

## Synthesis, structural characterization and properties of a series of heteropolyoxomolybdates: [AlMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>]<sup>3-</sup>, [GeMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>, [GeMo<sub>6</sub>O<sub>22</sub>(Hmal)<sub>3</sub>]<sup>7-</sup>, [SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>, [TeMo<sub>6</sub>O<sub>24</sub>]<sup>6-</sup>

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### TABLE OF CONTENT

**Table S1.** Thermogravimetric data for compounds **1-4**, **6-10**

**Figure S1.** TG curve of [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>3</sub>[AlMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>]·7H<sub>2</sub>O (**1**)

**Figure S2.** TG curve of [{Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>Na<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{H<sub>4</sub>Mo<sub>8</sub>O<sub>28</sub>}]·4H<sub>2</sub>O (**1a**)

**Figure S3.** TG curve of [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[Al(mal)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·Hmal·2H<sub>2</sub>O (**1b**)

**Figure S4.** TG curve of [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>6</sub>[TeMo<sub>6</sub>O<sub>24</sub>]·16H<sub>2</sub>O (**2**)

**Figure S5.** TG curve of Na<sub>2</sub>[Co(ox)(en)<sub>2</sub>]<sub>4</sub>[TeMo<sub>6</sub>O<sub>24</sub>]·16H<sub>2</sub>O (**3**)

**Figure S6.** TG curve of [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>4</sub>[GeMo<sub>12</sub>O<sub>40</sub>]·6H<sub>2</sub>O (**4**)

**Figure S7.** TG curve of [Co(ox)(en)<sub>2</sub>]<sub>4</sub>[GeMo<sub>12</sub>O<sub>40</sub>]·12H<sub>2</sub>O (**6**)

**Figure S8.** TG curve of [Co(ox)(en)<sub>2</sub>]<sub>4</sub>[SiMo<sub>12</sub>O<sub>40</sub>]·12H<sub>2</sub>O (**7**)

**Figure S9.** TG curve of Na<sub>4</sub>[Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>3</sub>[GeMo<sub>6</sub>O<sub>22</sub>(Hmal)<sub>3</sub>]·7.75H<sub>2</sub>O (**8**)

**Figure S10.** TG curve of [Co(NH<sub>3</sub>)<sub>6</sub>][Al(mal)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (**9**)

**Figure S11.** TG curve of [Co(en)<sub>3</sub>]<sub>2</sub>[Mo<sub>8</sub>O<sub>26</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (**10**)

**Table S2.** IR spectra data for compounds **1-4** i **6-10**

**Figure S12.** IR spectrum of [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>3</sub>[AlMo<sub>6</sub>(OH)<sub>6</sub>O<sub>18</sub>]·7H<sub>2</sub>O (**1**)

**Figure S13.** IR spectrum of [{Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>Na<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{H<sub>4</sub>Mo<sub>8</sub>O<sub>28</sub>}]·4H<sub>2</sub>O (**1a**)

**Figure S14.** IR spectrum of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_2[\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2]\cdot\text{Hmal}\cdot 2\text{H}_2\text{O}$  (**1b**)

**Figure S15.** TG curve of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_6[\text{TeMo}_6\text{O}_{24}]\cdot 16\text{H}_2\text{O}$  (**2**)

**Figure S16.** TG curve of  $\text{Na}_2[\text{Co}(\text{ox})(\text{en})_2]_4[\text{TeMo}_6\text{O}_{24}]\cdot 16\text{H}_2\text{O}$  (**3**)

**Figure S17.** IR spectrum of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_4[\text{GeMo}_{12}\text{O}_{40}]\cdot 6\text{H}_2\text{O}$  (**4**)

**Figure S18.** IR spectrum of  $[\text{Co}(\text{ox})(\text{en})_2]_4[\text{GeMo}_{12}\text{O}_{40}]\cdot 12\text{H}_2\text{O}$  (**6**)

**Figure S19.** IR spectrum of  $[\text{Co}(\text{ox})(\text{en})_2]_4[\text{SiMo}_{12}\text{O}_{40}]\cdot 12\text{H}_2\text{O}$  (**7**)

**Figure S20.** IR spectrum of  $\text{Na}_4[\text{Co}(\text{ox})(\text{NH}_3)_4]_3[\text{GeMo}_6\text{O}_{22}(\text{Hmal})_3]\cdot 7.75\text{H}_2\text{O}$  (**8**)

**Figure S21.** IR spectrum of  $[\text{Co}(\text{NH}_3)_6][\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$  (**9**)

**Figure S22.** IR spectrum of  $[\text{Co}(\text{en})_3]_2[\text{Mo}_8\text{O}_{26}(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 6\text{H}_2\text{O}$  (**10**)

**Table S3.** Crystallographic data of the obtained compounds **1**, **1a**, **1b**, **2**, **4**, **8**

**Table S4.** Crystallographic data of the obtained compounds **3**, **6**, **7**

**Table S5.** Crystallographic data of the obtained compounds **9** and **10**

**Figure. S23** Asymmetric unit (top) and packing of molecules (bottom) for compounds (**1**, **1a**, **1b**, **2**, **4**, **5**, **8**) containing  $[\text{Co}(\text{ox})(\text{NH}_3)_4]^+$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.

**Figure. S24** Asymmetric unit (top) and packing of molecules (bottom) for compounds (**3**, **6**, **7**) containing  $[\text{Co}(\text{ox})(\text{en})_2]^+$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.

**Figure. S25** Asymmetric unit (top) and packing of molecules (bottom) for compounds **9** and **10** containing  $[\text{Co}(\text{en})_3]^{3+}$  or  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.

**Table S6.** Hydrogen bonds formed between complex cations and anions in **1a**.

**Table S7.** Hydrogen bonds formed between complex cations and anions in **10**.

**Table S8.** Hydrogen bonds formed between complex cations and anions in **1b**

**Table S9.** Hydrogen bonds formed between complex cations and anions in **9**.

**Table S10.** Hydrogen bonds formed between complex cations and anions in **1**.

**Table S11.** Hydrogen bonds formed between complex cations and anions in **2**

**Table S12.** Hydrogen bonds formed between complex cations and anions in **3**.

**Table S13.** Hydrogen bonds formed between complex cations and anions in **6**

**Table S14.** Hydrogen bonds formed between complex cations and anions in **7**

**Figure S26.** Visible spectra degradation of safranin T in presence of compounds a) **4** without H<sub>2</sub>O<sub>2</sub> b) **5** without H<sub>2</sub>O<sub>2</sub> c) **1** in presence of H<sub>2</sub>O<sub>2</sub> d) **2** in presence of H<sub>2</sub>O<sub>2</sub>

**Figure S27.** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex **1**.

**Figure S28** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex **2**.

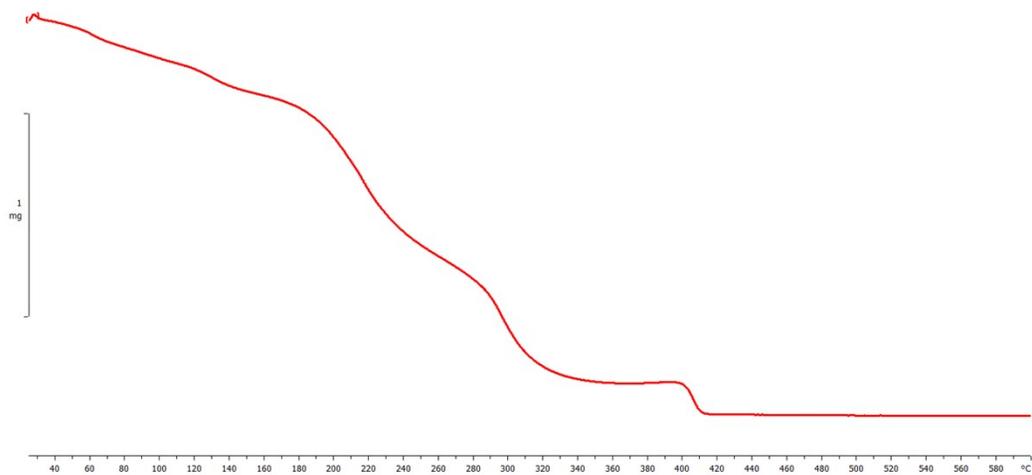
**Figure S29.** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex **4**.

**Figure S30.** PXRD patterns of compounds described in this work. The teal lines indicate patterns obtained by powder diffraction, while the black lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.

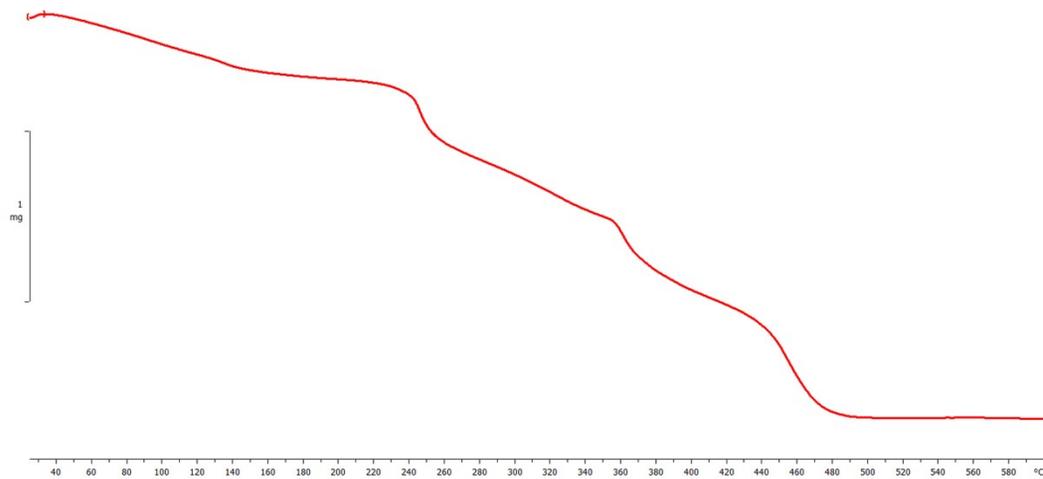
**Figure S31.** Comparison of the PXRD patterns before (dark blue) and after (light blue) the catalytic experiments for compounds **1, 2, 4, 5, 6** and **7**.

**Table S1:** Thermogravimetric data for compounds **1-4, 6-10**

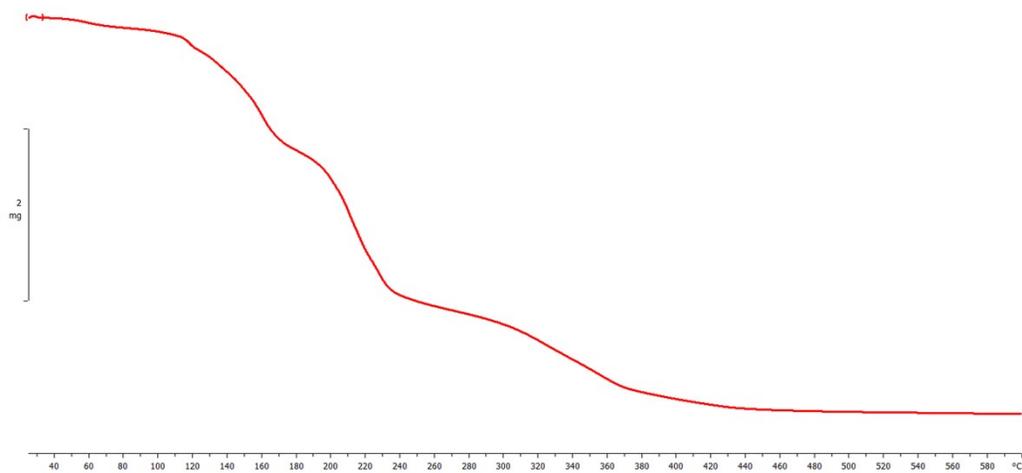
	<b>1<sup>st</sup></b>	<b>2<sup>nd</sup></b>	<b>3<sup>rd</sup></b>
<b>1</b>	33.21 %	2.84 %	
	34-365 °C	369-430 °C	
<b>1a</b>	4.46 %	23.67 %	
	42-193 °C	200-515 °C	
<b>1b</b>	75.31 %		
	32-508 °C		
<b>2</b>	8.98 %	29.07	5.49
	35-189 °C	191-348 °C	350-428 °C
<b>3</b>	10,45 %	34,89 %	
	30-198 °C	199-519 °C	
<b>4</b>	25.75 %		
	129-360 °C		
<b>6</b>	6.08 %	27.84 %	
	32-217 °C	219-487 °C	
<b>7</b>	5.88 %	29.25 %	
	29-214 °C	218-493 °C	
<b>8</b>	6.54 %	34.99 %	
	31-137 °C	138-421 °C	
<b>9</b>	2.82 %	73.61 °C	
	33-94 °C	99-453 °C	
<b>10</b>	5.59 %	20.60 %	4.91 %
	36-140 °C	157-314 °C	316-358 °C



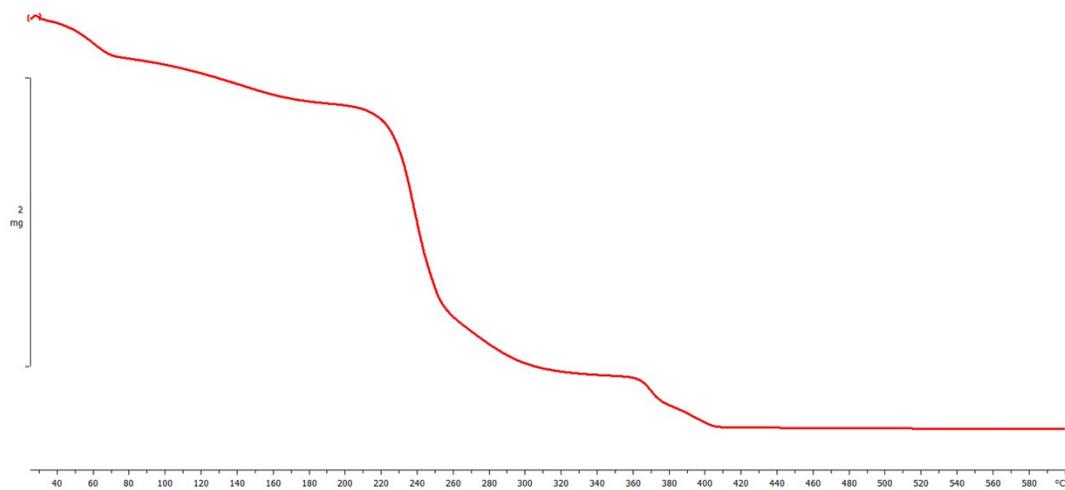
**Figure S1.** TG curve of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_3[\text{AlMo}_6(\text{OH})_6\text{O}_{18}] \cdot 7\text{H}_2\text{O}$  (**1**)



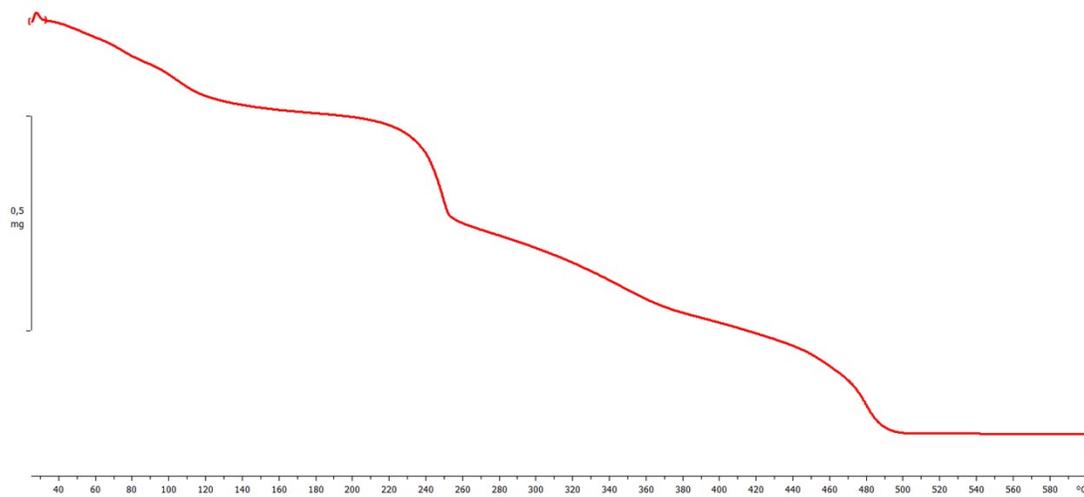
**Figure S2.** TG curve of  $[\{\text{Co}(\text{ox})(\text{NH}_3)_4\}_2\text{Na}_2(\text{H}_2\text{O})_6\{\text{H}_4\text{Mo}_8\text{O}_{28}\}] \cdot 4\text{H}_2\text{O}$  (**1a**)



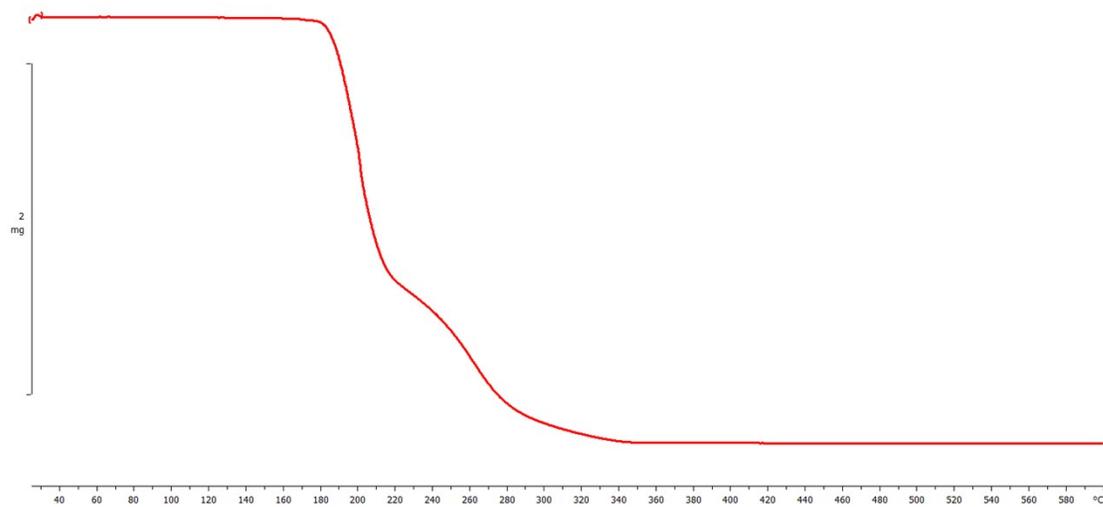
**Figure S3.** TG curve of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_2[\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2] \cdot \text{Hmal} \cdot 2\text{H}_2\text{O}$  (**1b**)



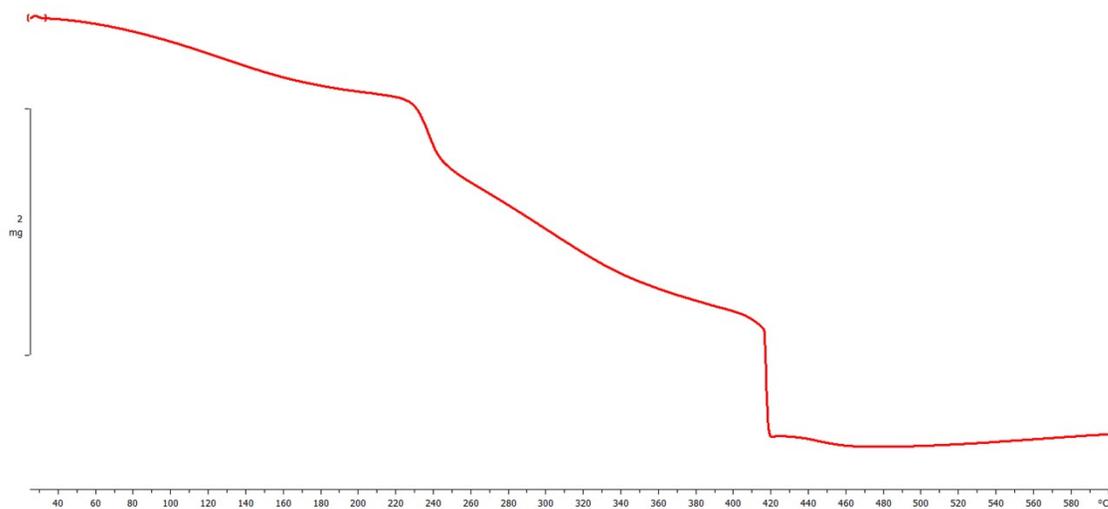
**Figure S4.** TG curve of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_6[\text{TeMo}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$  (**2**)



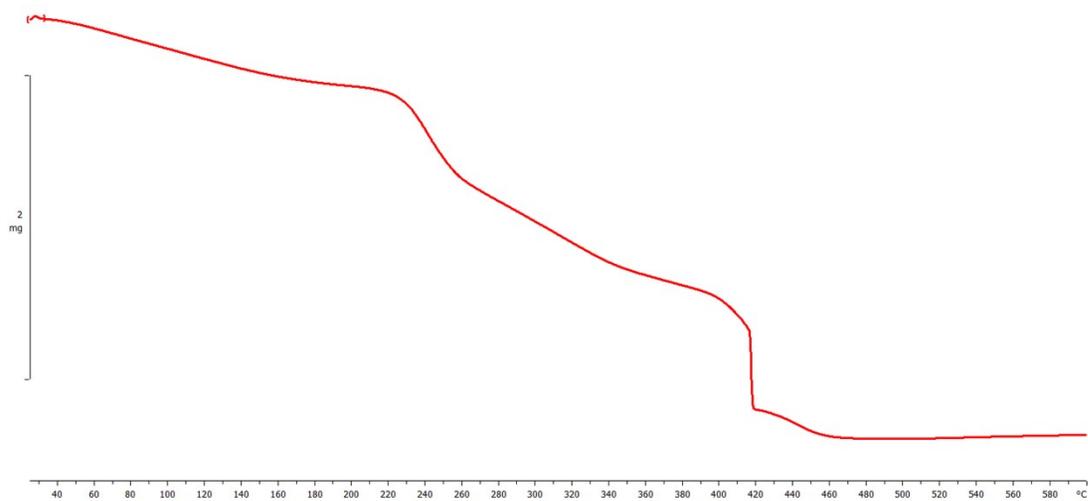
**Figure S5.** TG curve of  $\text{Na}_2[\text{Co}(\text{ox})(\text{en})_2]_4[\text{TeMo}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$  (**3**)



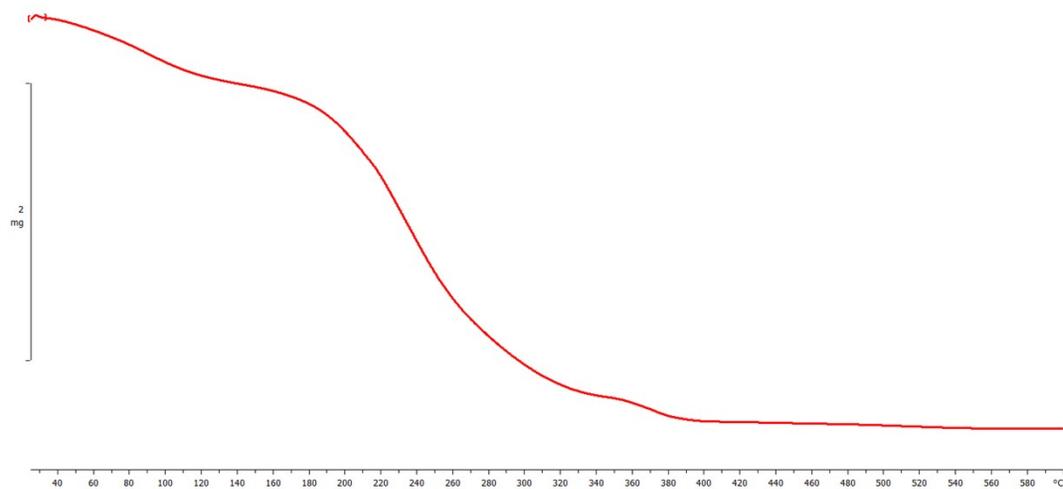
**Figure S6.** TG curve of  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_4[\text{GeMo}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$  (**4**)



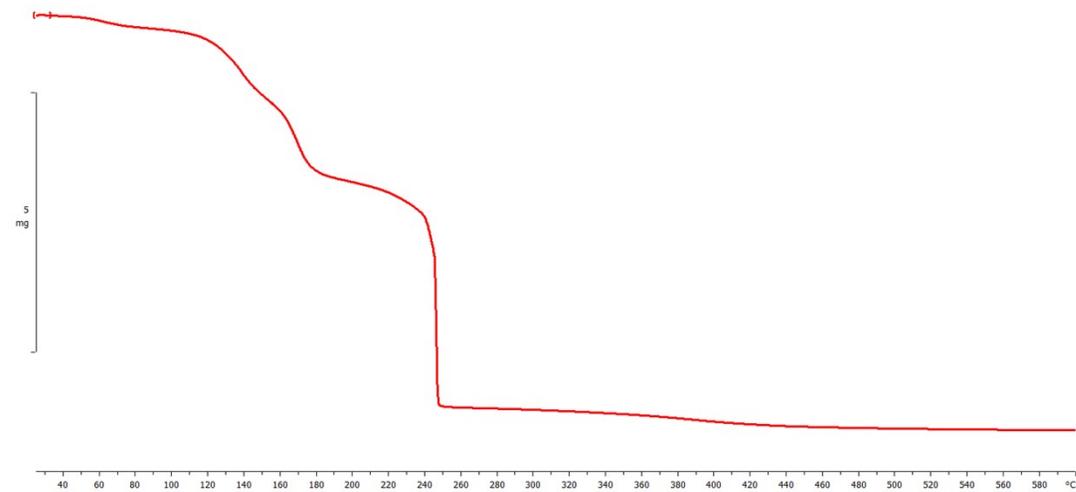
**Figure S7.** TG curve of  $[\text{Co}(\text{ox})(\text{en})_2]_4[\text{GeMo}_{12}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$  (6)



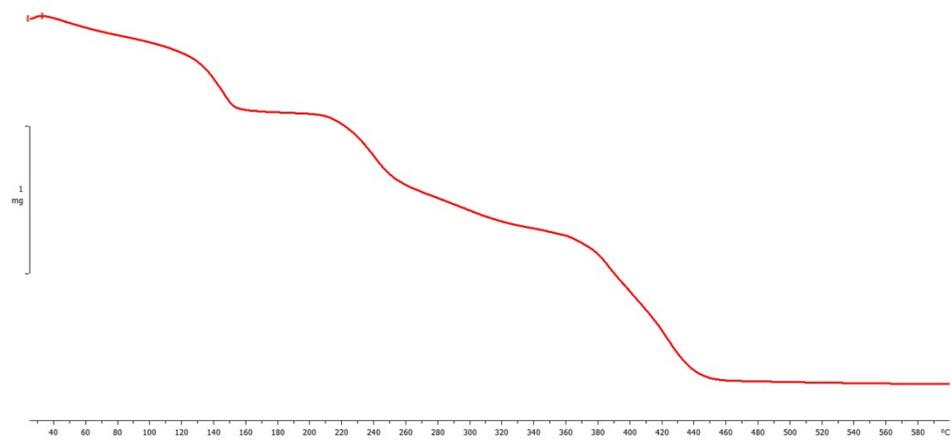
**Figure S8.** TG curve of  $[\text{Co}(\text{ox})(\text{en})_2]_4[\text{SiMo}_{12}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$  (7)



**Figure S9.** TG curve of  $\text{Na}_4[\text{Co}(\text{ox})(\text{NH}_3)_4]_3[\text{GeMo}_6\text{O}_{22}(\text{Hmal})_3] \cdot 7.75\text{H}_2\text{O}$  (**8**)



**Figure S10.** TG curve of  $[\text{Co}(\text{NH}_3)_6][\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (**9**)



**Figure S11.** TG curve of  $[\text{Co}(\text{en})_3]_2[\text{Mo}_8\text{O}_{26}(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (**10**)

**Table S2:** IR data of compounds **1-4**, **1a**, **6-10**

	$\nu_1(\text{Mo}=\text{O}_1)$ + $\nu_1(\text{Mo}=\text{O}_2)$	$\nu_1(\text{Mo}-\text{O}-\text{Mo})$ + $\nu_2(\text{Mo}-\text{O}-\text{Mo})$	$\nu(\text{Mo}-\text{O}$ in $\text{Mo}-\text{O}-\text{Mo})$ + $\nu(\text{Mo}-\text{O})$	$\nu_1(\text{N-H})$ + $\nu_1(\text{O-H})$	$\delta_1(\text{N-H})$	$\nu_1(\text{C-O})$	$\nu_1(\text{C-O})$ + $\nu(\text{C-C})$	$\nu_1(\text{O-H})$	$\nu_1(\text{M-O})$ + $\nu(\text{C-C})$	$\delta(\text{O-C=O})$ + $\nu(\text{M-O})$
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	953	797, 741	598							
$[\text{Co}(\text{en})_3]\text{Cl}_3$				3195, 3074			1735			
$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$				3215, 3111	1592				606-400	
$[\text{Co}(\text{C}_2\text{O}_4)(\text{en})_2]\text{CH}_2\text{O}$				3114, 3023			1744		524-460	
$[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_4](\text{NO}_3) \cdot \text{H}_2\text{O}$				3180-3492	1304, 1278		1632-1364		535-450	
Oxalic acid						1692, 1687	1464, 1377	2954 - 2854		
Malonic acid						1695	1432-1167	3026 - 2948		
$[\text{Co}(\text{ox})(\text{NH}_3)_4][\text{AlMo}_4(\text{OH})_4\text{O}_{10}] \cdot 7\text{H}_2\text{O}$ (1).	933, 909	888, 626	575	3286, 3139		1679, 1640	1416-1266		501-415	
$[\text{Co}(\text{ox})(\text{NH}_3)_4][\text{TeMo}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$ (2)	935, 893	851-646	564, 537	3282, 3170		1634, 1590	1397-1252		568-452	
$\text{Na}_2[\text{Co}(\text{ox})(\text{en})_2][\text{TeMo}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$ (3)	942, 890	823, 716	557, 533	3296, 3135		1665, 1559	1387, 1315, 1258		601-525	
$[\text{Co}(\text{ox})(\text{NH}_3)_4][\text{GeMo}_2\text{O}_{10}] \cdot 6\text{H}_2\text{O}$ (4)	932, 909	887	626, 576	3285, 3139		1697-1640	1363-1266		575-433	
$[\text{Co}(\text{ox})(\text{en})_2][\text{GeMo}_2\text{O}_{10}] \cdot 12\text{H}_2\text{O}$ (6)	922, 905	836	675, 510	3278, 3111		1618, 1598	1307, 1222		602-458	
$[\text{Co}(\text{ox})(\text{en})_2][\text{SiMo}_2\text{O}_{10}] \cdot 12\text{H}_2\text{O}$ (7)	991, 948	824, 769	561, 531	3491, 3186		1697 - 1585	1359 - 1252		561-531	
$\text{Na}_4[\text{Co}(\text{ox})(\text{NH}_3)_4][\text{GeMo}_6\text{O}_{22}(\text{Hmal})_3] \cdot 7.75\text{H}_2\text{O}$ (8)	944, 912	836, 787	689, 567	3300, 3091		1667-1568	1317, 1267		615-488	
$[\text{Co}(\text{NH}_3)_6][\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (9)				3203-2098		1579, 1508	1496-1408	2931-2862		
$[\text{Co}(\text{en})_3][\text{Mo}_6\text{O}_{24}(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (10)	987, 898	854, 760	535, 512	3240, 3120		1654-1540	1430-1279		544-428	
$[(\text{Co}(\text{ox})(\text{NH}_3)_4)_2\text{Na}_2(\text{H}_2\text{O})_2(\text{H}_4\text{Mo}_6\text{O}_{28})] \cdot 4\text{H}_2\text{O}$ (1a)	955 - 905	773 - 688	609, 560	3530 - 3181		1699 - 1647	1406 - 1242		570 - 486	
$[\text{Co}(\text{ox})(\text{NH}_3)_4][\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2] \cdot \text{Hmal} \cdot 2\text{H}_2\text{O}$ (1b)				3220-3098		1688, 1543	1444, 1398	2880-2768		

\* IR data of compounds **5** and **11** are described in the literature: **11** in V. Damjanović, J. Pisk, D. Kuzman, D. Agustin, V. Vrdoljak, V. Stilinović, M. Cindrić, *Dalton Trans.*, 2019, 48 p. 9974.; **5** in D. Kuzman, V. Damjanović, V. Stilinović, M. Cindrić, V. Vrdoljak, *New J. Chem.* 2021, 45, 19764

**Table S3.** Crystallographic data of the obtained compounds **1**, **1a**, **1b**, **2**, **4**, **8**

	<b>1</b>	<b>1a</b>	<b>1b</b>	<b>2</b>	<b>4</b>
Formula	C <sub>6</sub> H <sub>56</sub> AlCo <sub>3</sub> Mo <sub>6</sub> N <sub>12</sub> O <sub>43</sub>	C <sub>4</sub> H <sub>48</sub> Co <sub>2</sub> Mo <sub>8</sub> N <sub>8</sub> Na <sub>2</sub> O <sub>46</sub>	C <sub>13</sub> H <sub>37</sub> AlCo <sub>2</sub> N <sub>8</sub> O <sub>24</sub>	C <sub>12</sub> H <sub>104</sub> Co <sub>6</sub> Mo <sub>6</sub> N <sub>24</sub> O <sub>64</sub> Te	C <sub>8</sub> H <sub>60</sub> Co <sub>4</sub> GeMo <sub>12</sub> N <sub>16</sub> O <sub>61</sub>
<i>M<sub>r</sub></i>	1764.03	1875.86	834.34	2665.91	2832.31
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	tetragonal
Space group	C2/c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P-1	I4 <sub>1</sub> /a
<i>a</i> (Å)	22.3274(8)	11.03090(10)	11.5399(9)	11.2606(6)	16.67110(10)
<i>b</i> (Å)	10.0879(4)	19.19200(10)	6.9391(6)	11.9994(6)	16.67110(10)
<i>c</i> (Å)	20.9583(9)	11.10560(10)	19.323(2)	16.4793(4)	23.1637(2)
<i>α</i> (°)	90	90	90	72.528(3)	90
<i>β</i> (°)	100.860(4)	102.8930(10)	98.004(9)	70.557(4)	90
<i>γ</i> (°)	90	90	90	72.466(5)	90
<i>V</i> (Å <sup>3</sup> )	4636.0(3)	2291.84(3)	1532.3(2)	1952.02(17)	6437.78(10)
<i>Z</i>	4	2	2	1	4
Reflections unique	16123	85786	19815	28027	65855
Reflections observed [ <i>I</i> > 2 <i>σ</i> ( <i>I</i> )]	4589	4940	3263	8179	3492
Parameters	345	326	252	514	240
<i>R</i> <sub>1</sub> (obs)	0.0387	0.0439	0.0814	0.0861	0.0425
w <i>R</i> <sub>1</sub> (obs)	0.1036	0.0965	0.2241	0.2345	0.1141
<i>Goof</i>	1.073	1.191	1.049	1.008	1.046

	<b>8</b>
Formula	$C_{15}H_{54.5}Co_3GeMo_6N_{12}Na_4O_{53.75}$
$M_r$	2164.56
Crystal system	triclinic
Space group	P-1
$a$ (Å)	10.4262(2)
$b$ (Å)	14.6913(3)
$c$ (Å)	20.8988(5)
$\alpha$ (°)	106.021(2)
$\beta$ (°)	101.646(2)
$\gamma$ (°)	91.277(2)
$V$ (Å <sup>3</sup> )	3003.13(12)
$Z$	2
Reflections unique	46687
Reflections observed [ $I > 2\sigma(I)$ ]	12727
Parameters	882
$R_1(\text{obs})$	0.0723
$wR_1(\text{obs})$	0.1942
<i>Goof</i>	1.035

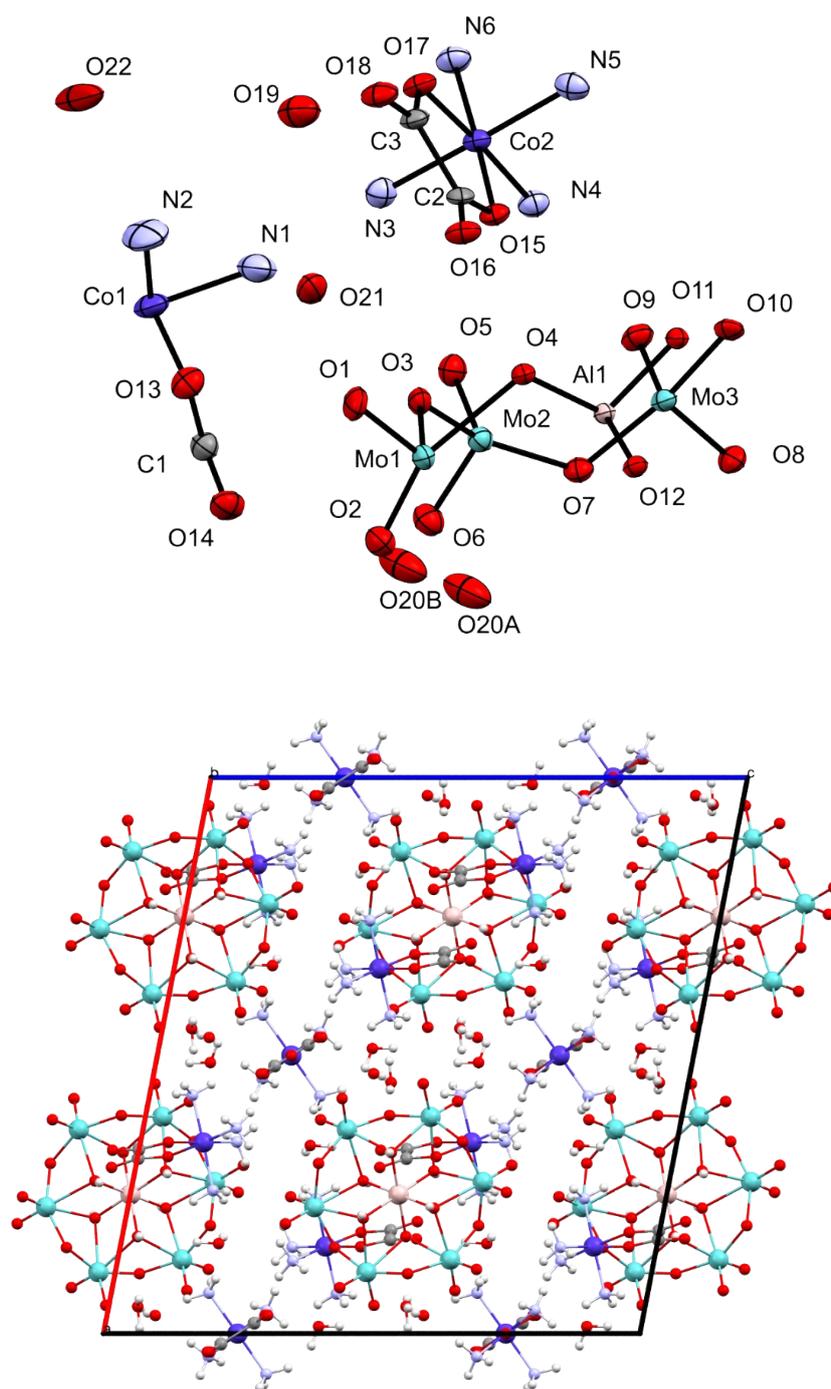
**Table S4.** Crystallographic data of the obtained compounds **3**, **6**, **7**

	<b>3</b>	<b>6</b>	<b>7</b>
Formula	C <sub>24</sub> H <sub>96</sub> Co <sub>4</sub> Mo <sub>6</sub> N <sub>16</sub> Na <sub>2</sub> O <sub>56</sub> Te	C <sub>24</sub> H <sub>88</sub> Co <sub>4</sub> GeMo <sub>12</sub> N <sub>16</sub> O <sub>68</sub>	C <sub>24</sub> H <sub>88</sub> Co <sub>4</sub> Mo <sub>12</sub> N <sub>16</sub> O <sub>68</sub> Si
<i>M<sub>r</sub></i>	2490.10	3148.69	3104.19
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	P2 <sub>1</sub> /n	I4 <sub>1</sub> /a
<i>a</i> (Å)	23.44470(10)	13.1320(7)	16.67110(10)
<i>b</i> (Å)	15.34869(6)	12.0745(7)	16.67110(10)
<i>c</i> (Å)	20.32150(8)	25.9671(16)	23.1637(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	97.3211(4)	93.300(5)	90
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	7252.98(5)	4110.6(4)	6437.78(10)
<i>Z</i>	4	2	4
Reflections unique	128517	35687	65855
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	7832	8715	3492
Parameters	523	552	240
<i>R</i> <sub>1</sub> (obs)	0.0345	0.0881	0.0434
w <i>R</i> <sub>1</sub> (obs)	0.0912	0.2148	0.1182
<i>Goof</i>	1.054	1.049	1.063

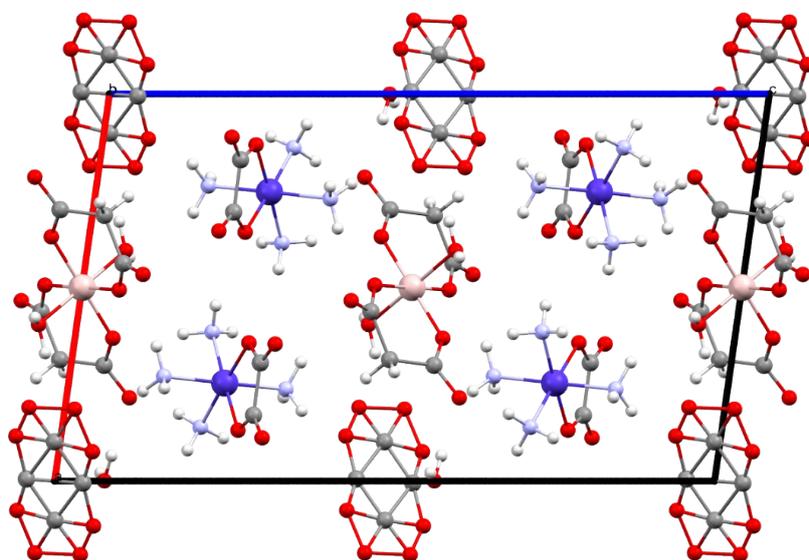
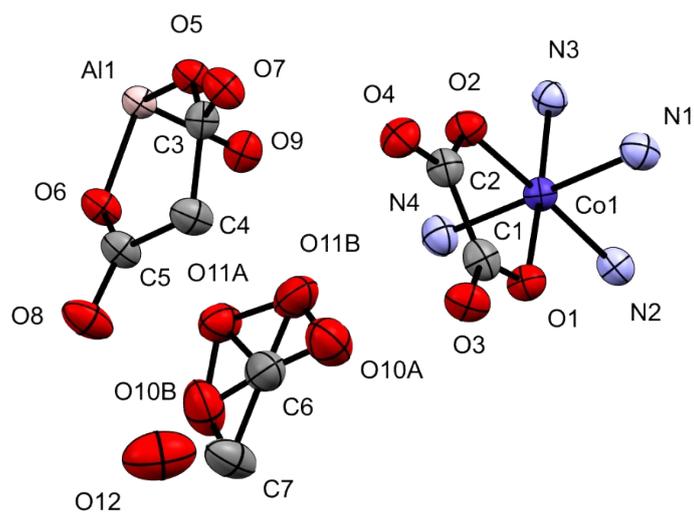
**Table S5.** Crystallographic data of the obtained compounds **9** and **10**

	<b>9</b>	<b>10</b>
Formula	C <sub>6</sub> H <sub>28</sub> AlCoN <sub>8</sub> O <sub>17</sub>	C <sub>12</sub> H <sub>64</sub> Cl <sub>2</sub> Co <sub>2</sub> Mo <sub>8</sub> N <sub>12</sub> O <sub>34</sub>
<i>M<sub>r</sub></i>	570.27	1877.02
Crystal system	monoclinic	triclinic
Space group	Cc	P-1
<i>a</i> (Å)	7.00218(5)	11.4453(6)
<i>b</i> (Å)	21.64748(14)	14.1720(7)
<i>c</i> (Å)	13.63824(10)	15.4608(6)
$\alpha$ (°)	90	88.228(4)
$\beta$ (°)	98.6221(7)	87.964(4)
$\gamma$ (°)	90	82.297(4)
<i>V</i> (Å <sup>3</sup> )	2043.92(2)	2482.7(2)
<i>Z</i>	4	2
Reflections unique	30650	36477
Reflections observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4248	10433
Parameters	423	650
<i>R</i> <sub>1</sub> (obs)	0.0244	0.0431
w <i>R</i> <sub>1</sub> (obs)	0.0634	0.1087

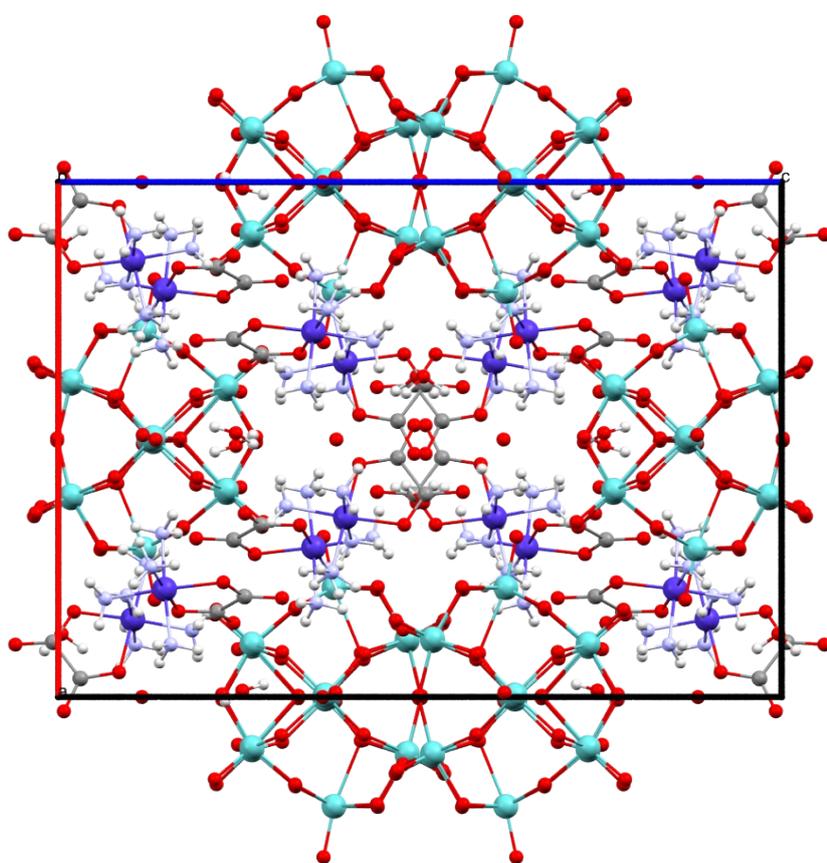
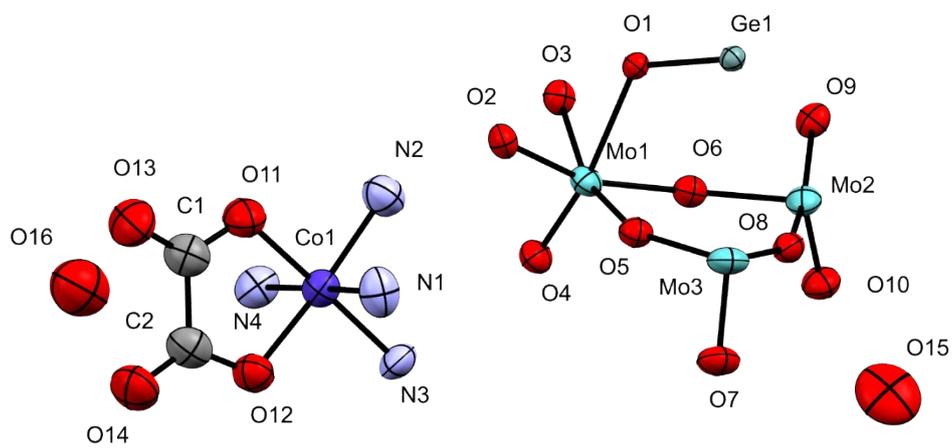
<i>Goof</i>	1.038	1.051
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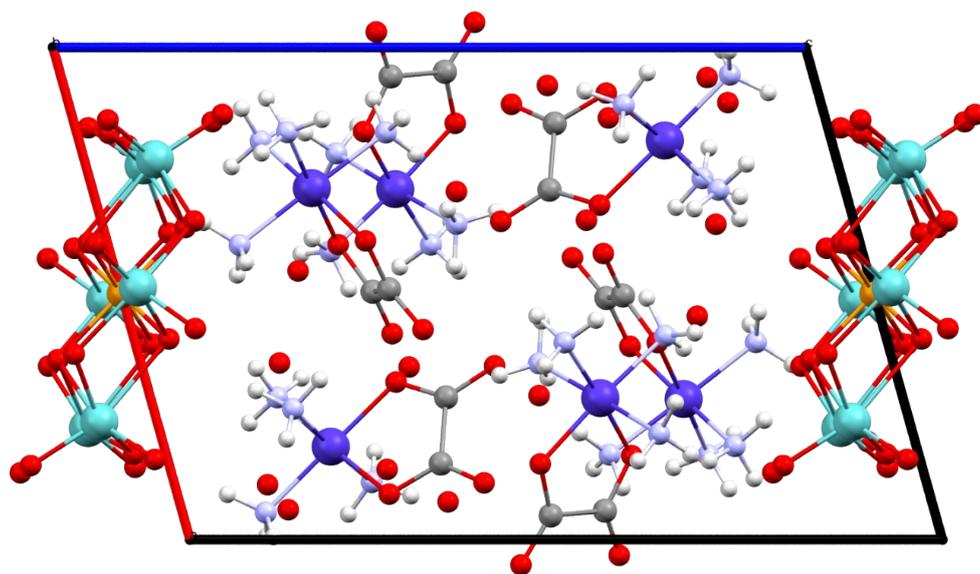
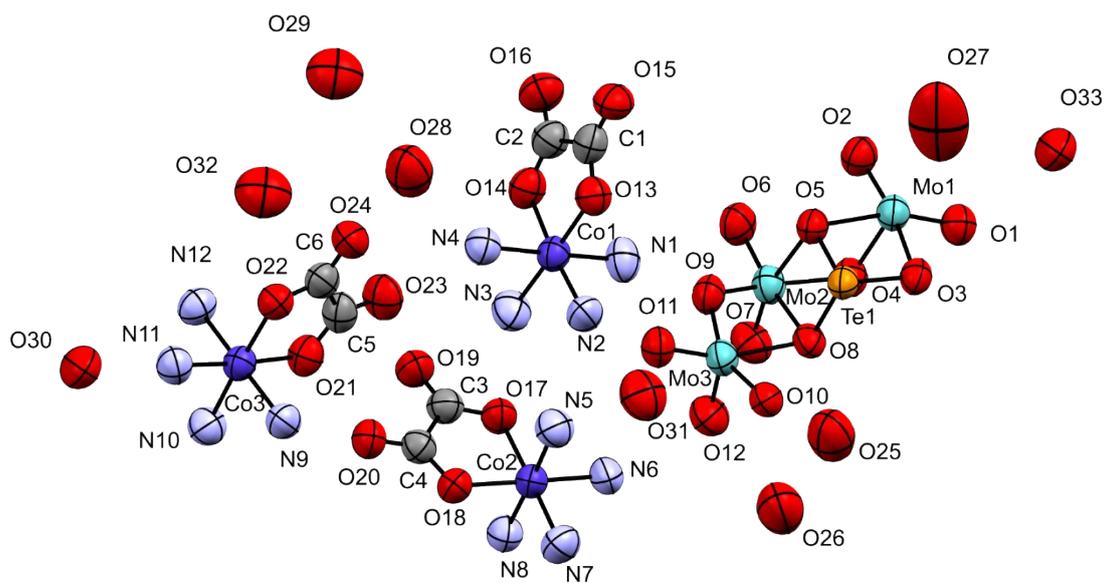
(a)  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_3[\text{AlMo}_6(\text{OH})_6\text{O}_{18}] \cdot 7\text{H}_2\text{O}$  (**1**)



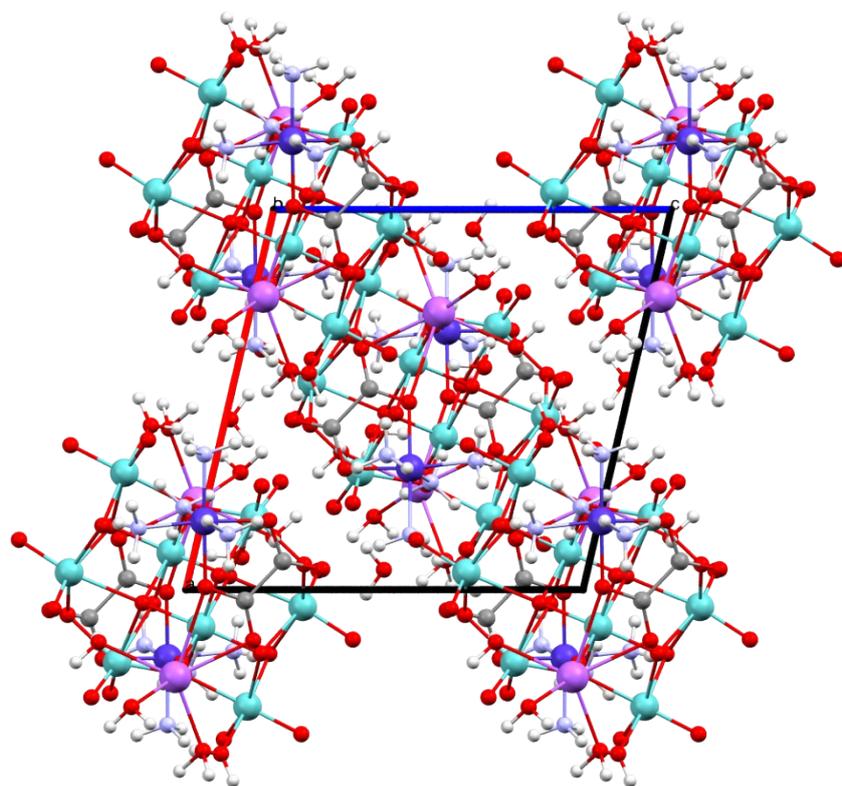
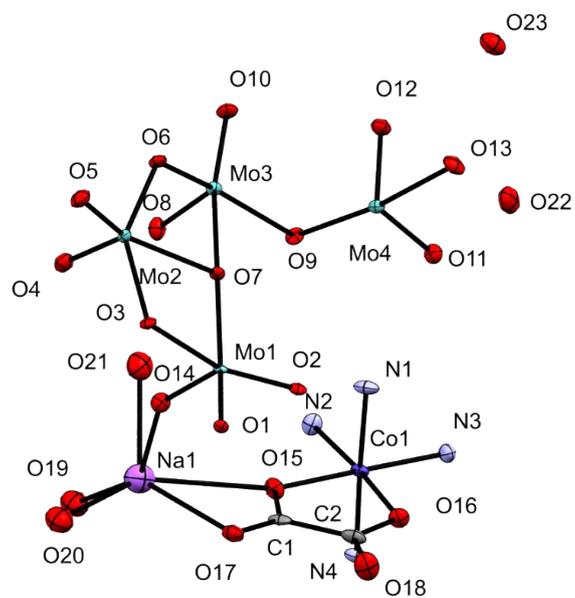
(b)  $[\text{Co}(\text{ox})(\text{NH}_3)_4]_2[\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2] \cdot \text{Hmal} \cdot 2\text{H}_2\text{O}$  (**1b**)



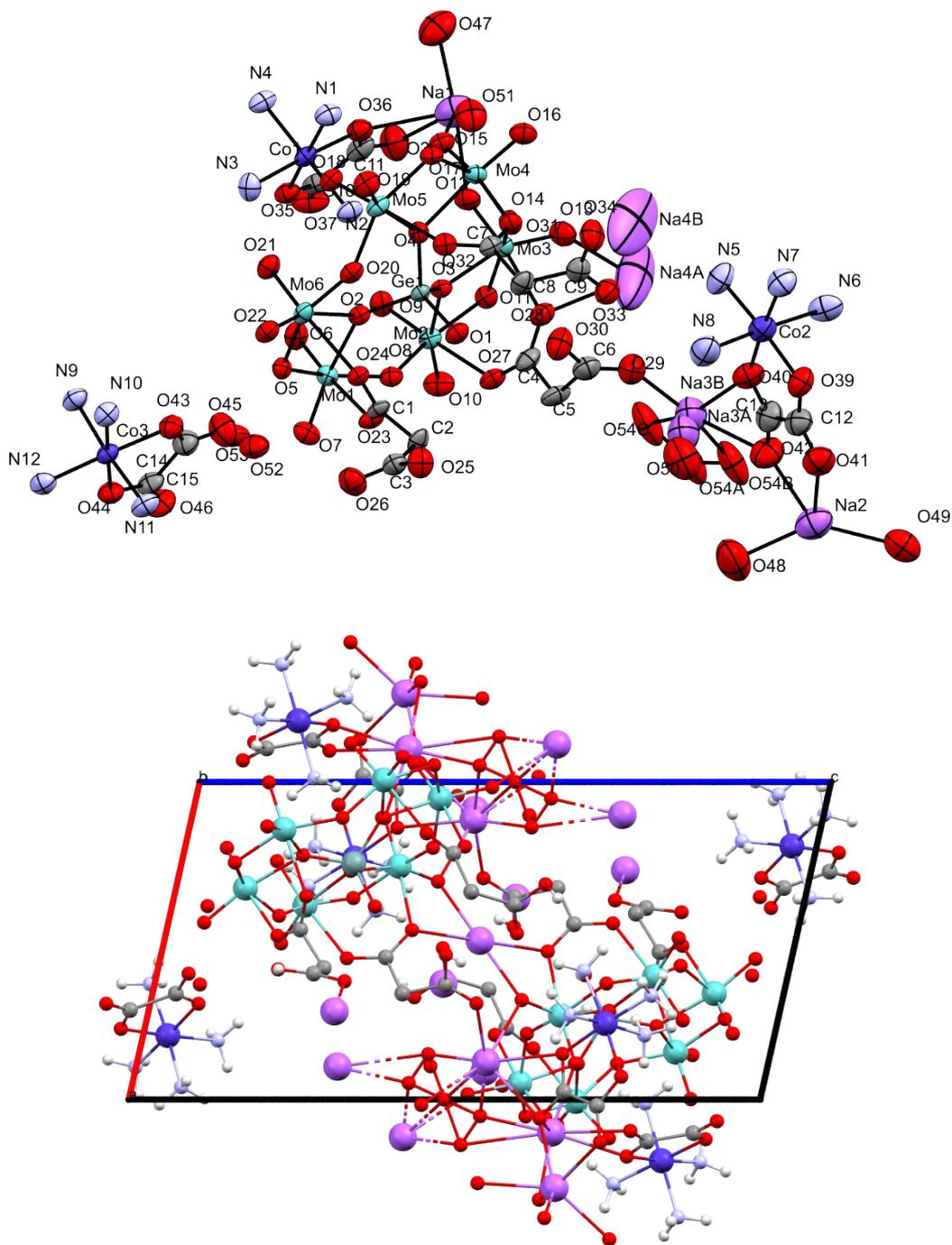
(c) [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>4</sub>[GeMo<sub>12</sub>O<sub>40</sub>]·6H<sub>2</sub>O (**4**)



(d) [Co(ox)(NH<sub>3</sub>)<sub>4</sub>]<sub>6</sub>[TeMo<sub>6</sub>O<sub>24</sub>]·16H<sub>2</sub>O (2)

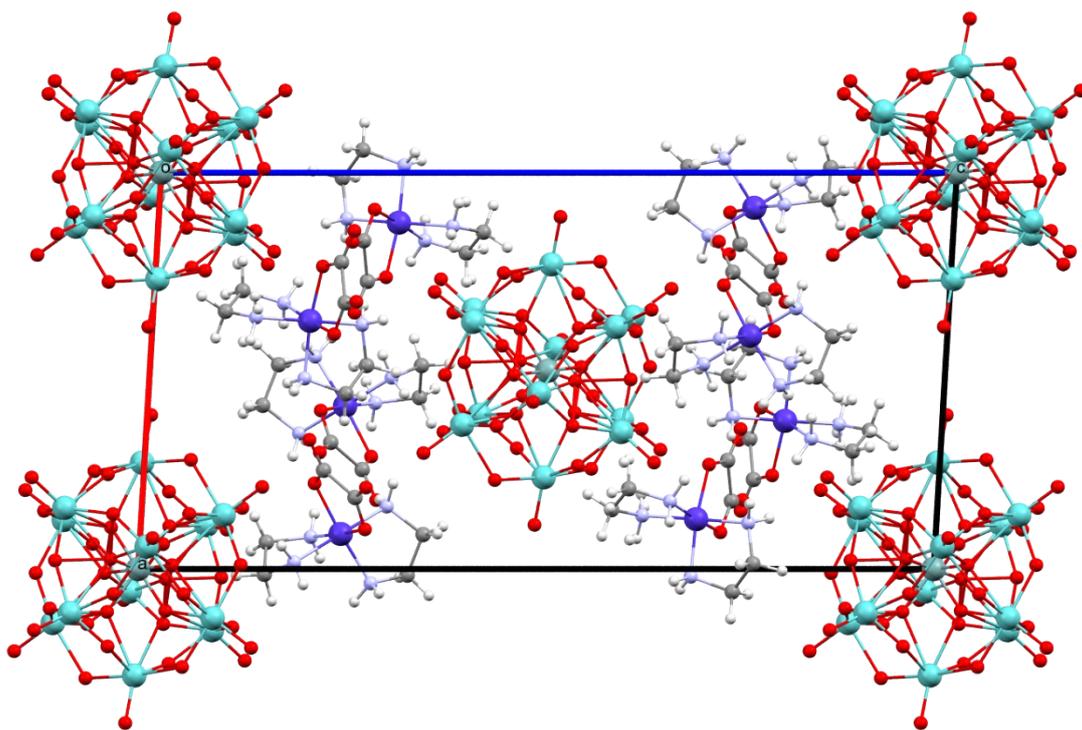
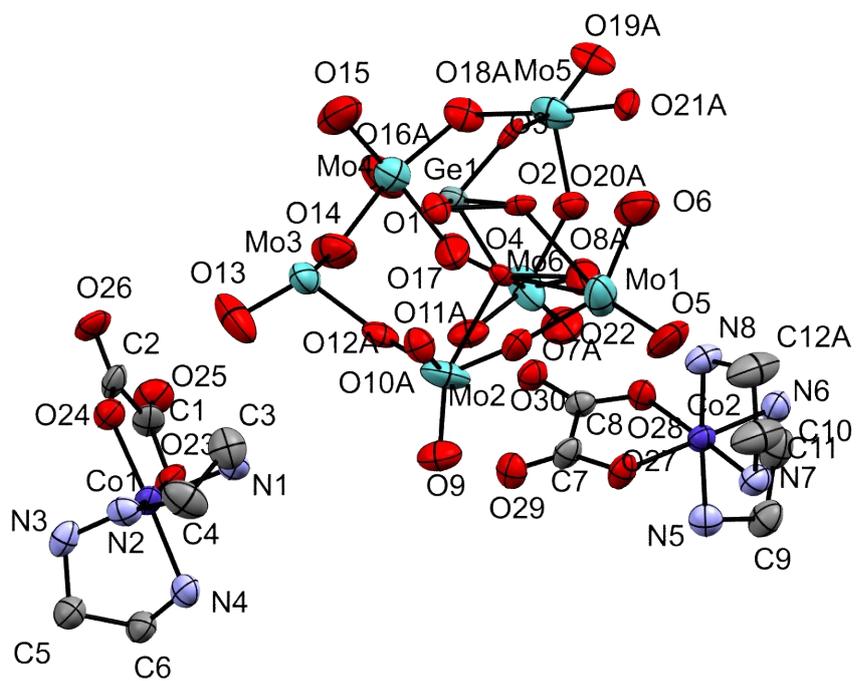


(e)  $[\{\text{Co}(\text{ox})(\text{NH}_3)_4\}_2\text{Na}_2(\text{H}_2\text{O})_6\{\text{H}_4\text{Mo}_8\text{O}_{28}\}]\cdot 4\text{H}_2\text{O}$  (**1a**)

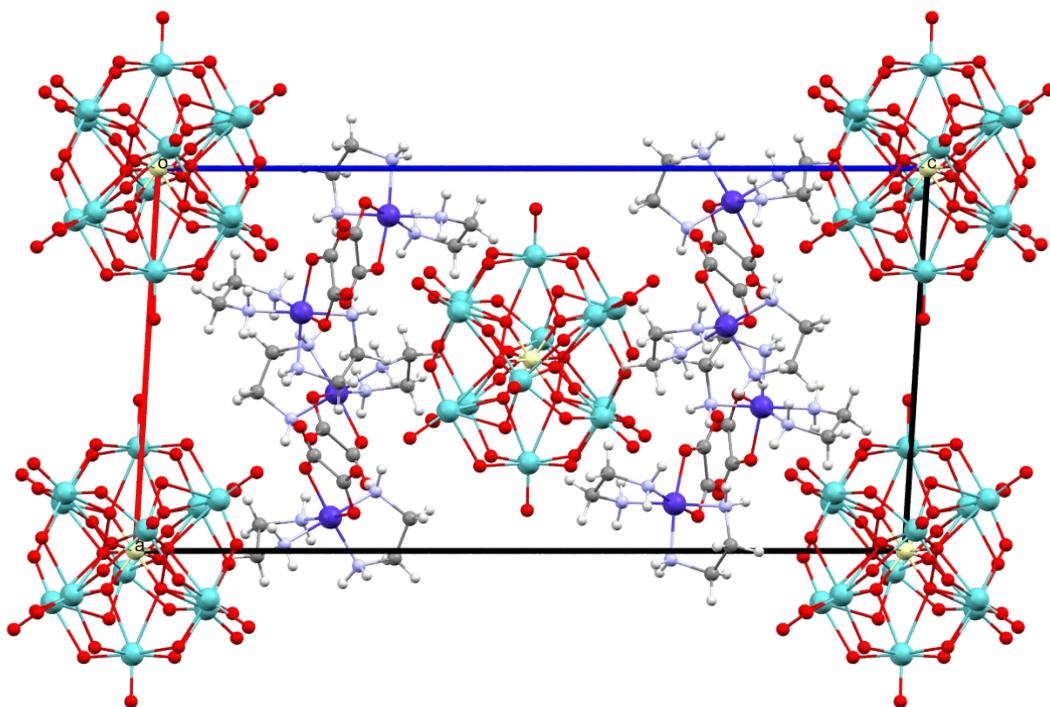
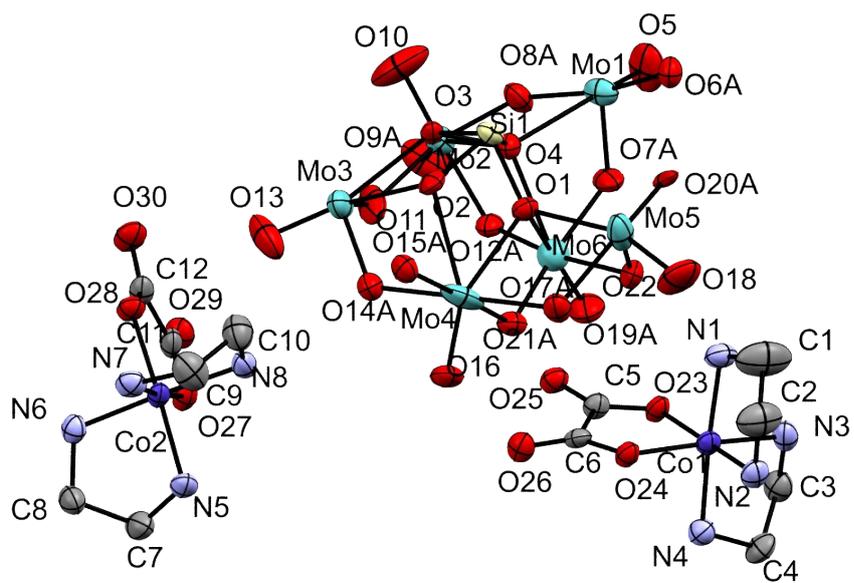


(f)  $\text{Na}_4[\text{Co}(\text{ox})(\text{NH}_3)_4]_3[\text{GeMo}_6\text{O}_{22}(\text{Hmal})_3] \cdot 7.75\text{H}_2\text{O}$  (**8**)

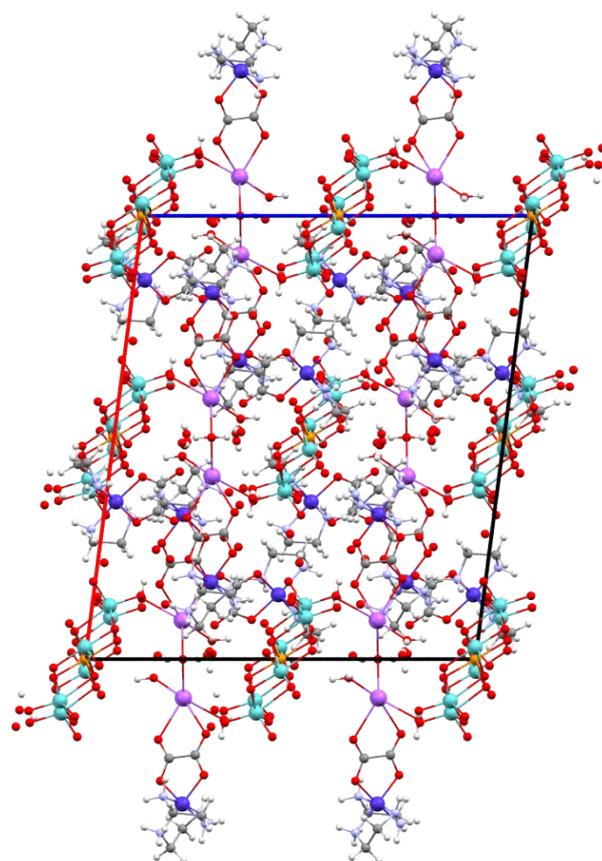
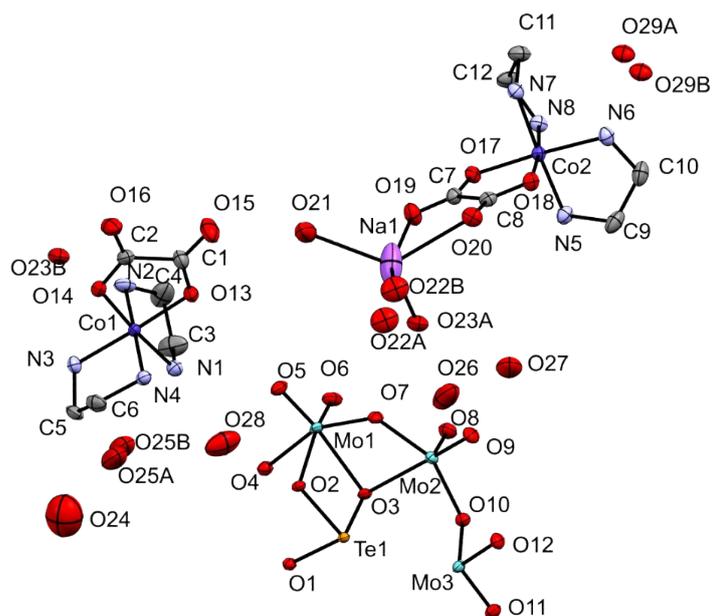
**Figure. S23** Asymmetric unit (top) and packing of molecules (bottom) for compounds (**1**, **1a**, **1b**, **2**, **4**, **5**, **8**) containing  $[\text{Co}(\text{ox})(\text{NH}_3)_4]^+$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.



(a) [Co(ox)(en)<sub>2</sub>]<sub>4</sub>[GeMo<sub>12</sub>O<sub>40</sub>]<sub>4</sub>·12H<sub>2</sub>O (**6**)

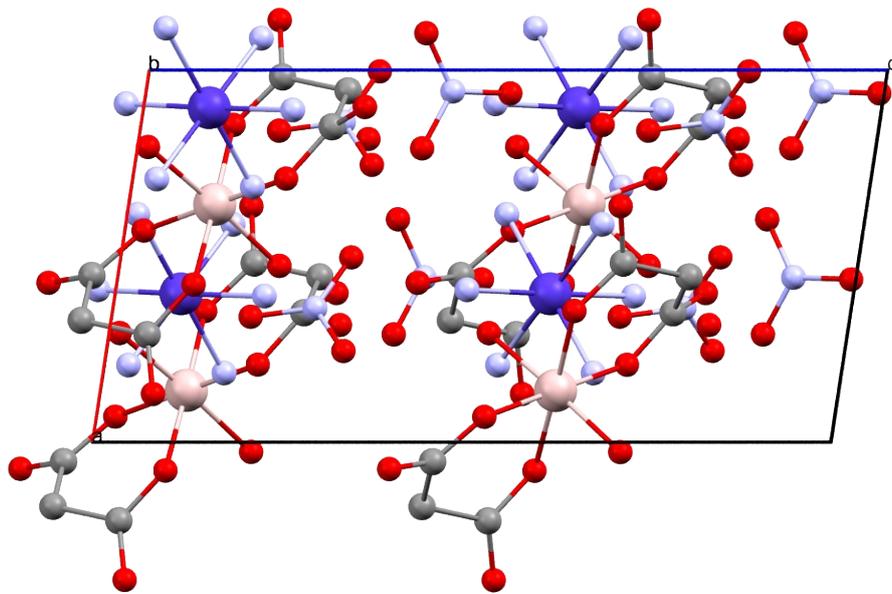
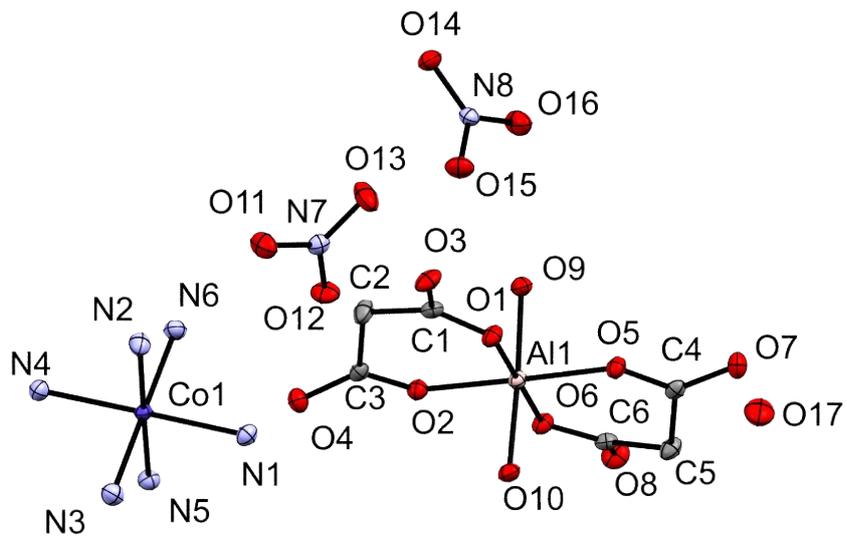


(b)  $[\text{Co}(\text{ox})(\text{en})_2]_4[\text{SiMo}_{12}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$  (7)

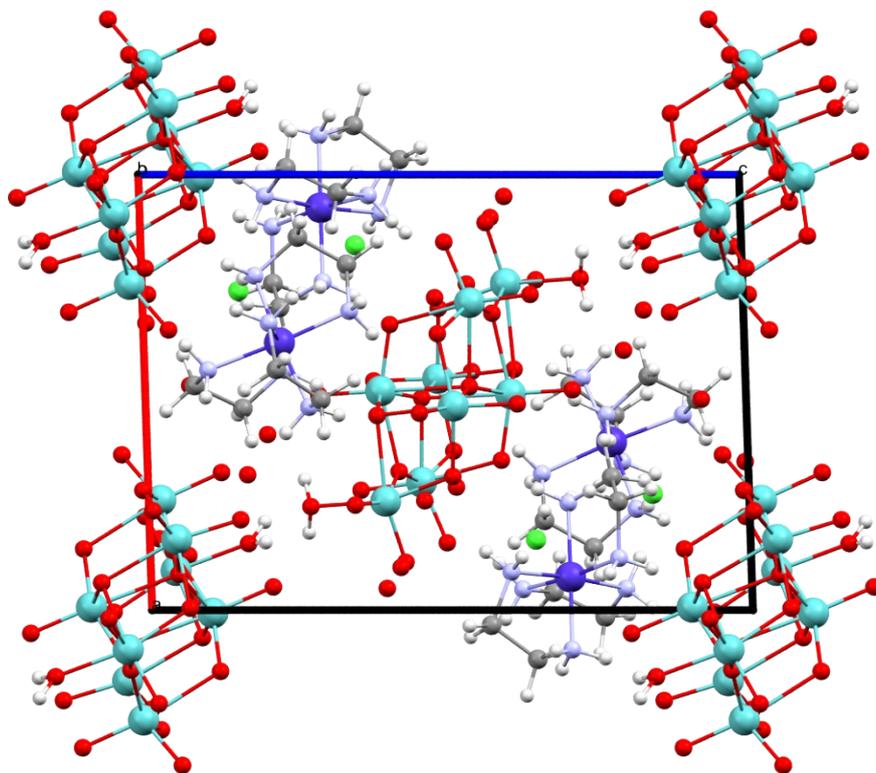
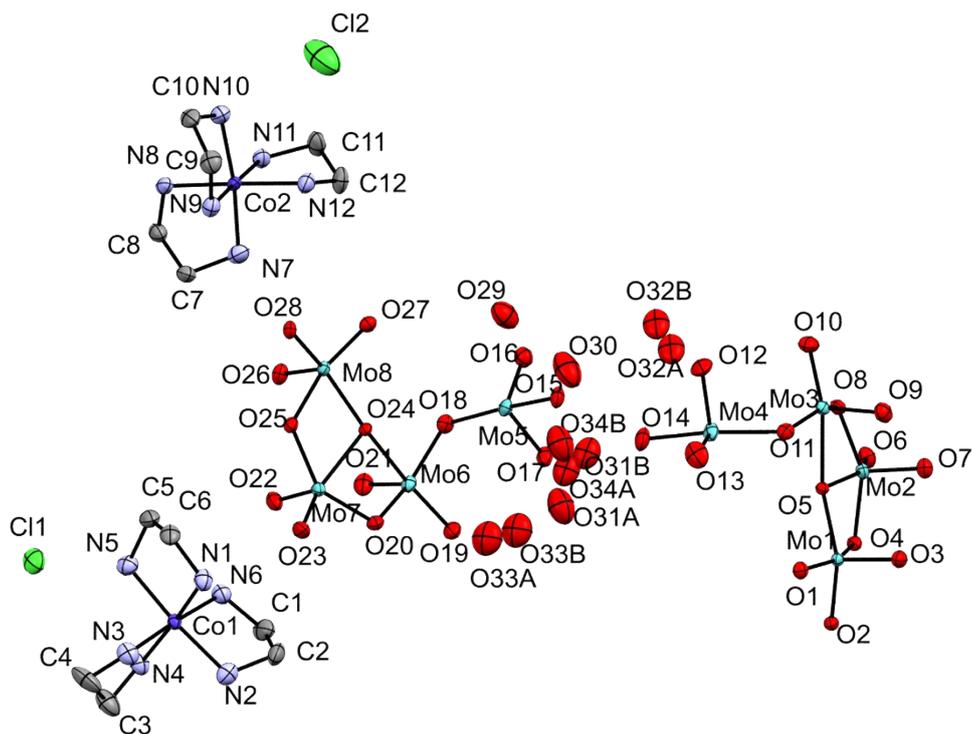


(c)  $\text{Na}_2[\text{Co}(\text{ox})(\text{en})_2]_4[\text{TeMo}_6\text{O}_{24}] \cdot 16\text{H}_2\text{O}$  (**3**)

**Figure. S24** Asymmetric unit (top) and packing of molecules (bottom) for compounds (**3**, **6**, **7**) containing  $[\text{Co}(\text{ox})(\text{en})_2]^+$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.



(a)  $[\text{Co}(\text{NH}_3)_6][\text{Al}(\text{mal})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (**9**)



(b)  $[\text{Co}(\text{en})_3]_2[\text{Mo}_8\text{O}_{26}(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (**10**)

**Figure. S25** Asymmetric unit (top) and packing of molecules (bottom) for compounds **9** and **10** containing  $[\text{Co}(\text{en})_3]^{3+}$  or  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation characterized in this work. Atoms are shown as thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted from the asymmetric unit for clarity.

**Table S6.** Hydrogen bonds formed between complex cations and anions in **1a**.

Donor–H…Acceptor	H-bond length / Å
N1–H1A…O11 <sup>a</sup>	3.047(8)
N1–H1A…O17 <sup>b</sup>	2.918(8)
N1–H1B…O5 <sup>c</sup>	3.054(8)
N1–H1C…O2 <sup>a</sup>	3.074(7)
N2–H2A…O17 <sup>b</sup>	3.089(8)
N2–H2A…O20 <sup>b</sup>	3.031(9)
N2–H2C…O1 <sup>b</sup>	2.931(7)
N3–H3A…O18 <sup>b</sup>	2.851(8)
N3–H3B…O10 <sup>d</sup>	3.268(8)
N3–H3C…O8 <sup>e</sup>	2.968(8)
N4–H4A…O10 <sup>d</sup>	3.164(8)
N4–H4A…O12 <sup>d</sup>	3.132(8)
N4–H4B…O12 <sup>f</sup>	3.076(8)
N4–H4C…O4 <sup>e</sup>	3.314(7)
O19–H19A…O18	2.751(8)
O19–H19B…O10	2.865(8)
O20–H20A…O21	2.854(9)
O21–H21A…O16	2.810(8)
O21–H21B…O8 <sup>a</sup>	2.943(8)

<sup>a</sup> x,y,z; <sup>b</sup> -1/2+x,3/2-y,-1/2+z; <sup>c</sup> 1-x,1-y,1-z; <sup>d</sup> 1/2-x,1/2+y,1/2-z; <sup>e</sup> -1/2+x,3/2-y,1/2+z; <sup>f</sup> 1/2+x,3/2-y,1/2+z

**Table S7.** Hydrogen bonds formed between complex cations and anions in **10**.

Donor–H…Acceptor	H-bond length / Å
N1–H1A…O9 <sup>a</sup>	2.857(8)
N1–H1B…O22 <sup>b</sup>	2.846(7)
N2–H2A…O16 <sup>c</sup>	3.101(8)
N2–H2A…O18 <sup>c</sup>	2.960(7)
N3–H3A…O11 <sup>a</sup>	2.934(8)
N4–H4A…O18 <sup>c</sup>	3.237(8)
N4–H4B…O27 <sup>c</sup>	3.067(7)
N5–H5A…O11 <sup>a</sup>	3.058(7)
N6–H6A…O23 <sup>d</sup>	3.093(7)
N7–H7B…O28 <sup>b</sup>	2.833(7)
N8–H8A…O7 <sup>e</sup>	2.980(7)
N8–H8B…O8 <sup>f</sup>	2.977(7)
N8–H8B…O10 <sup>f</sup>	3.258(7)
N9–H9A…O7 <sup>e</sup>	2.871(8)
N9–H9B…O19 <sup>g</sup>	2.980(8)
N10–H10B…O1 <sup>h</sup>	3.084(7)
N10–H10B…O8 <sup>f</sup>	3.229(8)
N11–H11B…O2 <sup>h</sup>	2.857(7)
N11–H11B…O10 <sup>f</sup>	3.042(8)
N12–H12B…O19 <sup>g</sup>	3.217(7)
N12–H12B…O20 <sup>g</sup>	2.951(7)
O14–H14A…O15 <sup>b</sup>	2.5352(9)
O14–H14B…O17 <sup>b</sup>	2.987(5)
O14–H14B…O3 <sup>i</sup>	3.033(4)

O15–H15A...O26 <sup>g</sup>	3.270(5)
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<sup>a</sup> 1+x,y,-1+z; <sup>b</sup> x,y,z; <sup>c</sup> 1+x,y,-1+z; <sup>d</sup> 2-x,1-y,1-z; <sup>e</sup> 1+x,-1+y,-1+z; <sup>f</sup> -x,1-y,1-z; <sup>g</sup> 1-x,1-y,1-z; <sup>h</sup> x,-1+y,-1+z; <sup>i</sup> -x,2-y,2-z

**Table S8.** Hydrogen bonds formed between complex cations and anions in **1b**.

Donor–H...Acceptor	H-bond length / Å
N1–H1A...O8 <sup>a</sup>	3.072(7)
N1–H1B...O5 <sup>b</sup>	2.952(7)
N1–H1B...O7 <sup>b</sup>	3.347(7)
N1–H1C...O10B <sup>c</sup>	3.326(6)
N1–H1C...O11A <sup>c</sup>	2.950(12)
N2–H2A...O3 <sup>d</sup>	2.962(7)
N2–H2B...O3 <sup>e</sup>	3.158(7)
N2–H2C...O8 <sup>c</sup>	3.053(7)
N3–H3A...O4 <sup>d</sup>	3.019(7)
N3–H3B...O6 <sup>c</sup>	3.045(7)
N4–H4A...O11B <sup>f</sup>	3.120(14)
N4–H4B...O3 <sup>d</sup>	3.207(7)
N4–H4B...O4 <sup>d</sup>	3.075(7)
N4–H4C...O7 <sup>d</sup>	3.289(7)
O9–H9A...O11A <sup>f</sup>	2.736(11)
O9–H9A...O11B <sup>f</sup>	2.477(13)
O9–H9B...O7 <sup>d</sup>	2.634(6)

<sup>a</sup> x,3/2-y,1/2+z; <sup>b</sup> 1-x,-1/2+y,3/2-z; <sup>c</sup> x,1/2-y,1/2+z; <sup>d</sup> x,-1+y,z; <sup>e</sup> -x,-1/2+y,3/2-z; <sup>f</sup> x,y,z

**Table S9.** Hydrogen bonds formed between complex cations and anions in **9**.

Donor–H...Acceptor	H-bond length / Å
N1–H1A...O12 <sup>a</sup>	2.970(3)
N1–H1B...O13 <sup>b</sup>	3.117(4)
N1–H1C...O4 <sup>a</sup>	2.979(3)
N1–H1C...O8 <sup>c</sup>	3.131(3)
N2–H2B...O11 <sup>a</sup>	2.901(3)
N2–H2C...O9 <sup>c</sup>	3.333(3)
N2–H2C...O13 <sup>c</sup>	2.950(3)
N3–H3A...O12 <sup>c</sup>	3.103(3)
N3–H3B...O6 <sup>c</sup>	3.242(3)
N3–H3B...O8 <sup>c</sup>	3.368(3)
N3–H3C...O16 <sup>d</sup>	3.055(3)
N4–H4A...O3 <sup>e</sup>	3.052(3)
N4–H4B...O12 <sup>c</sup>	3.003(3)
N4–H4C...O7 <sup>f</sup>	3.170(3)

N5–H5A...O7 <sup>f</sup>	3.149(3)
N5–H5B...O11 <sup>b</sup>	3.023(3)
N5–H5B...O16 <sup>d</sup>	2.954(3)
N5–H5C...O14 <sup>b</sup>	3.092(3)
N5–H5C...O15 <sup>b</sup>	3.323(3)
N6–H6A...O3 <sup>e</sup>	3.067(3)
N6–H6B...O14 <sup>b</sup>	3.044(3)
N6–H6C...O12 <sup>a</sup>	3.108(3)
O9–H9A...O4 <sup>g</sup>	2.639(3)
O9–H9B...O15 <sup>a</sup>	2.746(3)
O9–H9B...O16 <sup>a</sup>	3.011(3)
O10–H10A...O3 <sup>h</sup>	2.629(3)
O10–H10B...O7 <sup>c</sup>	2.667(3)

<sup>a</sup> x,y,z; <sup>b</sup> 1/2+x,3/2-y,1/2+z; <sup>c</sup> 1+x,y,z; <sup>d</sup> 3/2+x,3/2-y,1/2+z; <sup>e</sup> 1/2+x,1/2+y,z; <sup>f</sup> 3/2+x,1/2+y,z; <sup>g</sup> -1+x,y,z; <sup>h</sup> x,1-y,1/2+z

**Table S10.** Hydrogen bonds formed between complex cations and anions in **1**.

Donor–H...Acceptor	H-bond length / Å
N1–H1B...O1 <sup>a</sup>	2.907(7)
N3–H3A...O14 <sup>b</sup>	2.840(6)
N3–H3B...O6 <sup>c</sup>	3.276(6)
O4–H4...O16 <sup>a</sup>	2.743(5)
N4–H4A...O14 <sup>b</sup>	2.944(6)
N4–H4B...O5 <sup>a</sup>	3.305(6)
N4–H4B...O9 <sup>a</sup>	2.931(6)
N4–H4C...O8 <sup>d</sup>	3.028(6)
N5–H5A...O8 <sup>e</sup>	3.148(6)
N5–H5A...O16 <sup>f</sup>	2.933(6)
N6–H6A...O8 <sup>e</sup>	3.246(6)
N6–H6B...O7 <sup>e</sup>	3.248(6)
N6–H6C...O14 <sup>b</sup>	3.128(6)

O11–H11...O18 <sup>a</sup>	2.758(5)
O12–H12...O15 <sup>f</sup>	2.880(4)

<sup>a</sup>  $x, y, z$ ; <sup>b</sup>  $x, 1-y, -1/2+z$ ; <sup>c</sup>  $1-x, 1-y, 1-z$ ; <sup>d</sup>  $1/2-x, -1/2+y, 1/2-z$ ; <sup>e</sup>  $x, -1+y, z$ ; <sup>f</sup>  $1/2-x, 3/2-y, 1-z$

**Table S11.** Hydrogen bonds formed between complex cations and anions in **2**.

Donor–H…Acceptor	H-bond length / Å
N1–H1A…O4 <sup>a</sup>	3.019(13)
N1–H1C…O6 <sup>b</sup>	2.991(14)
N2–H2A…O22 <sup>c</sup>	3.189(11)
N2–H2B…O9 <sup>b</sup>	2.999(12)
N2–H2C…O17 <sup>b</sup>	3.050(12)
N3–H3A…O23 <sup>b</sup>	3.024(14)
N3–H3C…O1 <sup>a</sup>	3.055(14)
N4–H4A…O19 <sup>c</sup>	3.162(11)
N4–H4A…O20 <sup>c</sup>	3.064(12)
N4–H4B…O24 <sup>c</sup>	3.371(12)
N4–H4C…O24 <sup>b</sup>	3.077(12)
N5–H5A…O24 <sup>c</sup>	3.093(14)
N5–H5B…O11 <sup>b</sup>	3.037(14)
N6–H6B…O2 <sup>d</sup>	3.088(12)
N6–H6B…O10 <sup>e</sup>	3.177(11)
N6–H6C…O12 <sup>b</sup>	2.872(15)
N7–H7B…O10 <sup>e</sup>	3.228(12)
N7–H7B…O5 <sup>d</sup>	2.992(13)
N8–H8A…O15 <sup>d</sup>	3.069(12)
N8–H8B…O2 <sup>d</sup>	3.083(11)
N8–H8B…O5 <sup>d</sup>	3.245(11)
N8–H8B…O6 <sup>d</sup>	3.055(13)
N9–H9A…O20 <sup>f</sup>	3.128(13)
N9–H9B…O20 <sup>b</sup>	3.150(12)
N9–H9C…O15 <sup>d</sup>	3.173(12)
N10–H10B…O16 <sup>d</sup>	3.004(13)
N11–H11B…O9 <sup>c</sup>	3.112(12)
N11–H11B…O13 <sup>c</sup>	3.066(12)

<sup>a</sup> 1-x,1-y,2-z; <sup>b</sup> x,y,z; <sup>c</sup> 2-x,1-y,1-z; <sup>d</sup> 1+x,y,z; <sup>e</sup> 2-x,-y,2-z; <sup>f</sup> 3-x,1-y,1-z

**Table S12.** Hydrogen bonds formed between complex cations and anions in **3**.

Donor–H…Acceptor	H-bond length / Å
N1–H1A…O5 <sup>a</sup>	3.045(4)
N1–H1B…O11 <sup>b</sup>	2.999(4)
N2–H2B…O6 <sup>c</sup>	3.026(4)
N3–H3B…O17 <sup>c</sup>	3.091(4)
N3–H3B…O19 <sup>c</sup>	2.976(4)
N4–H4A…O11 <sup>b</sup>	3.033(4)
N4–H4B…O20 <sup>d</sup>	3.055(14)
N5–H5B…O3 <sup>e</sup>	3.057(4)
N5–H5B…O8 <sup>e</sup>	3.155(4)
N6–H6B…O9 <sup>f</sup>	3.039(4)
N6–H6B…O12 <sup>f</sup>	2.928(4)
N7–H7A…O16 <sup>d</sup>	2.997(5)
N7–H7B…O9 <sup>f</sup>	2.934(4)
N8–H8A…O2 <sup>g</sup>	2.951(4)

<sup>a</sup> x,y,z; <sup>b</sup> 1-x,1-y,1-z; <sup>c</sup> 1-x,-y,1-z; <sup>d</sup> 1-x,y,1/2-z; <sup>e</sup> 3/2-x,1/2-y,1-z; <sup>f</sup> 3/2-x,-1/2+y,1/2-z; <sup>g</sup> 1/2+x,-1/2+y,z

**Table S13.** Hydrogen bonds formed between complex cations and anions in **6**.

Donor–H…Acceptor	H-bond length / Å
N1–H1A…O25 <sup>a</sup>	3.066(14)
N1–H1B…O12B <sup>b</sup>	3.091(19)
N1–H1B…O13 <sup>b</sup>	3.087(18)
N2–H2B…O30 <sup>c</sup>	2.941(12)
N3–H3A…O29 <sup>d</sup>	2.945(13)
N3–H3B…O9 <sup>d</sup>	2.988(14)
N4–H4A…O26 <sup>a</sup>	2.941(13)
N5–H5A…O29 <sup>e</sup>	3.116(14)
N5–H5A…O30 <sup>e</sup>	3.178(12)
N5–H5B…O17 <sup>e</sup>	3.035(17)

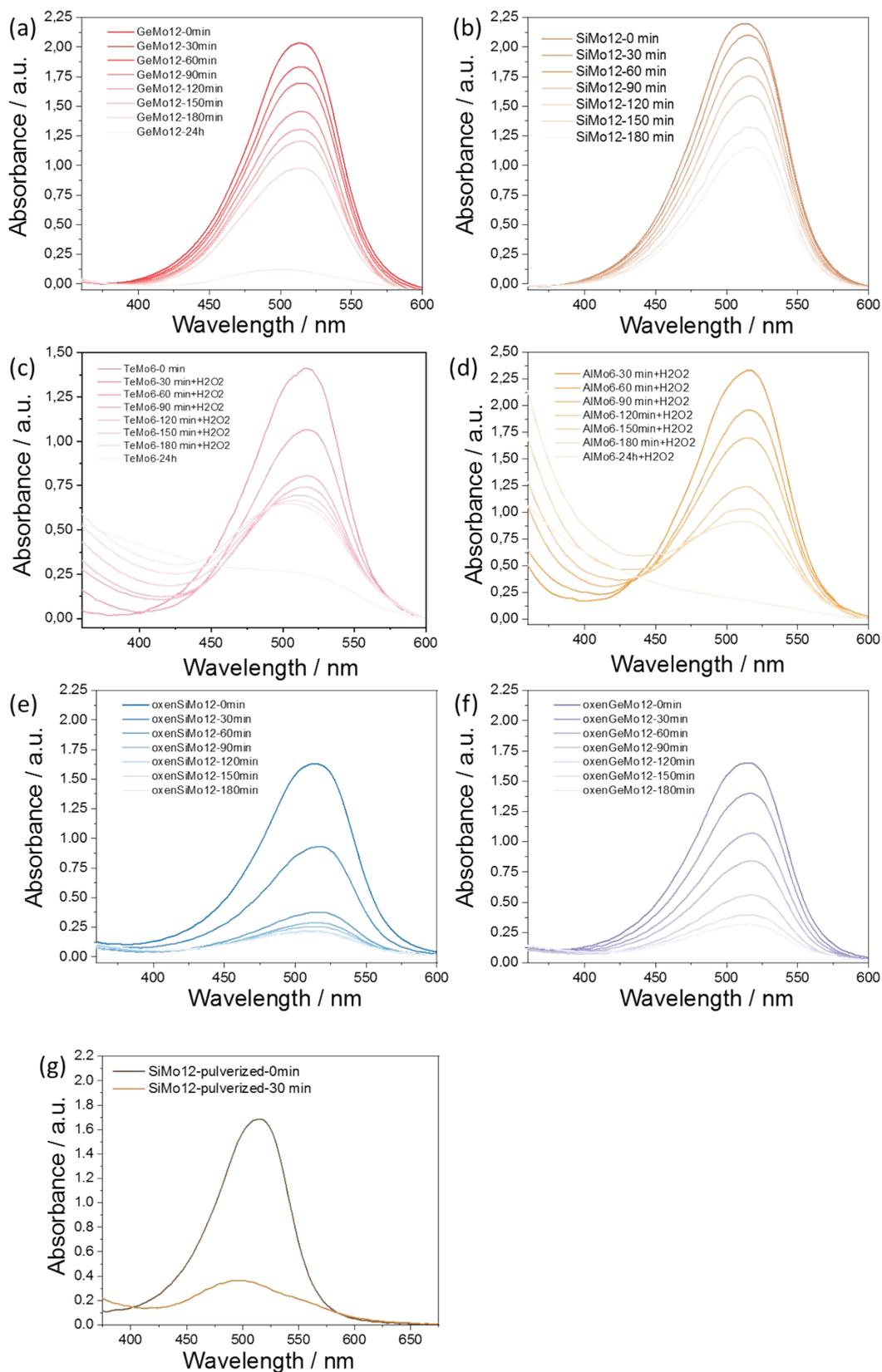
N6–H6A…O25 <sup>e</sup>	2.940(14)
N7–H7A…O16A <sup>f</sup>	3.12(3)
N7–H7A…O16B <sup>f</sup>	3.07(3)
N7–H7A…O30 <sup>e</sup>	3.143(13)
N8–H8AB…O22 <sup>b</sup>	2.927(16)

<sup>a</sup> 3/2-x,1/2+y,1/2-z; <sup>b</sup> x,y,z; <sup>c</sup> 1+x,y,z; <sup>d</sup> 3/2-x,-1/2+y,1/2-z; <sup>e</sup> 1/2-x,1/2+y,1/2-z; <sup>f</sup> x,1+y,z

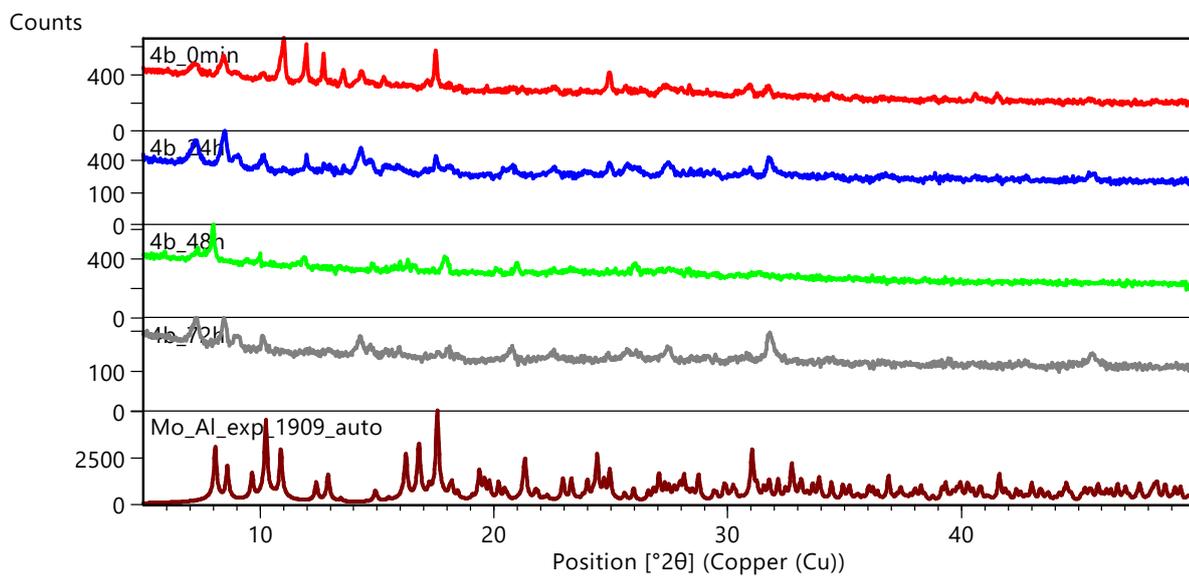
**Table S14.** Hydrogen bonds formed between complex cations and anions in **7**.

Donor–H…Acceptor	H-bond length / Å
N1–H1B…O22 <sup>a</sup>	2.928(13)
N2–H2A…O9A <sup>b</sup>	3.01(2)
N2–H2A…O9B <sup>b</sup>	3.092(18)
N2–H2A…O25 <sup>c</sup>	3.214(9)
N3–H3A…O29 <sup>c</sup>	2.968(10)
N4–H4A…O25 <sup>c</sup>	3.188(9)
N4–H4A…O26 <sup>c</sup>	3.112(9)
N4–H4B…O12A <sup>c</sup>	2.869(18)
N4–H4B…O12B <sup>c</sup>	3.216(17)
N5–H5A…O30 <sup>d</sup>	2.915(10)
N6–H6A…O26 <sup>e</sup>	2.933(9)
N6–H6B…O16 <sup>e</sup>	3.009(11)
N7–H7A…O26 <sup>e</sup>	3.193(10)
N7–H7B…O25 <sup>f</sup>	2.911(9)
N8–H8A…O29 <sup>d</sup>	3.076(10)
N8–H8B…O13 <sup>a</sup>	3.079(14)
N8–H8B…O14A <sup>a</sup>	3.105(16)

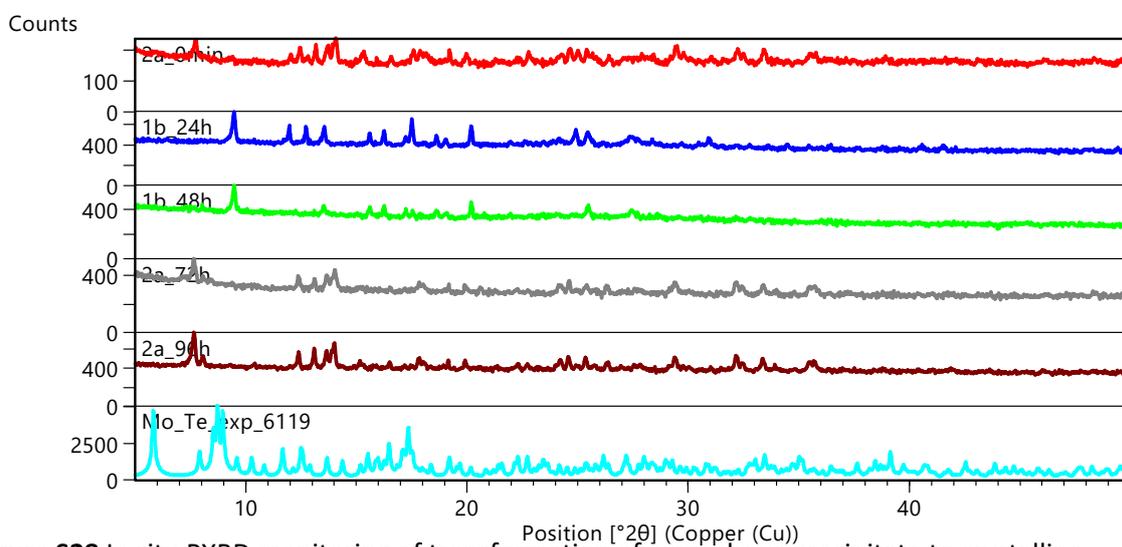
<sup>a</sup> x,y,z; <sup>b</sup> x,1+y,z; <sup>c</sup> 1/2-x,1/2+y,1/2-z; <sup>d</sup> 3/2-x,1/2+y,1/2-z; <sup>e</sup> 3/2-x,-1/2+y,1/2-z; <sup>f</sup> 1+x,y,z



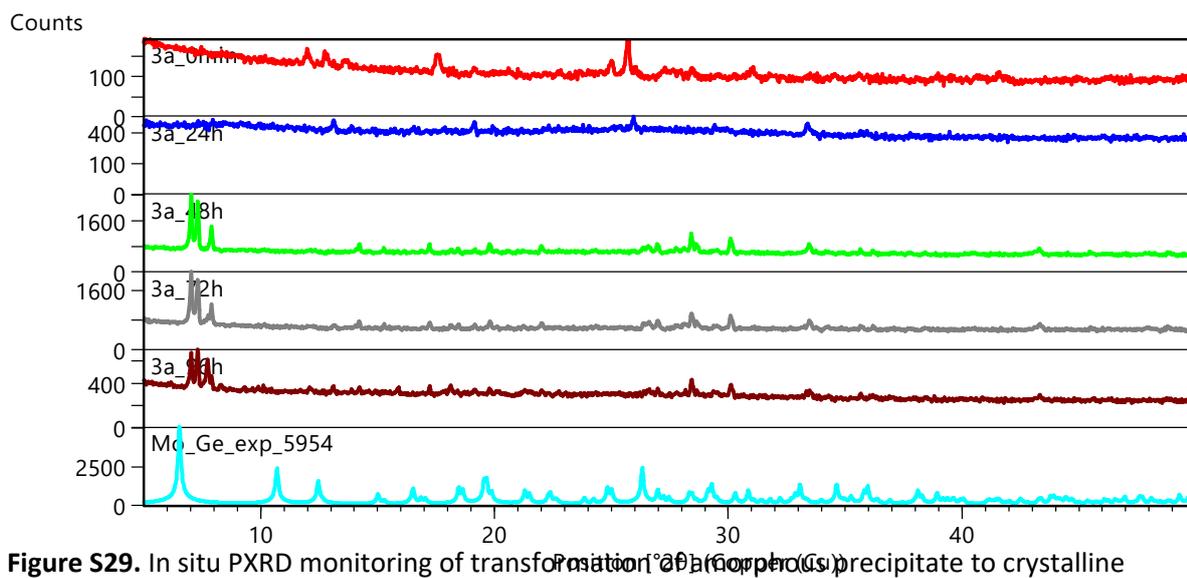
**Figure S26.** Visible spectra degradation of sofranin T in the presence of compounds a) **4** b) **5** e) **6** and f) **7** after irradiation; c) **1** and d) **2** in presence of H<sub>2</sub>O<sub>2</sub> after irradiation; g) catalytic test with compound **5** after pulverization in mortar



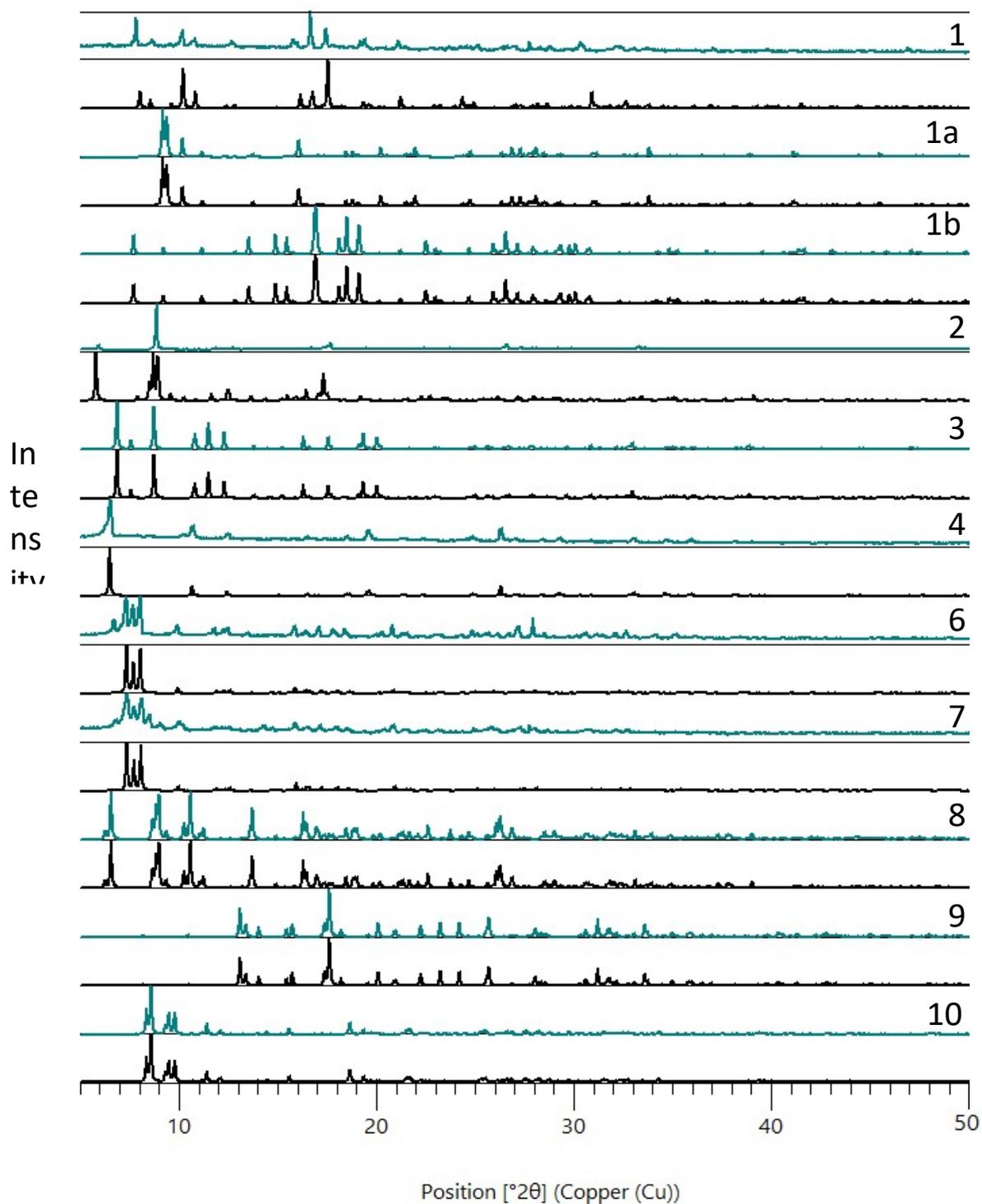
**Figure S27.** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex 1.



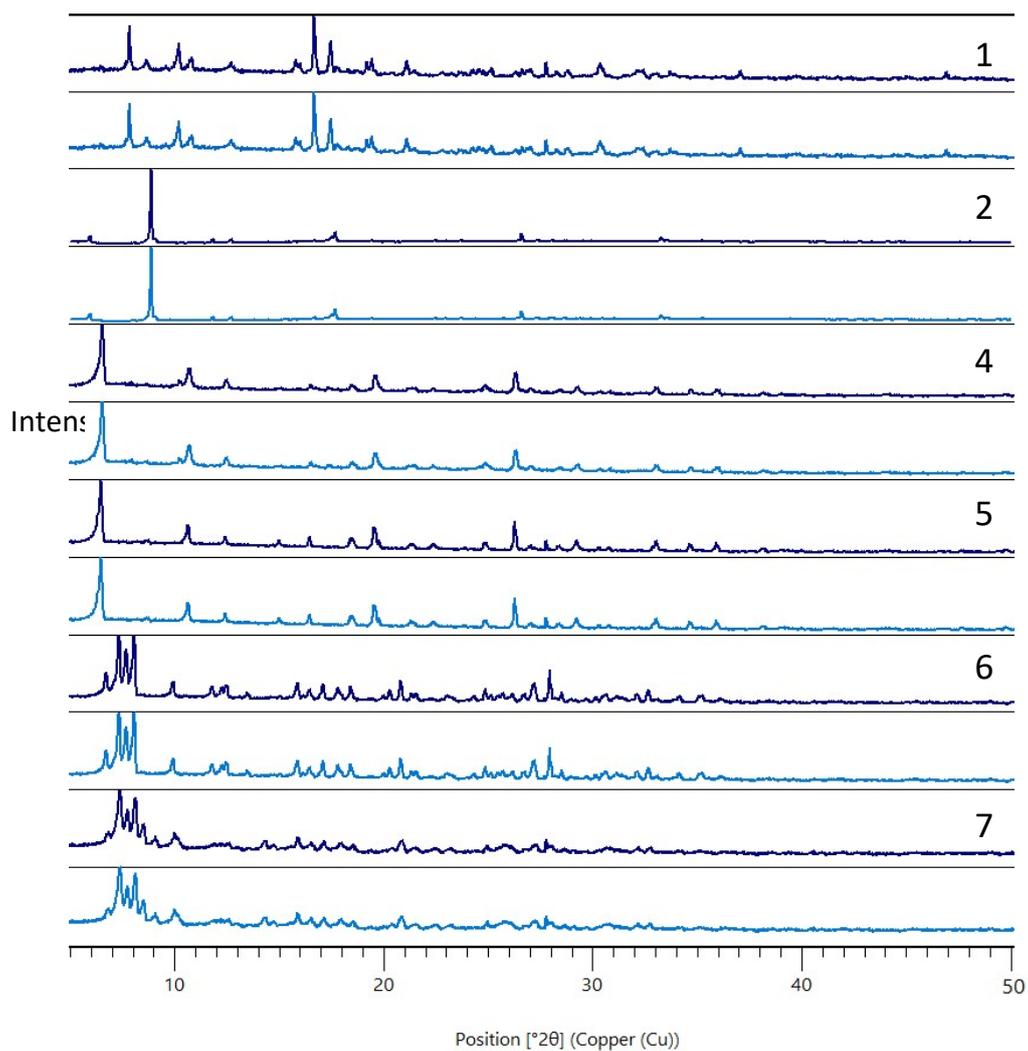
**Figure S28** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex 2.



**Figure S29.** In situ PXRD monitoring of transformation of amorphous precipitate to crystalline complex 4.



**Figure S30.** PXRD patterns of compounds described in this work. The teal lines indicate patterns obtained by powder diffraction, while the black lines indicate patterns calculated from the X-ray single-crystal structures of the corresponding compounds.



**Figure S31.** Comparison of the PXRD patterns before (dark blue) and after (light blue) the catalytic experiments for compounds **1**, **2**, **4**, **5**, **6** and **7**.