

## Supramolecular assembling of oxalatomolybdates controlled by hydrogen bonding potential of Co(III) – ammine cations

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### TABLE OF CONTENT:

**Table S1.** Crystal data and summary of experimental details for single crystal diffraction experiments for compounds 1 – 4c.

**Figure S1** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 1.

**Figure S2** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 2.

**Figure S3** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 2a.

**Figure S4** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 3.

**Figure S5** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 4.

**Figure S6** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 4a.

**Figure S7** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 4b.

**Figure S8** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of 4c.

**Table S2** Thermogravimetric data for 1–4 and 1a–4c complexes

**Figure S9** TG\_curve\_ Complex 1

**Figure S10** TG\_curve\_ Complex 1a

**Figure S11** TG\_curve\_ Complex 2

**Figure S12** TG\_curve\_ Complex 2a

**Figure S13** TG\_curve\_ Complex 3

**Figure S14** TG\_curve\_ Complex 3a

**Figure S15** TG\_curve\_ Complex 4

**Figure S16** TG\_curve\_ Complex 4a

**Figure S17** TG\_curve\_ Complex 4b

**Figure S18** TG\_curve\_ Complex 4c

**Figure S19** IR spectrum of pink mixture of CoMoO<sub>n</sub> oxides (after thermogravimetric measurement of 1)

**Figure S20** PXRD data of CoMoO<sub>4</sub> oxides obtained after combustion of compounds 1, 1a, 4 and 4c

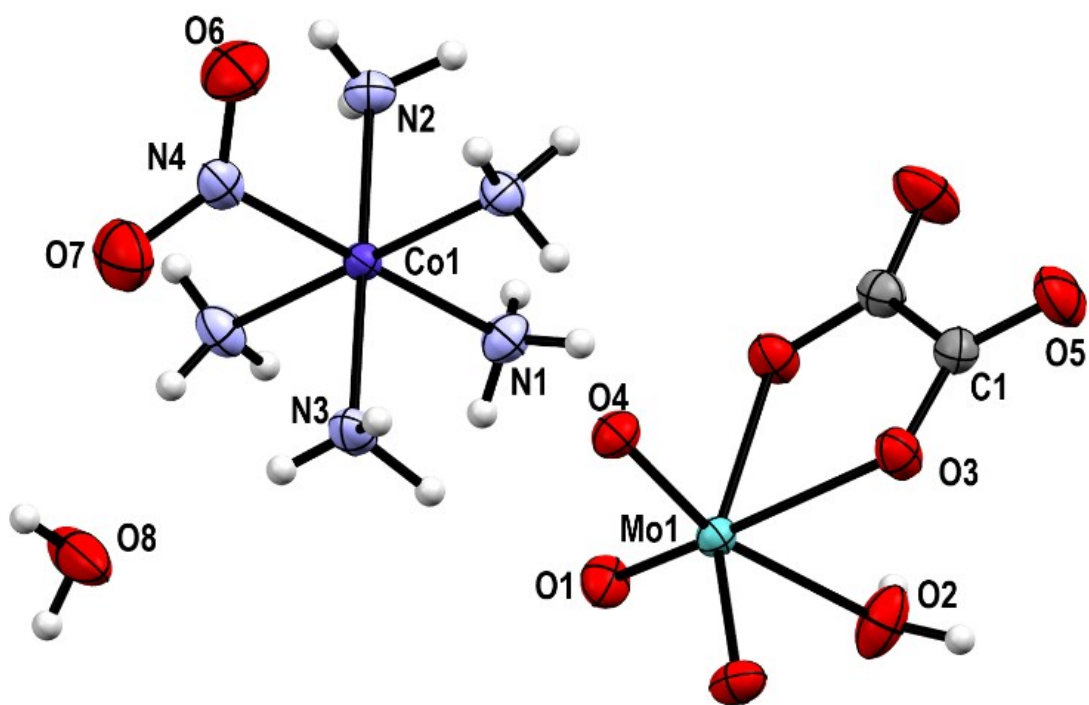
**Table S1.** Crystal data and summary of experimental details for single crystal diffraction experiments for compounds **1 – 4c**.

	(1)	(2)	(2a)	(3)
Formula	C <sub>2</sub> H <sub>19</sub> CoMoN <sub>6</sub> O <sub>11</sub>	C <sub>8</sub> Mo <sub>4</sub> O <sub>28</sub> ·2(C <sub>2</sub> H <sub>2</sub> MoO <sub>8</sub> )·4(CoH <sub>18</sub> N <sub>6</sub> )·10(H <sub>2</sub> O)	C <sub>8</sub> H <sub>2</sub> Mo <sub>4</sub> O <sub>28</sub> ·2(CoH <sub>18</sub> N <sub>6</sub> )·6(H <sub>2</sub> O)	C <sub>18</sub> H <sub>64</sub> Co <sub>2</sub> Mo <sub>3</sub> N <sub>12</sub> O <sub>29</sub>
<i>M<sub>r</sub></i>	458.10	2252.48	1360.22	1318.49
Crystal system, space group	Orthorhombic, <i>Pnma</i>	Triclinic, <i>P</i> -1	Orthorhombic, <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	Orthorhombic, <i>Pna2<sub>1</sub></i>
<i>T</i> /K	295	150	150	295
<i>a</i> / Å	27.0371 (12)	10.2131 (3)	10.5531 (3)	13.5465 (3)
<i>b</i> / Å	7.9845 (3),	13.1299 (4)	16.1106 (6)	11.6910 (3)
<i>c</i> / Å	6.4776 (3)	13.2356 (3)	23.2787 (7)	28.9847 (7)
<i>α</i> / °	90	79.390 (2)	90	90
<i>β</i> / °	90	84.259 (2)	90	90
<i>γ</i> / °	90	77.997 (2)	90	90
<i>V</i> / Å <sup>3</sup>	1398.37 (10)	1702.85 (8)	3957.8 (2)	4590.37 (19)
<i>Z</i>	4	1	4	4
Radiation type	Mo <i>Kα</i>	Mo <i>Kα</i>	Mo <i>Kα</i>	Mo <i>Kα</i>
<i>μ</i> / mm <sup>-1</sup>	2.15	2.14	2.17	1.61
Crystal size / mm <sup>3</sup>	0.65 × 0.31 × 0.06	0.23 × 0.20 × 0.10	0.71 × 0.19 × 0.14	0.16 × 0.15 × 0.14
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	9126, 1628, 1468	12170, 7387, 5877	30194, 8629, 7889	23742, 9938, 7811
<i>R</i> <sub>int</sub>	0.027	0.020	0.029	0.031
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.022, 0.054, 1.08	0.023, 0.047, 0.91	0.020, 0.043, 0.96	0.031, 0.069, 0.91
No. of reflections	1628	7387	8629	9938
No. of parameters	150	636	592	584
Δρ <sub>max</sub> , Δρ <sub>min</sub> / e Å <sup>-3</sup>	0.37, -0.73	0.48, -0.53	0.37, -0.48	0.64, -0.51

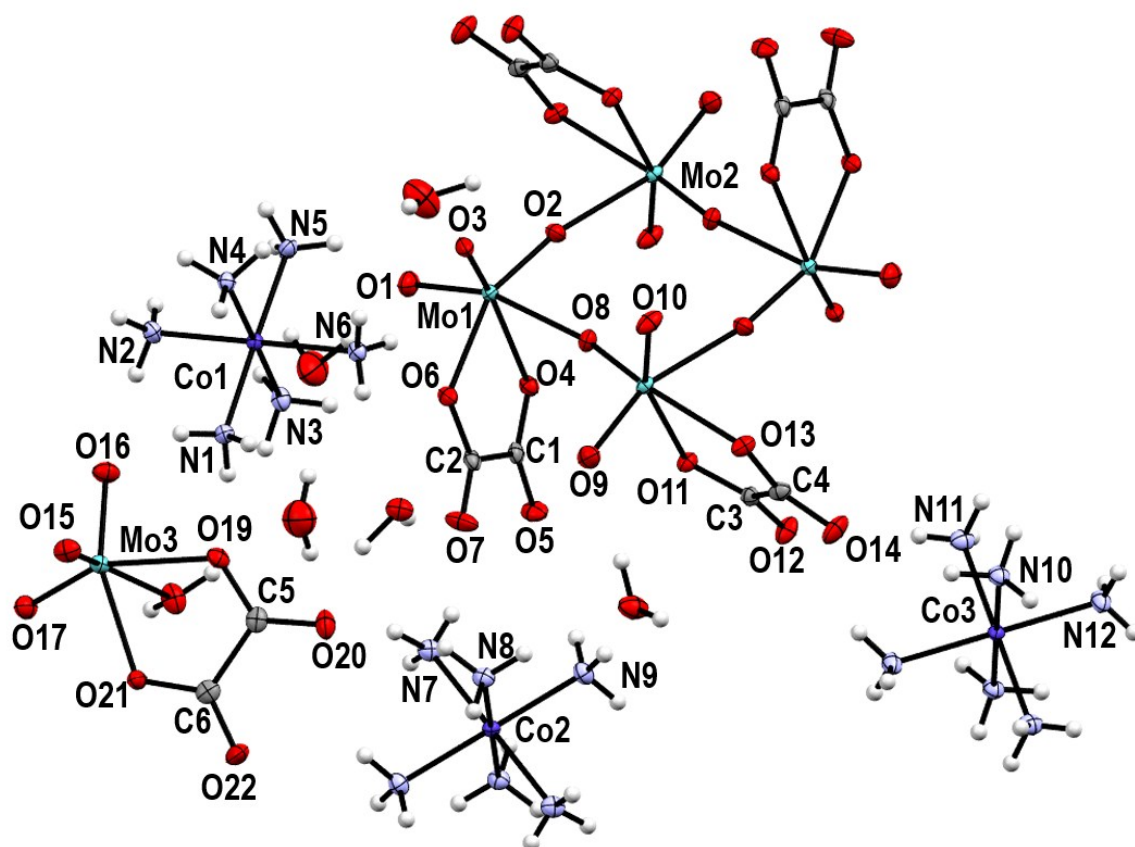
**Table S1. cont.**

	(4)	(4a)	(4b)	(4c)
Formula	C <sub>20</sub> H <sub>60</sub> Co <sub>2</sub> Mo <sub>4</sub> N <sub>12</sub> O <sub>33</sub>	C <sub>4</sub> H <sub>4</sub> Mo <sub>2</sub> O <sub>15</sub> ·2(C <sub>6</sub> H <sub>16</sub> CoN <sub>4</sub> O <sub>4</sub> )·4(H <sub>2</sub> O)	C <sub>16</sub> H <sub>46</sub> Co <sub>2</sub> Mo <sub>2</sub> N <sub>8</sub> O <sub>28</sub>	C <sub>14</sub> H <sub>48</sub> Co <sub>2</sub> Mo <sub>8</sub> O <sub>23</sub>

$M_r$	1498.42	1090.33	1108.35	910.40
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Orthorhombic, $Pbcn$	Triclinic, $P-1$
$T/K$	295	295	295	295
$a / \text{\AA}$	13.5099 (10),	12.8719 (10),	10.7699 (5),	10.0883 (12),
$b / \text{\AA}$	17.5536 (10),	10.4734 (7),	22.3609 (9),	11.9280 (13),
$c / \text{\AA}$	9.9621 (8)	14.5744 (10)	15.1262 (8)	15.268 (4)
$\alpha / ^\circ$	90	90	90	67.802 (7)
$\beta / ^\circ$	87.737 (6)	112.997 (8)	90	86.402 (2)
$\gamma / ^\circ$	90	90	90	75.04 (1)
$V / \text{\AA}^3$	2360.6 (3)	1808.7 (2)	3642.8 (3)	1642.2 (5)
$Z$	2	2	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
$\mu / \text{mm}^{-1}$	1.83	1.69	1.68	1.48
Crystal size / $\text{mm}^3$	$0.24 \times 0.07 \times 0.04$	$0.79 \times 0.16 \times 0.03$	$0.29 \times 0.21 \times 0.06$	$0.73 \times 0.35 \times 0.21$
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9053, 4106, 2202	19135, 3921, 2800	26808, 3969, 2979	11506, 6948, 4549
$R_{\text{int}}$	0.056	0.079	0.078	0.055
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.053, 0.141, 0.89	0.046, 0.125, 0.98	0.042, 0.095, 1.03	0.057, 0.138, 0.91
No. of reflections	4106	3921	3969	6948
No. of parameters	343	256	296	475
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / \text{e \AA}^{-3}$	1.29, -0.93	1.49, -0.96	0.63, -0.59	1.44, -1.57



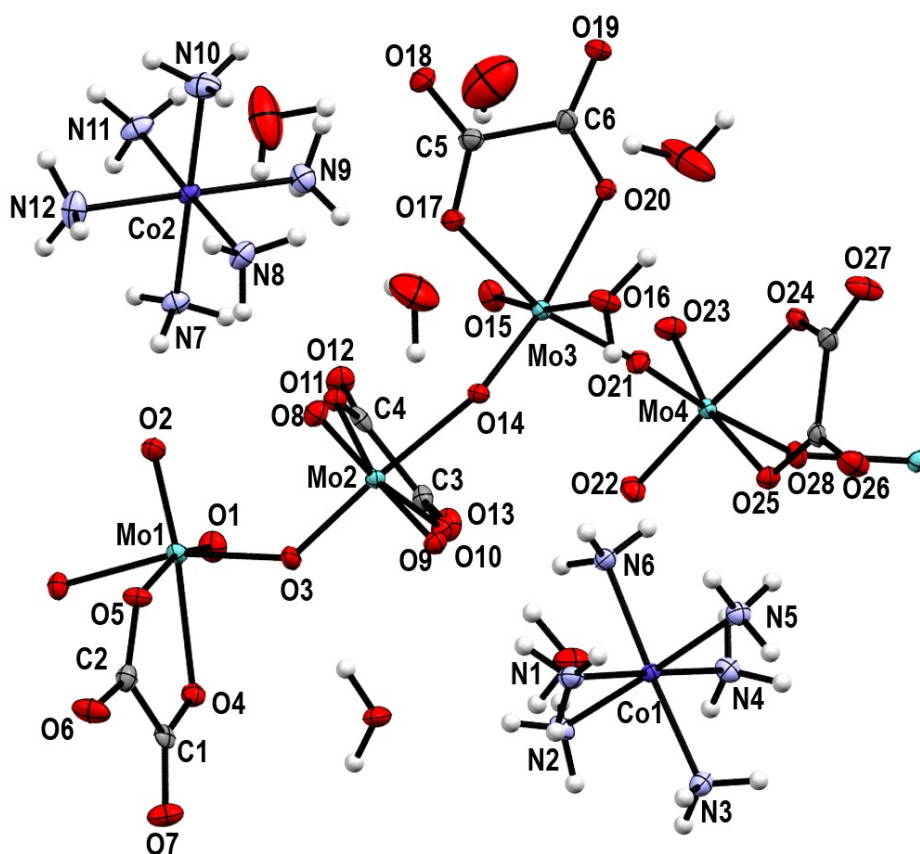
**Figure S1** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **1**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii.



**Figure S2** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **2**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules have been omitted for clarity.

**Structural description of the  $[\text{Mo}_4\text{O}_{12}(\text{ox})_4]^{8-}$  cyclic tetramer:**

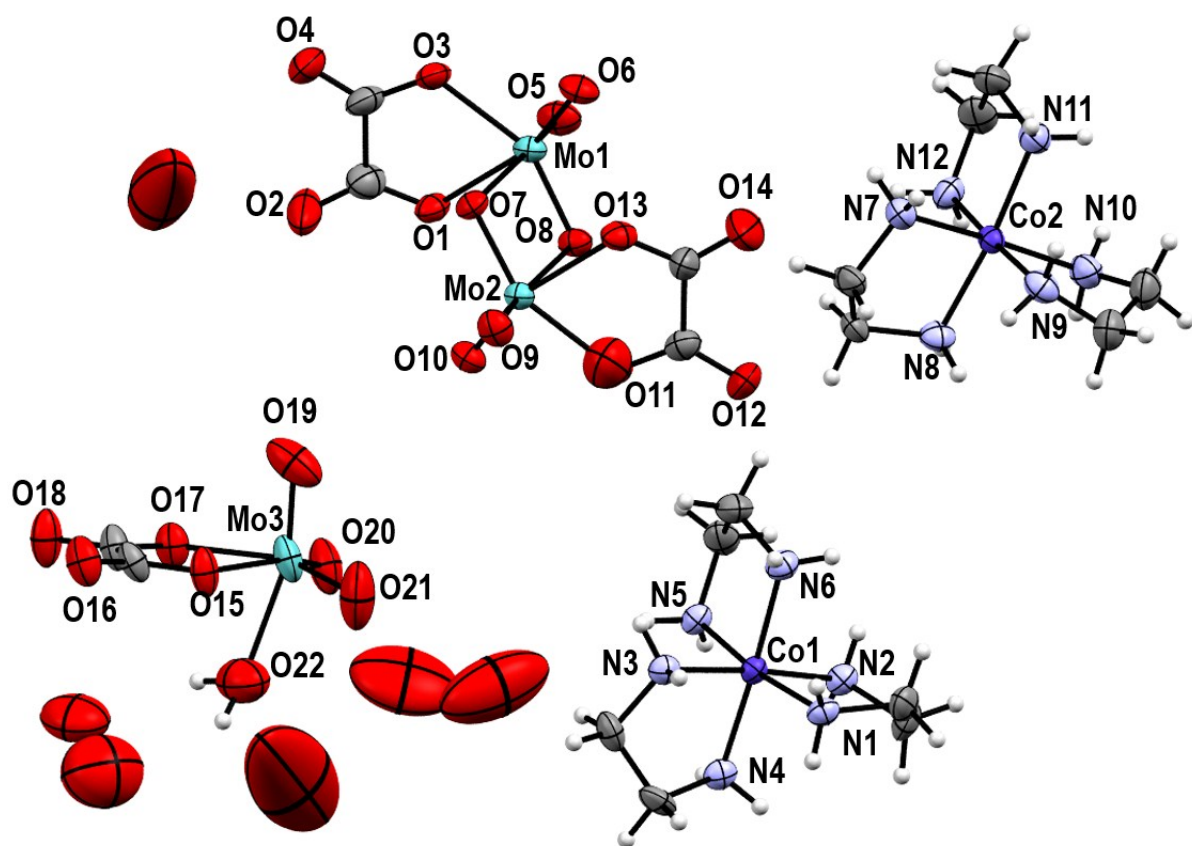
Each molybdenum atom is coordinated by an oxalate anion, two terminal and two bridging oxo ligands. The four molybdenum atoms of  $[\text{Mo}_4\text{O}_{12}(\text{ox})_4]^{8-}$  are coplanar and constitute a parallelogram closely approaching a regular square with Mo-Mo distances of 3.97 and 3.95 Å and the acute angle of 88.45°, with the bridging oxygen atoms lying approximately in the same plane. The Mo-O bond lengths alternate within the ring, each oxygen (and each molybdenum) forming one shorter (1.738 and 1.757 Å) and one longer bond (2.228 and 2.247 Å). As the former bond length corresponds to a Mo=O double bond, the  $[\text{Mo}_4\text{O}_{12}(\text{ox})_4]^{8-}$  tetramer can be described as derivative of  $[\text{MoO}_3(\text{ox})(\text{H}_2\text{O})]^{2-}$ , formed by replacing the coordinated water molecules by oxo ligand of another  $[\text{MoO}_3(\text{ox})]^{2-}$  core.



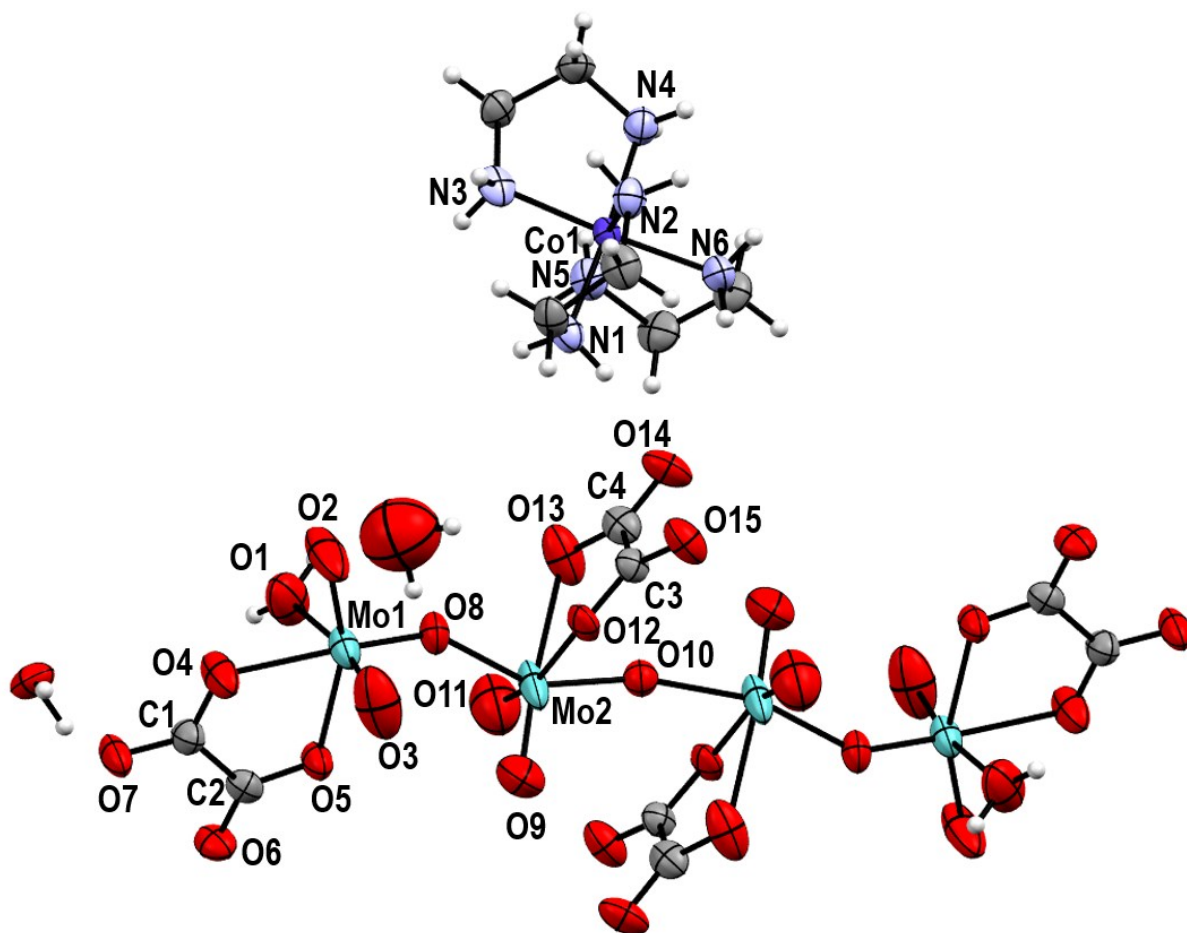
**Figure S3** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **2a**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules have been omitted for clarity.

**Structural description of the  $[\text{Mo}_4\text{O}_{11}(\text{ox})_4(\text{H}_2\text{O})]_n^{6n-}$  polymer:**

$[\text{Mo}_4\text{O}_{11}(\text{ox})_4(\text{H}_2\text{O})]_n^{6n-}$  differs from the previously reported  $[\text{MoO}_3(\text{C}_2\text{O}_4)]_n^{2n-}$  polymer by being partly protonated, *i.e.* every fourth  $[\text{MoO}_3(\text{C}_2\text{O}_4)]^{2-}$  subunit is replaced by a  $\text{MoO}_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})$ . This has a pronounced effect on the structure of the polymer – whereas  $[\text{MoO}_3(\text{C}_2\text{O}_4)]_n^{2n-}$  is usually linear with equal Mo–O bonds,  $[\text{Mo}_4\text{O}_{11}(\text{ox})_4(\text{H}_2\text{O})]_n^{6n-}$  is strongly corrugated and forms a highly elongated helix about a crystallographic  $2_1$  axis. The reason for this is that while the bridging oxo ligands are placed *trans* one to another in every  $[\text{MoO}_3(\text{C}_2\text{O}_4)]^{2-}$  subunit, they are in a *cis* position in  $\text{MoO}_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})$ . This also affects the lengths of the Mo–O bonds with the bridging oxo ligands – the two formed by the protonated subunit being the shortest (1.775 and 1.780 Å) and the rest falling in the 1.836–2.095 Å range.



**Figure S4** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **3**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules and carbon atoms have been omitted for clarity.

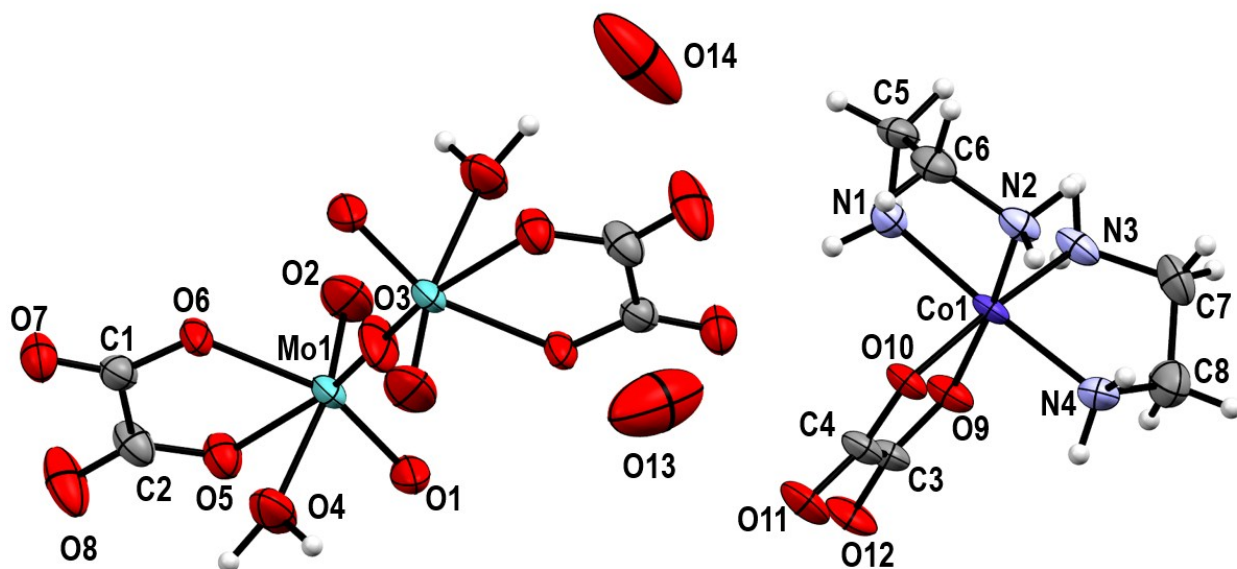


**Figure S5** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **4**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules and carbon atoms have been omitted for clarity.

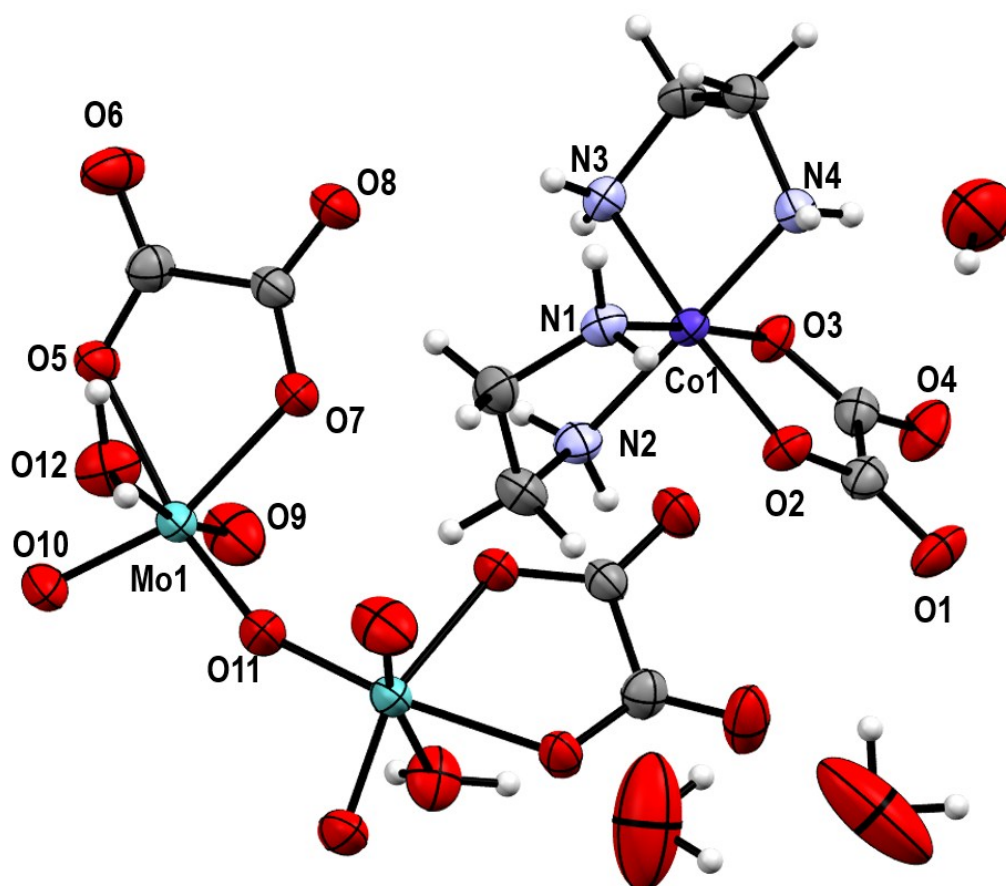
**Structural description of the  $[\text{Mo}_4\text{O}_8(\mu\text{-O})_3(\text{ox})_4(\text{H}_2\text{O})_2]^{6-}$  linear tetramer:**

$[\text{Mo}_4\text{O}_8(\mu\text{-O})_3(\text{ox})_4(\text{H}_2\text{O})_2]^{6-}$  is a linear tetramer with two pairs of inequivalent molybdenum subunits. The terminal molybdenum ions are coordinated by a water molecule, an oxalate anion, two terminal and one bridging oxo ligands. Between these molybdenum subunits is a pair of bridging subunits where the molybdenum ions are coordinated by an oxalate anion, two terminal and two bridging oxo ligands. Unlike in the cyclic tetramer all Mo–O bonds with the bridging oxo ligands are of approximately equal lengths and lie in the 1.811–1.986 Å range. The two angles in Mo–O–Mo unit are obtuse (144° for the angle to the terminal and 157° for the angle between the central subunits). The ion lies on a crystallographic inversion center, with the central oxygen atom displaced from the center by *ca.* 0.37 Å, because of which it appears to be disordered over two positions with equal occupancies.

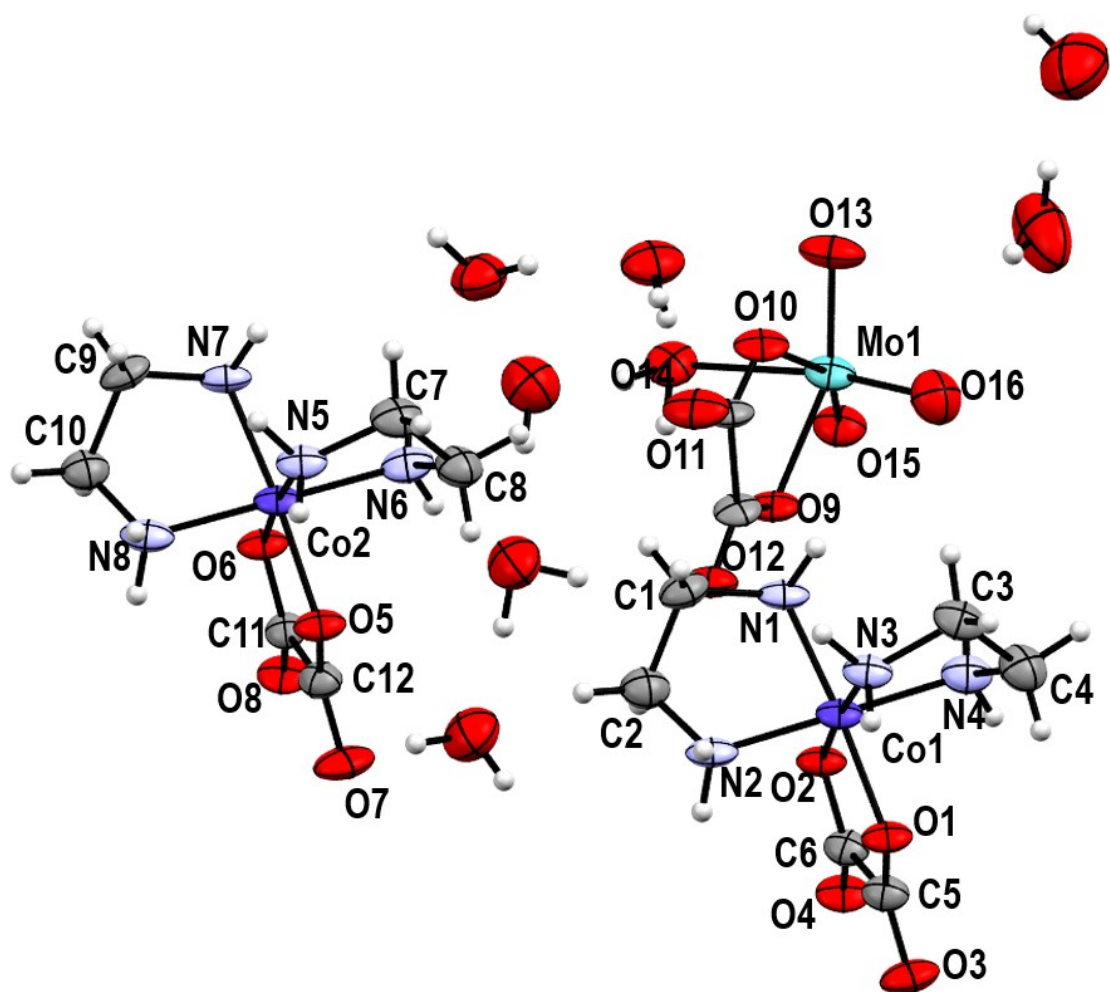




**Figure S6** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **4a**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii.



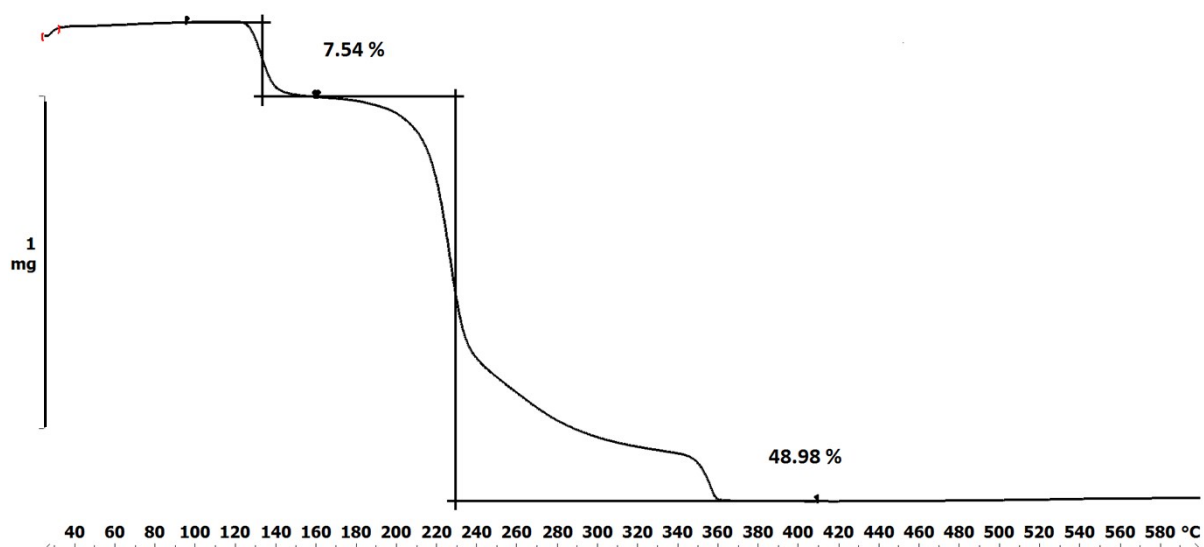
**Figure S7** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **4b**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules and carbon atoms have been omitted for clarity.



**Figure S8** ORTEP plot of the extended asymmetric unit with the atom labeling scheme of **4c**. Displacement ellipsoids shown at 50% probability and hydrogen atoms are shown as small spheres of arbitrary radii. Labels for solvent molecules have been omitted for clarity.

**Table S2.** Thermogravimetric data for 1–4 and 1a–4c complexes

	Dehydration/°C	exp. (%)	calc. (%)	Pyrolysis	exp. (%)	calc. (%)
1	98-169	7.54	7.86	168-412	48.98	47.78
1a	41-194	6.16	6.59	194-410	52.21	53.12
2	94-186	8.98	9.15	186-457	52.69	51.65
2a	45-210	7.98	9.27	210-410	50.15	53.35
3	43-212	5.11	6.27	213-495	44.85	41.95
3a	41-132	6.42	8.32	190-482	51.16	48.85
4	45-189	6.76	7.21	205-450	50.68	48.43
4a	68-167	10.66	9.91	200-550	41.43	40.15
4b	47-153	12.19	12.79	192-560	40.68	38.86
4c	39-135	15.08	16.71	157-493	36.28	34.07



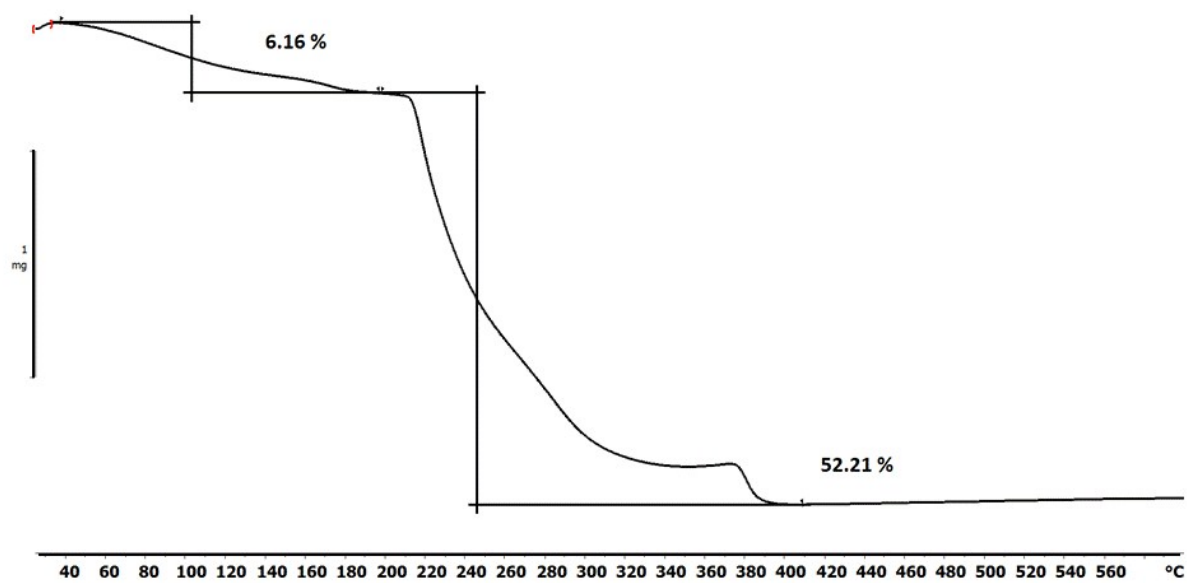


Figure S10 TG\_curve\_Complex 1a

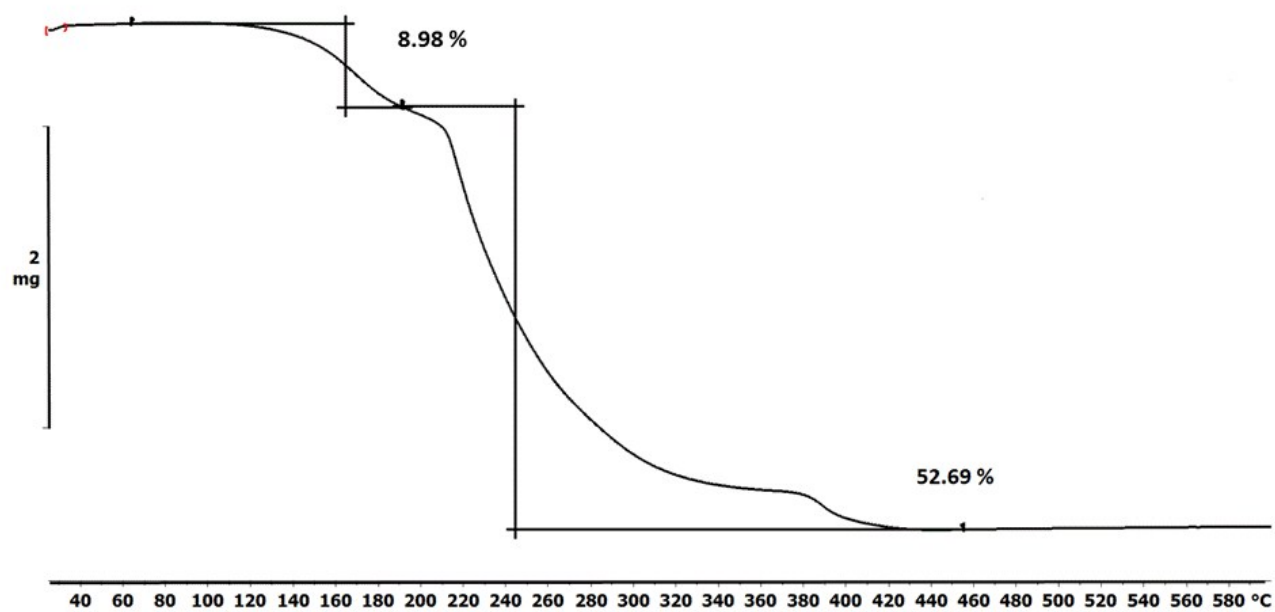


Figure S11 TG\_curve\_Complex 2

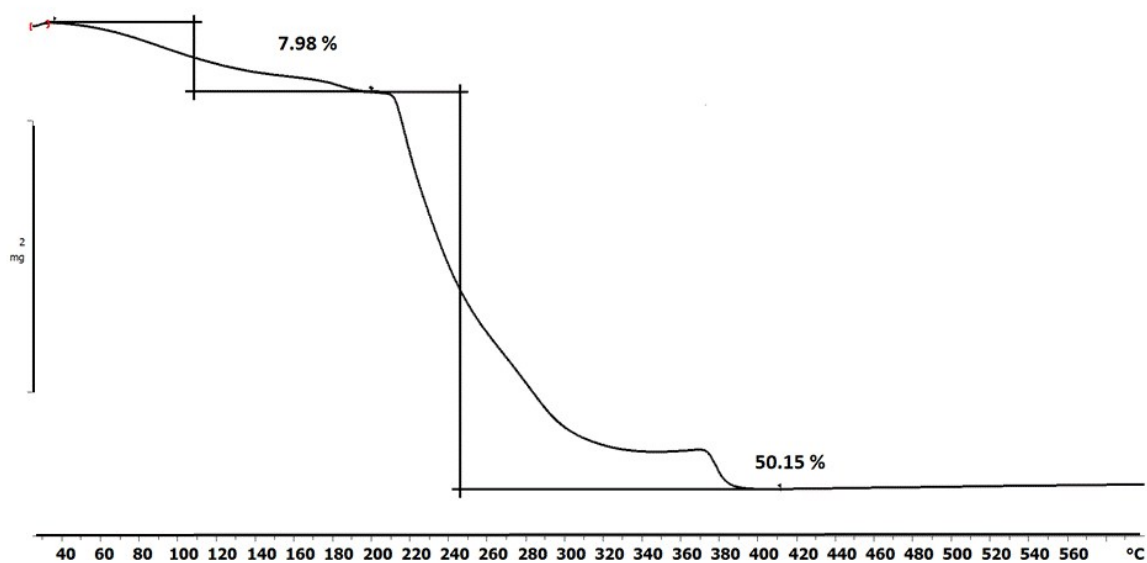
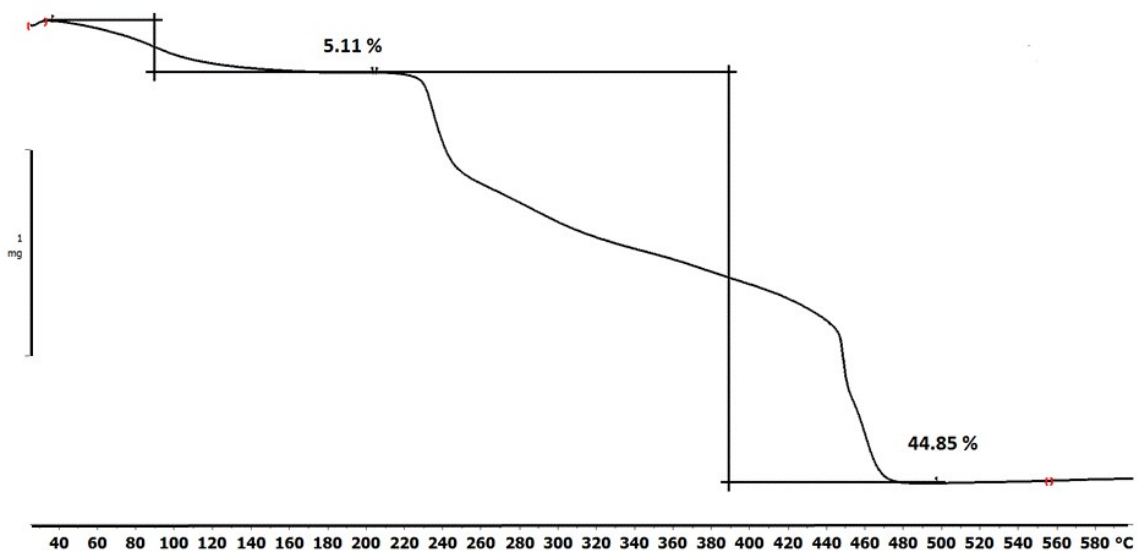


Figure S12 TG\_curve\_Complex 2a



S13 TG\_curve\_Complex 3

Figure

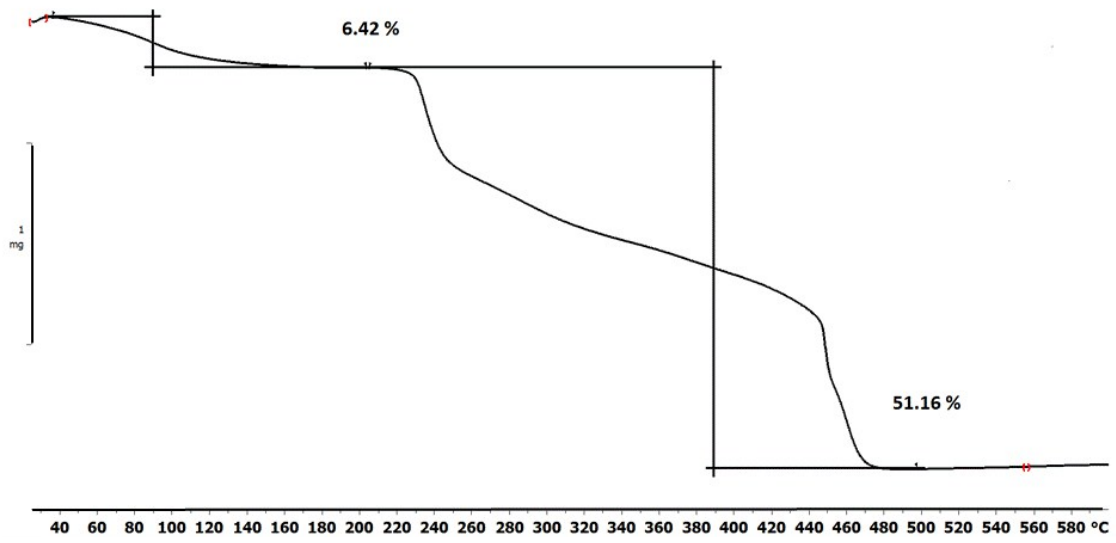


Figure S14 TG\_curve\_Complex 3a

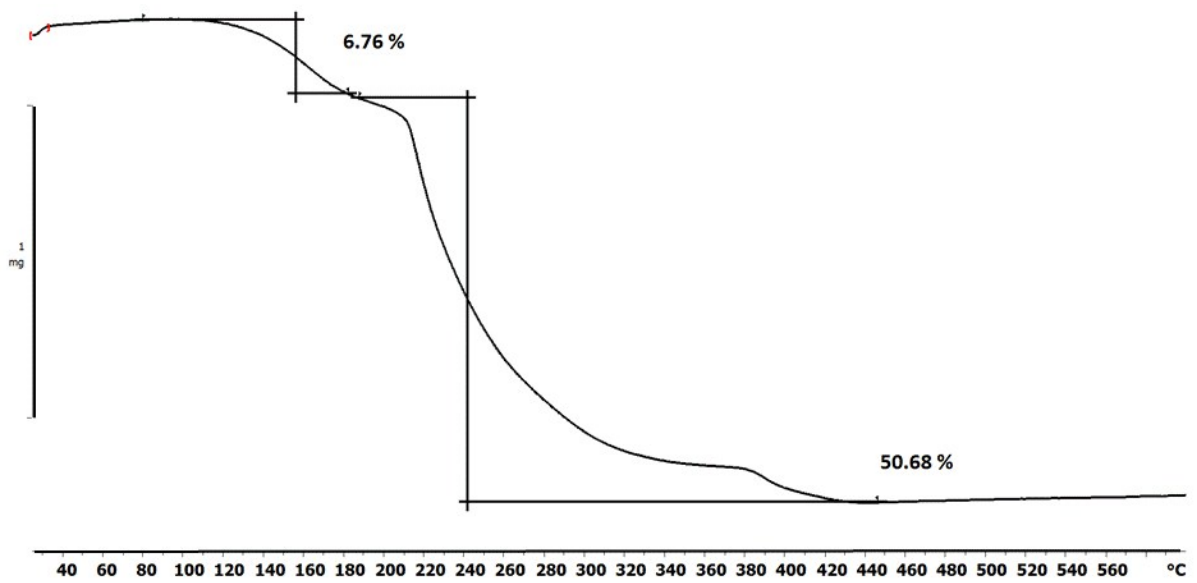


Figure S15 TG\_curve\_Complex 4

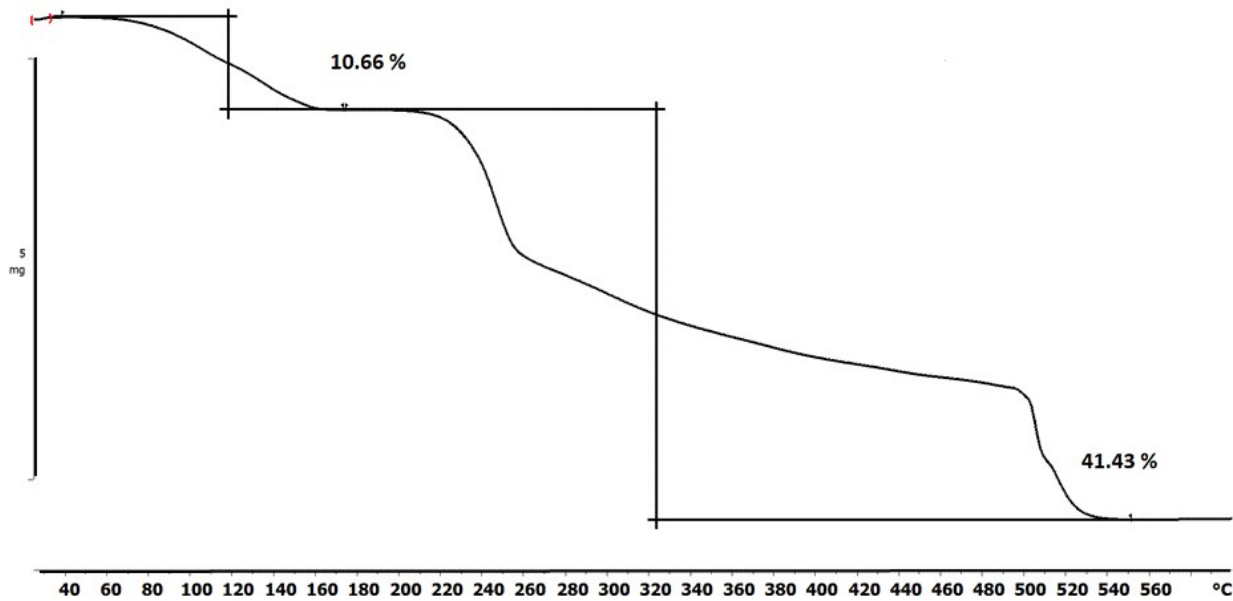


Figure S16 TG\_curve\_Complex 4a

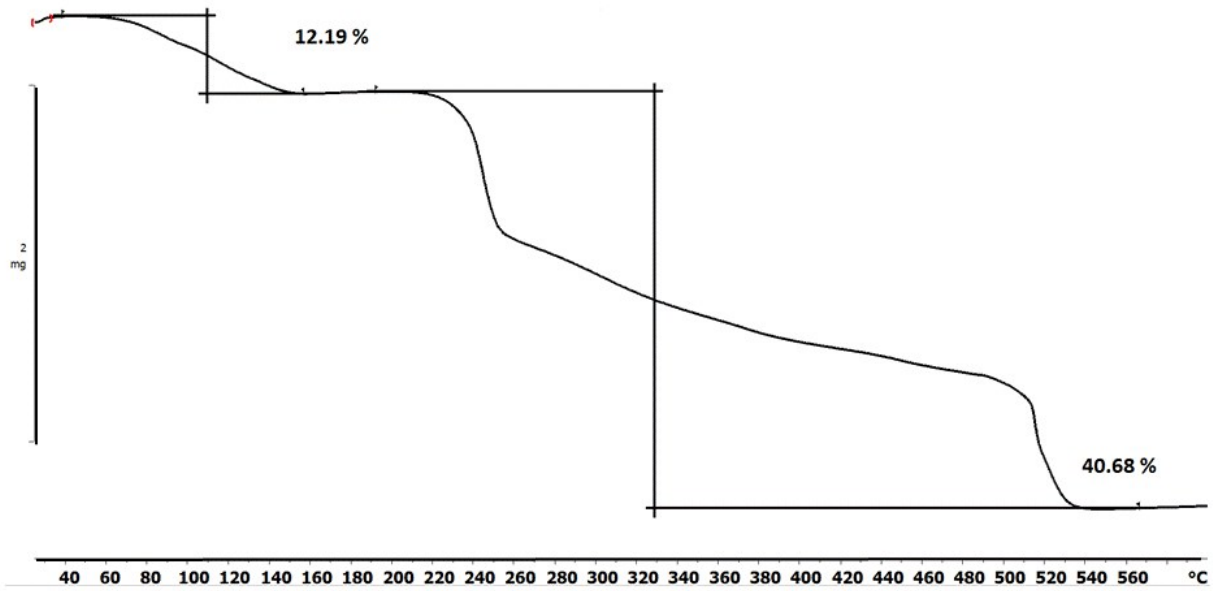


Figure S17 TG\_curve\_Complex 4b

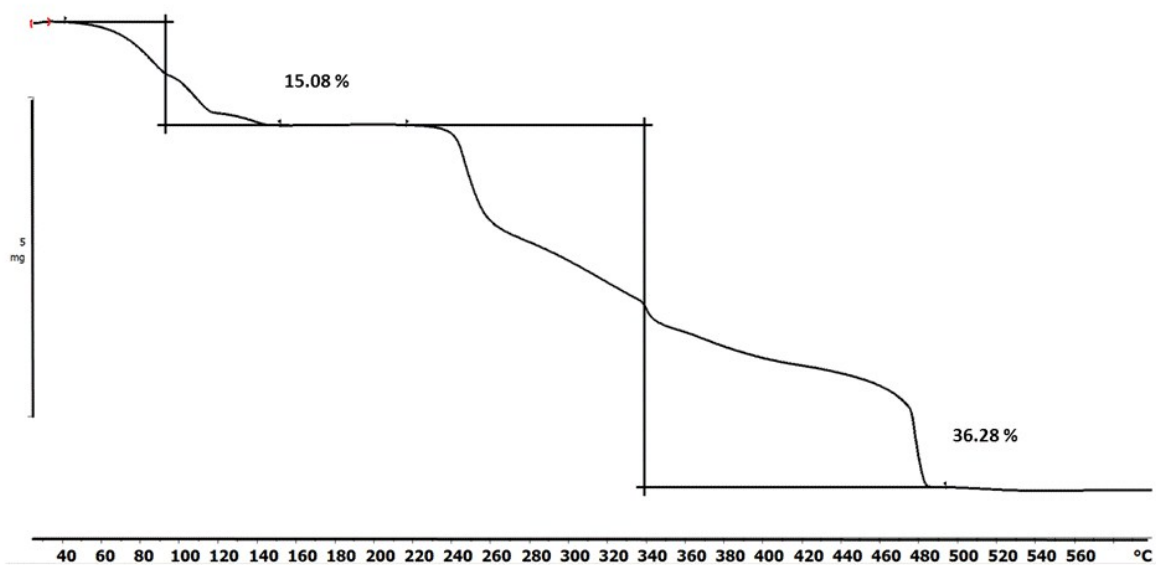


Figure S18 TG\_curve\_ Complex 4c

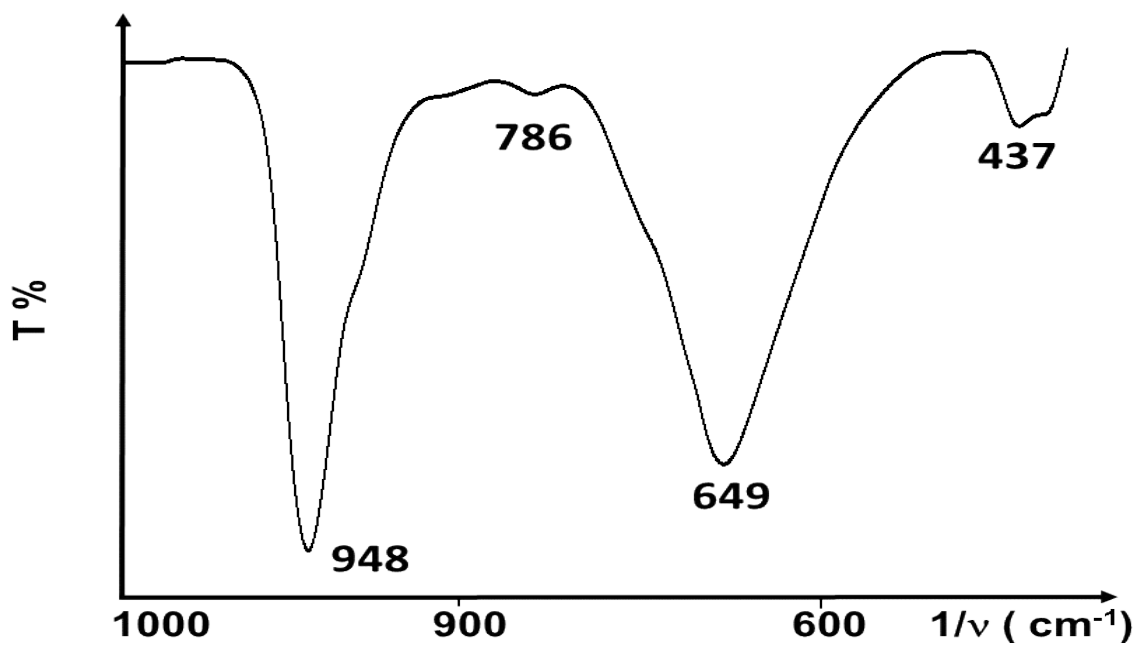
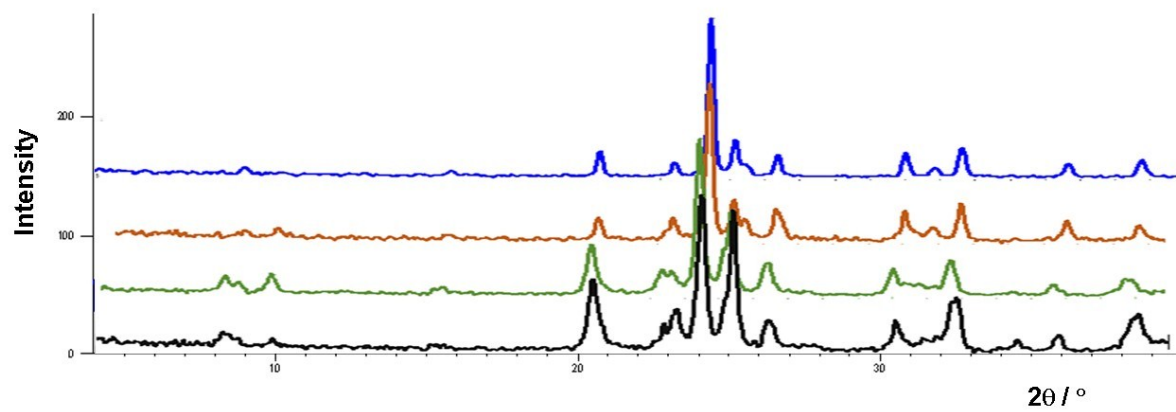


Figure S19 IR spectrum of pink mixture of  $\text{CoMoO}_n$  oxides (after termogravimetric measurement of 1)





**Figure S20** PXRD data of CoMoO<sub>4</sub> oxides obtained after combustion of compounds **1** (black), **1a** (green), **4** (brown) and **4c** (blue)