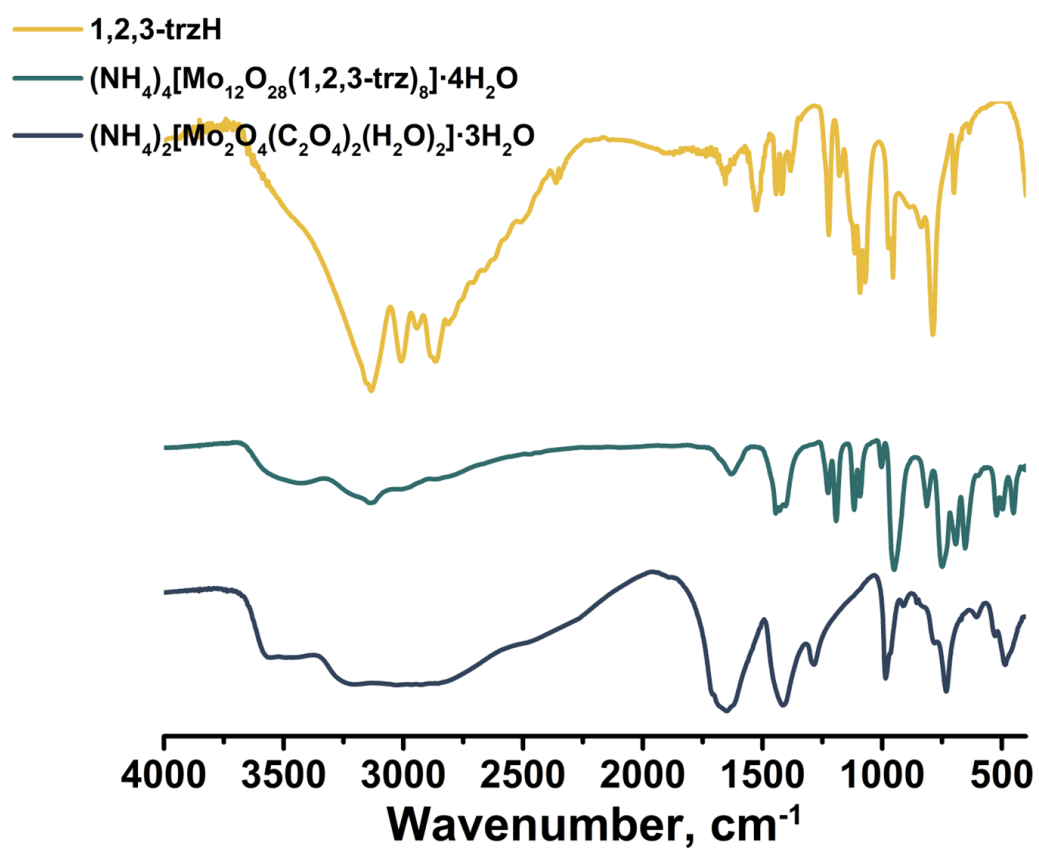


Figure S18. FTIR spectra of **2** in comparison with pyrazole and initial cluster.



**Figure S19.** FTIR spectra of **3** in comparison with pyrazole and initial cluster.

## Thermogravimetric analysis

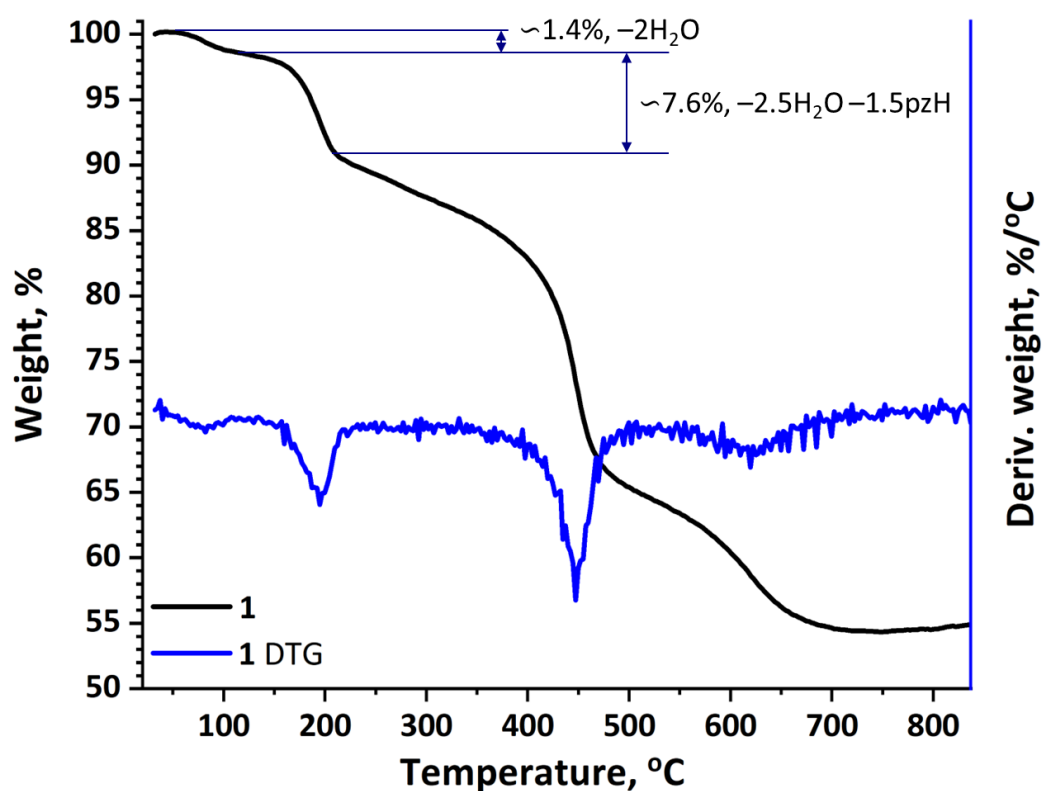


Figure S20. TGA and DTG curves of **1**. Heating rates of 10 °C·min<sup>-1</sup>.

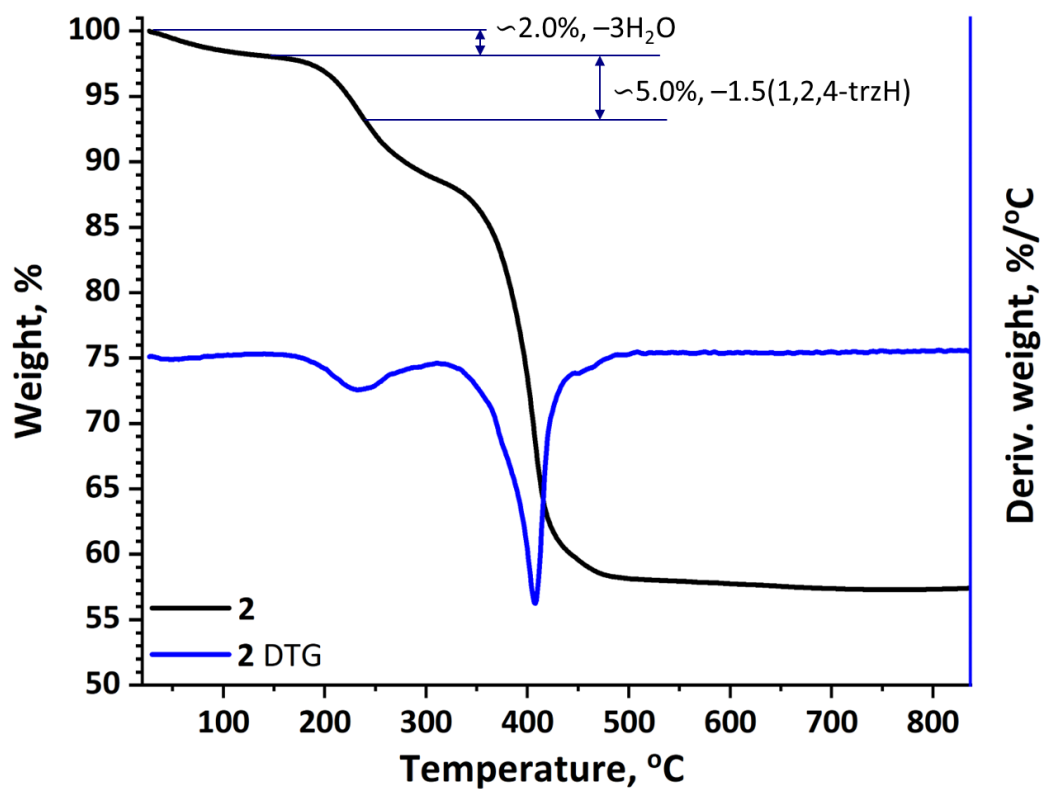
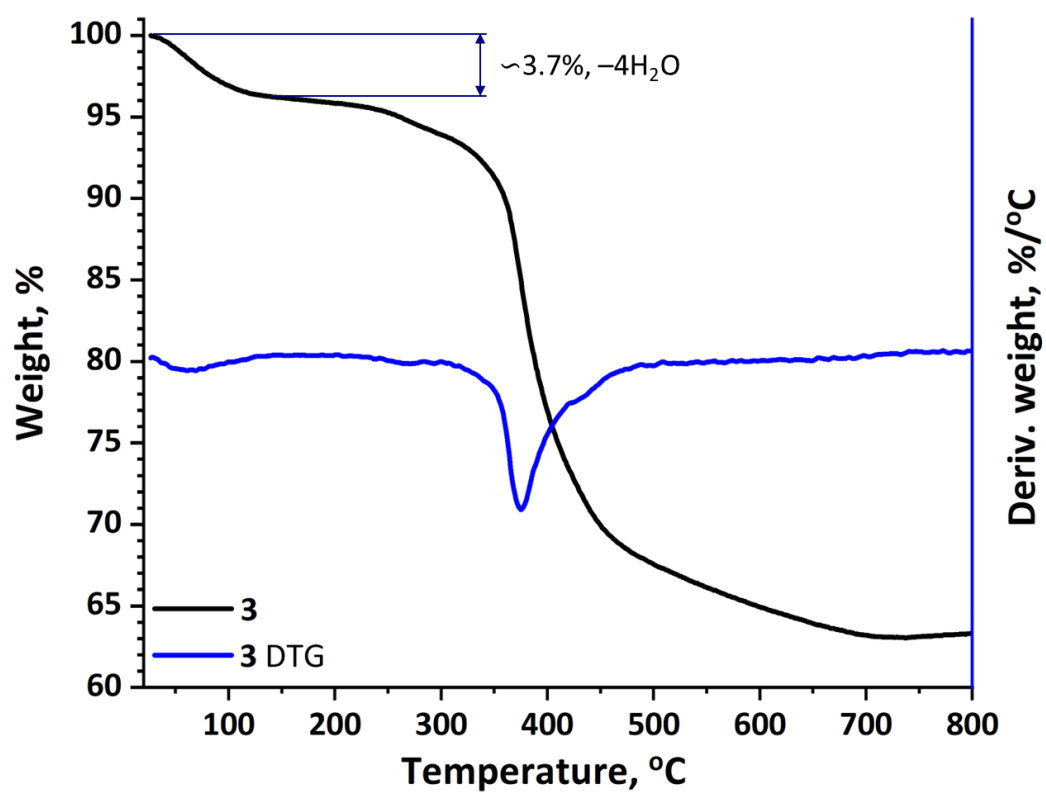
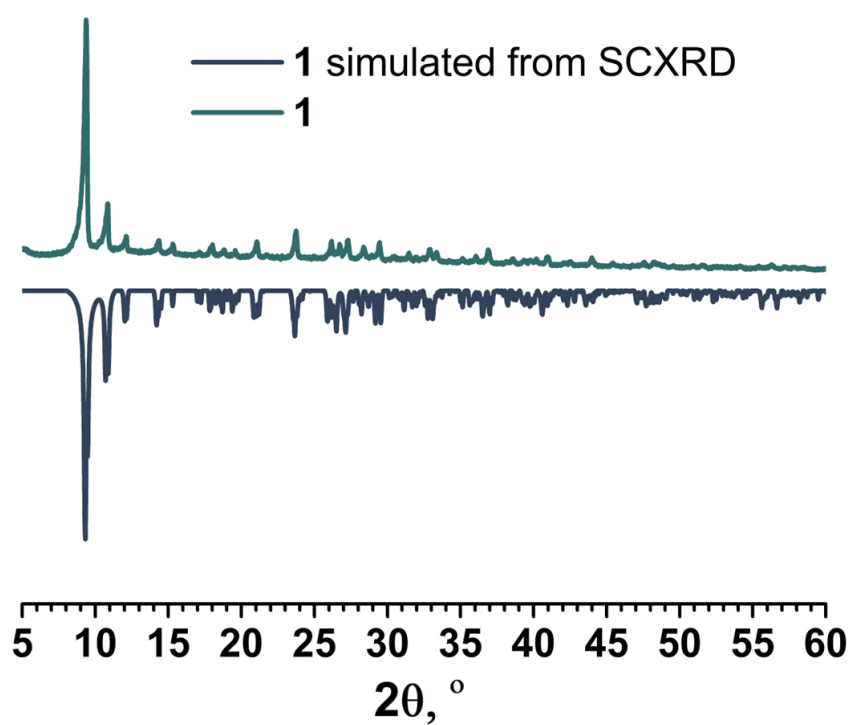


Figure S21. TGA and DTG curves of **2**. Heating rates of 10 °C·min<sup>-1</sup>.

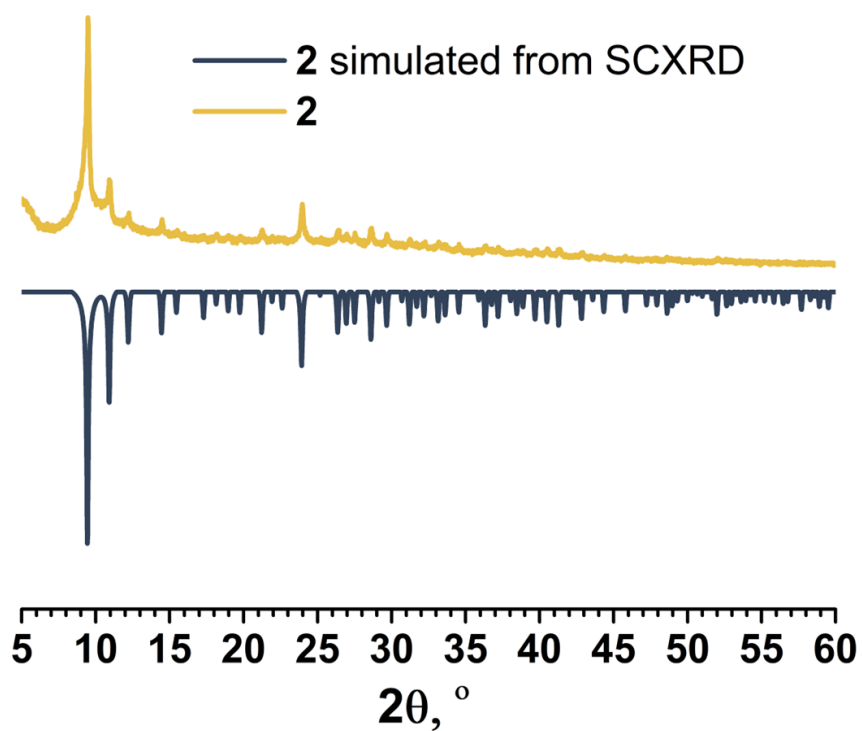


**Figure S22.** TGA and DTG curves of **3**. Heating rates of 10 °C·min<sup>-1</sup>.

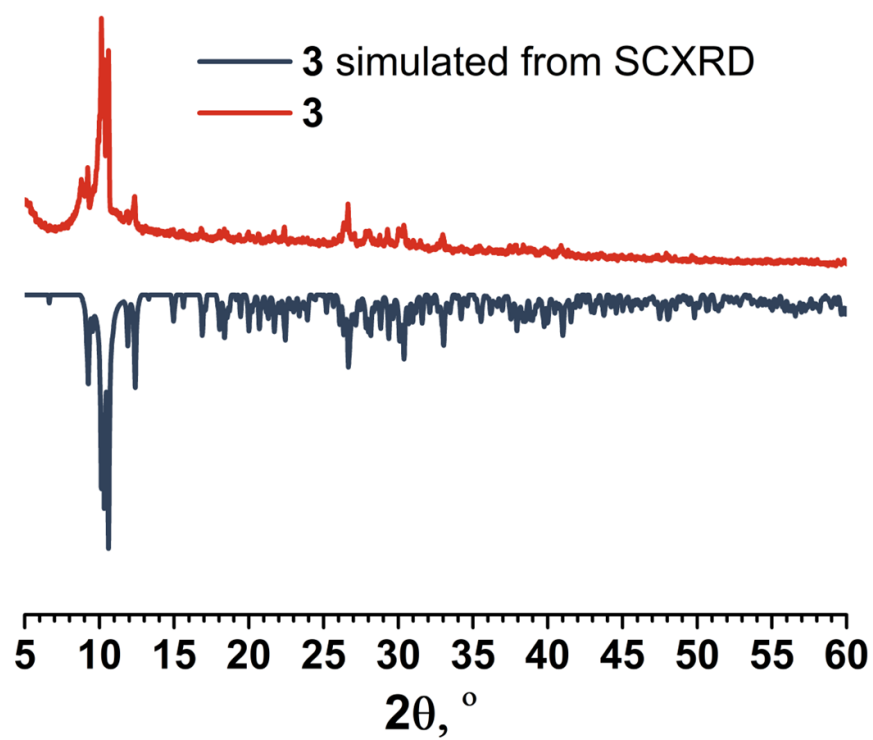
## Powder X-ray diffraction analysis



**Figure S23.** XRPD pattern of **1** in comparison with calculated one from the SCXRD data.



**Figure S24.** XRPD pattern of **2** in comparison with calculated one from the SCXRD data.



**Figure S25.** XRPD pattern of **3** in comparison with calculated one from the SCXRD data.



## Crystal structure data

**Table S3.** Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis for  $(\text{NH}_4)_4[\text{Mo}_{12}\text{O}_{28}(\text{pz})_8] \cdot 1.5\text{pzH} \cdot 4.5\text{H}_2\text{O}$  (**1**),  $(\text{NH}_4)_4[\text{Mo}_{12}\text{O}_{28}(1,2,4\text{-trz})_8] \cdot 10\text{H}_2\text{O}$  (**2**) and  $(\text{NH}_4)_4[\text{Mo}_{12}\text{O}_{28}(1,2,3\text{-trz})_8] \cdot 4\text{H}_2\text{O}$  (**3**).

Compound	<b>1</b>	<b>2</b>	<b>3</b>
CCDC	2299185	2299187	2299186
Empirical formula	$\text{C}_{28.5}\text{H}_{55}\text{Mo}_{12}\text{N}_{23}\text{O}_{32.5}$	$\text{C}_{16}\text{H}_{52}\text{Mo}_{12}\text{N}_{28}\text{O}_{38}$	$\text{C}_{16}\text{H}_{40}\text{Mo}_{12}\text{N}_{28}\text{O}_{32}$
Formula weight	2391.23	2396.13	2288.04
Temperature, K	150(2)	150(2)	150(2)
Crystal system	Trigonal	Cubic	Monoclinic
Space group	$R\bar{3}c$	$I\bar{4}3d$	$P2_1/n$
$a$ , Å	38.3453(15)	26.6106(4)	11.7496(4)
$b$ , Å	38.3453(15)	26.6106(4)	21.5118(7)
$c$ , Å	22.8946(11)	26.6106(4)	22.6938(7)
$\alpha$ , °	90	90	90
$\beta$ , °	90	90	102.1740(10)
$\gamma$ , °	120	90	90
$V$ , Å <sup>3</sup>	29153(3)	18843.6(8)	5607.0(3)
$Z$	18	12	4
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	2.452	2.534	2.710
$\mu$ , mm <sup>-1</sup>	2.338	2.420	2.696
$F(000)$	20718	13824	4368
Crystal size	0.12 × 0.10 × 0.10	0.06 × 0.06 × 0.06	0.10 × 0.08 × 0.08
2 $\theta$ range for data collection, °	1.850 to 33.172	2.165 to 30.495	1.893 to 33.158
Index ranges	$-58 \leq h \leq 58$	$-37 \leq h \leq 37$	$-18 \leq h \leq 18$
	$-58 \leq k \leq 45$	$-38 \leq k \leq 37$	$-33 \leq k \leq 33$
	$-35 \leq l \leq 35$	$-38 \leq l \leq 38$	$-28 \leq l \leq 34$
Reflections collected	184771	180189	74359
Independent reflections	24695 [ $R_{\text{int}} = 0.0853$ ]	4789 [ $R_{\text{int}} = 0.0811$ ]	21345 [ $R_{\text{int}} = 0.0520$ ]
Data/restraints/parameters	24695/19/918	4789/24/254	21345/30/832
Goodness-of-fit on $F^2$	1.069	1.131	1.063
$R_1 / wR_2(I > 2\sigma(I))$	0.0514/0.1212	0.0243/0.0549	0.0385/0.0850
$R_1 / wR_1$ (all data)	0.0580/0.1249	0.0275/0.0565	0.0606/0.0914
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e·Å <sup>-3</sup> )	2.197/−2.089	0.640/−0.506	1.260/−1.537

## References

1. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson and J. Trotter, *Inorg. Chem.*, 1993, **32**, 5176–5182.
2. B. Modec, J. V. Brenčič, L. Golič and L. M. Daniels, *Polyhedron*, 2000, **19**, 1407-1414.