Aqueous solution as a *playground* of $\{MoO_4\}$, $\{Mo_4O_{12}\}$, $\{Mo_8O_{26}\}$, $\{Mo_8V_5O_{40}\}$ and $\{V_7Mo_2O_{27}\}$ species in the presence of carboxylic acids and $[Co(C_2O_4)(NH_3)_4]^+$ or $[Co(en)_3]^{3+}$ cations

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Table S1. Reactions of $Na_2MoO_4 \cdot 2H_2O$ and $[Co(C_2O_4)(NH_3)_4]NO_3 \cdot H_2O$ with 1.22, 2.44, 7.93, and 15.90 mmol of acetic acid.

Solution based methods	Precursors / Acid	Mo : Co : Acid / mmol	Products
Room temperature	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / CH_3COOH	5 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 12H_2O$ (1) $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 10H_2O$ (2)
		5 : 2 : 2.44	
		5 : 2 : 7.93	
		5 : 2 : 15.90	
Reflux	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / CH_3COOH	5 : 2 : 1.22 5 : 2 : 2.44	$[Co(C_2O_4)(NH_{3)4}]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n\cdot 6nH_2O$ (3)
		5 : 2 : 7.93	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 12H_2O$ (1) $[Co(C_2O_4)(NH_{3)4}]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n\cdot 6nH_2O$ (3)
		5 : 2 : 15.90	$[Co(C_2O_4)(NH_3)_4]_8[\beta\text{-}Mo_8O_{26}(H_2O)_2][\gamma\text{-}Mo_8O_{26}]\cdot 12H_2O$ (4) $[Co(C_2O_4)(NH_3)_4]_8[\gamma\text{-}Mo_8O_{26}(H_2O)_2]\cdot 6H_2O$ (5)
Solvothermal at 110 °C	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / CH_3COOH	5 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 12H_2O$ (1) $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 10H_2O$ (2)
		5 : 2 : 2.44	
		5 : 2 : 7.93	
		5 : 2 : 15.90	

Table S2. Reactions of $Na_2MoO_4{\cdot}2H_2O$ and $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ with 1.22, 2.44, 7.93, and 15.90 mmol of succinic acid.

Solution based methods	Precursors / Acid	Mo : Co : Acid / mmol	Products
Room temperature	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n{\cdot}6nH_2O$ (3)
		5 : 2 : 2.44	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}12H_2O$ (1)
		5 : 2 : 7.93 5 : 2 : 15.90	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}4H_2O{\cdot}C_4H_6O_4$ (6)
Reflux	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n{\cdot}6nH_2O$ (3)
		5 : 2 : 2.44	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}12H_2O$ (1), $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\ 4H_2O{\cdot}C_4H_6O_4$ (6) $[Co(C_2O_4)(NH_3)_4]_4[\gamma\text{-}Mo_8O_{26}(H_2O)_2]{\cdot}12H_2O$ (7) $[Co(C_2O_4)(NH_3)_4]_{2n}[Mo_4O_{12}(C_4H_4O_4)]_n{\cdot}3nH_2O$ (8)
		5 : 2 : 7.93 5 : 2 : 15.90	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}4H_2O{\cdot}C_4H_6O_4$ (6)
Solvothermal at 110 °C	Na_2MoO_4 / $[Co(C_2O_4)(NH_3)_4]NO_3$ / $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n{\cdot}6nH_2O$ (3)
		5 : 2 : 2.44	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}4H_2O{\cdot}C_4H_6O_4$ (6)
		5 : 2 : 7.93 5 : 2 : 15.90	$[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]{\cdot}4H_2O{\cdot}C_4H_6O_4$ (6) $[Co(C_2O_4)(NH_3)_4]_{4n}[\gamma\text{-}Mo_8O_{26}]_2{\cdot}9nH_2O$ (9)

Table S3. Reactions of $Na_2MoO_4 \cdot 2H_2O$ and $[Co(CO_3)(NH_3)_4](NO_3) \cdot H_2O$ with 1.22, 2.44, 7.93, and 15.90 mmol of acetic or succinic acid.

Solution based methods	Precursors / Acid	Mo : Co : Acid / mmol	Products
Room temperature	Na_2MoO_4 / $[Co(CO_3)(NH_3)_4]^+$ / CH_3COOH or $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	$[Mo_5Co_2O_{17}(HCO_3)(H_4C_4O_4H)(NH_3)_7] \cdot 5H_2O$ (10) $[Mo_5Co_2O_{18}(NH_3)_7] \cdot 5H_2O$ (11)
		5 : 2 : 2.44	
		5 : 2 : 7.93	
		5 : 2 : 15.90	
Reflux	Na_2MoO_4 / $[Co(CO_3)(NH_3)_4]^+$ / CH_3COOH or $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	unindentified black-brown precipitate
		5 : 2 : 2.44	
		5 : 2 : 7.93	$[Mo_5Co_2O_{17}(HCO_3)(H_4C_4O_4H)(NH_3)_7] \cdot 5H_2O$ (10) $[Mo_5Co_2O_{18}(NH_3)_7] \cdot 5H_2O$ (11)
		5 : 2 : 15.90	
Solvothermal at 110 °C	Na_2MoO_4 / $[Co(CO_3)(NH_3)_4]NO_3$ / CH_3COOH or $HOOCCH_2CH_2COOH$	5 : 2 : 1.22	unidentified black-brown precipitate
		5 : 2 : 2.44	
		5 : 2 : 7.93	$[Mo_5Co_2O_{17}(HCO_3)(H_4C_4O_4H)(NH_3)_7] \cdot 5H_2O$ (10) $[Mo_5Co_2O_{18}(NH_3)_7] \cdot 5H_2O$ (11)
		5 : 2 : 15.90	

Table S4. Reactions of $Na_2MoO_4 \cdot 2H_2O$, NH_4VO_3 and $[Co(C_2O_4)(NH_3)_4](NO_3) \cdot H_2O$ or $[Co(CO_3)(NH_3)_4](NO_3) \cdot H_2O$ with 1.22, 2.44, 7.93, and 15.90 mmol of succinic acid.

Solution based methods	Precursors / Acid	Mo : Co : V : Acid / mmol	Products
Room temperature / Reflux / Solvothermal at 110 °C / accelerated milling	Na_2MoO_4 / NH_4VO_3 $[Co(C_2O_4)(NH_3)_4]^+$ / CH_3COOH	5 : 2 : 2 : 1.22	$[Co(C_2O_4)(NH_3)_4]_2[H_2Mo_8V_5O_{40}Na_2(H_2O)_8] \cdot 5.5H_2O$(12)
		5 : 2 : 2 : 2.44	
		5 : 2 : 2 : 7.93	
		5 : 2 : 2 : 15.90	
Room temperature / Reflux / Solvothermal at 110 °C	Na_2MoO_4 / NH_4VO_3 $[Co(C_2O_4)(NH_3)_4]^+$ / $HOOCCH_2CH_2COOH$	5 : 2 : 2 : 1.22	heterogenous solid mixture
		5 : 2 : 2 : 2.44	
		5 : 2 : 2 : 7.93	
		5 : 2 : 2 : 15.90	
Room temperature / Reflux / Solvothermal at 110 °C	Na_2MoO_4 / NH_4VO_3 $[Co(CO_3)(NH_3)_4]^+$ / $HOOCCH_2CH_2COOH$	5 : 2 : 2 : 1.22	heterogenous solid mixture
		5 : 2 : 2 : 2.44	
		5 : 2 : 2 : 7.93	
		5 : 2 : 2 : 15.90	

Table S5. Reactions of $Na_2MoO_4{\cdot}2H_2O$, NH_4VO_3 and $[Co(en)_3]Cl_3$ or $[Co(CO_3)(NH_3)_4](NO_3){\cdot}H_2O$ with 1.22, 2.44, 7.93, and 15.90 mmol of succinic acid.

Solution based methods	Precursors / Acid	Mo : Co : Acid / mmol	Products
Room temperature / Reflux / Solvothermal at 110 °C	Na_2MoO_4 / NH_4VO_3 $[Co(en)_3]^{3+}$ / CH_3COOH or $HOOCCH_2CH_2COOH$	5 : 2 : 2: 1.22	heterogenous solid mixture
		5 : 2 : 2: 2.44	
		5 : 2 : 2: 7.93	
		5 : 2 : 2: 15.90	
Accelerated ageing	Na_2MoO_4 / NH_4VO_3 $[Co(en)_3]^{3+}$ / CH_3COOH or $HOOCCH_2CH_2COOH$ or without acid	5 : 2 : 2: 1.22	$Na_3[Co(en)_3][HV_7Mo_2O_{27}]{\cdot}18H_2O$ (13).
		5 : 2 : 2: 2.44	
		5 : 2 : 2: 7.93	
		5 : 2 : 2: 15.90	

Table S6. TG data of compounds **1-4**, **6-8**, **10-12**

	1st	2nd	3rd
1	9.15 %	18.56 %	6.28 %
	36-146 °C	146-316 °C	316-361 °C
2	8.46 %	19.23 %	7.09 %
	46-155 °C	155-316 °C	316-398 °C
3	5.22 %	19.49 %	5.88 %
	37-166 °C	166-287 °C	287-353 °C
4	22.86 %	12.12 %	10.93 %
	126-206 °C	206-297 °C	297-434 °C
6	24.34 %	10.98 %	4.23 %
	36-103 °C	103-331 °C	331-499 °C
7	23.34 %	10.78 %	
	33-291 °C	291-383 °C	
8	4.95 %	23.71 %	11.17 %
	39-100 °C	120-300 °C	320-385 °C
10	8.11 %	21.19 %	9.02 %
	28-155 °C	155-298 °C	298-395 °C
11	9.14 %	10.58 %	1.64 %
	32-154 °C	154-298 °C	298-365 °C
12	6.89 %	24.16 °C	3.52 %
	40-282 °C	282-342 °C	342-389 °C

*Mass of compounds **5**, **9** and **13** was insufficient for thermogravimetric analysis

Table S7. IR data for compounds **1-13**

	ν_s (M=O_t) + ν_a (Mo=O_t) M = Mo or/ and V	ν_s (M–O–M) + ν_a(M–O–M) M = Mo or/ and V	ν(Mo–O in Mo–O–Mo) M = Mo or/ and V	ν_s(N-H) + ν_s(O-H)	δ_s(N-H)	ν_s(C-O)	ν_s (C-O) + ν(C-C)
$Na_2MoO_4 \cdot 2H_2O$	953	797, 741	598				
$[Co(C_2O_4)(NH_3)_4]NO_3 \cdot H_2O$				3180, 3269, 3492	1304, 1278		1632, 1417, 1364
$[Co(CO_3)(NH_3)_4]NO_3 \cdot H_2O$				3297	1382, 1281	1612	
$[Co(en)_3]Cl_3$							
Succinic acid						1719, 1723	1575, 1566, 1550, 1398,
1	956, 900	800, 762	536, 481	3297-2927	1311, 1222	1705, 1668	1381, 1318
2	955, 935	809, 788	540, 488	3498, 3281	1345, 1239	1734, 1700	1402, 1346
3	944, 935	778, 765	525, 483	3493 - 3185	1345, 1198	1669,1654	1430, 1322
4	935, 912	802, 777	540, 478	3387, 3289	1334, 1190	1672, 1666	1423, 1311
5	980, 841	800, 756	555, 467	3100-2890	1300, 1298	1700, 1687	1513, 1470
6	977, 908	810, 798	567, 544	3308, 3198	1309, 1234	1718, 1744	1560, 1499, 1359
7	954, 902	796,765	535, 474	3390, 3076	1299, 1198	1704, 1680	1393, 1326, 1249
8	976, 891	786, 770	555, 467	3100-2890	1300, 1298	1700, 1687	1513, 1470
9	993, 945, 899	756, 723	525,483	3493 - 3185	1320, 1222	1723, 1698	1500, 1455
10	882, 822	832, 722	538, 474	2990-2879	1329, 1220	1699, 1685	1307, 1289
11	884, 841	836, 831	575, 484	3278	1278, 1234		
12	938, 874	825, 803	687, 648	3125	1311, 1264	1698, 1672	1409
13	945, 853	824, 769	665, 627	3230, 3125	1324, 1222		

Table S8. Analytical data of compounds **1-4**, **6-8**, **10-13**

(Compound) molecular formula	Analytical data													
	$w_{calcd.}$ (%)							$w_{exp.}$ (%)						
	Co	Mo	Na	V	C	H	N	Co	Mo	Na	V	C	H	N
(**1**) $C_8H_{72}Co_4Mo_8N_{16}O_{54}$	10.43	33.96			4.25	3.21	9.92	10.36	33.73			4.17	2.72	9.88
(**2**) $C_8H_{68}Co_4Mo_8N_{16}O_{52}$	10.60	34.52			4.32	3.08	10.08	10.45	34.23			4.18	3.01	9.89
(**3**) $C_8H_{68}Co_4Mo_8N_{16}Na_2O_{55}$	10.17	33.12	1.98		4.14	2.96	9.67	10.22	33.07	1.89		4.03	2.87	9.54
(**4**) $C_{16}H_{124}Co_8Mo_{16}N_{32}O_{98}$	10.86	35.37			4.43	2.88	10.59	11.02	35.97			4.41	2.79	10.39
(**6**) $C_{12}H_{62}Co_4Mo_8N_{16}O_{50}$	10.55	34.36			6.45	2.80	10.03	10.47	34.58			6.52	2.67	10.18
(**7**) $C_8H_{76}Co_4Mo_8N_{16}O_{56}$	10.27	33.43			4.18	3.34	9.76	10.20	33.14			4.15	3.23	9.58
(**8**) $C_8H_{34}Co_2Mo_4N_8O_{27}$	10.02	32.64			8.17	2.91	9.53	10.12	32.44			8.05	2.81	9.38
(**10**) $C_5H_{37}Co_2Mo_5N_7O_{29}$	9.38	38.16			4.78	2.97	7.80	9.22	38.20			4.55	2.81	7.88
(**11**) $H_{31}Co_2Mo_5N_7O_{23}$	10.76	43.81				2.85	8.96	10.57	43.87				2.73	8.81
(**12**) $C_6H_{57}Co_3Mo_8N_{12}Na_2O_{62.5}V_5$	6.98	30.28	1.81	10.08	2.84	2.27	6.63	6.88	30.09	1.89	10.10	2.83	2.22	6.75
(**13**) $C_6H_{60}CoMo_2N_6Na_3O_{45}V_7$	3.65	11.90	4.28	22.11	4.47	3.75	5.21	3.33	11.45	4.18	22.05	4.40	3.62	5.11

*Mass of compounds **5** and **9** was insufficient for elemental analysis

	4	**5**	**6**
Formula	$C_{16}H_{124}Co_8Mo_{16}N_{32}O_{98}$	$C_8H_{64}Co_4Mo_8N_{16}O_{50}$	$C_{12}H_{62}Co_4Mo_8N_{16}O_{50}$
M_r	4339.94	2187.99	2234.01
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*–1	$P2_1/c$	*P*–1
a/Å	11.7837(3)	9.99760(10)	8.4824(2)

Table S9. Crystallographic data for compounds **1-9**, and **11;** for **12** and **13** are given data for unit cell

	1	**2**	**3**
Formula	$C_8H_{72}Co_4Mo_8N_{16}O_{54}$	$C_8H_{68}Co_4Mo_8N_{16}O_{52}$	$C_8H_{68}Co_4Mo_8N_{16}Na_2O_{55}$
M_r	2260.05	2224.02	2318.16
Crystal system	triclinic	triclinic	triclinic
Space group	*P*–1	*P*–1	*P*–1
a/Å	8.51130(10)	8.51020(10)	9.4465(3)
b/Å	13.7625(2)	13.7353(2)	10.7769(3)
c/Å	13.9561(2)	13.95510(10)	15.2702(4)
α/°	93.0160(10)	95.0810(10)	106.856(2)
β/°	107.3180(10)	107.1720(10)	93.852(2)
γ/°	103.2230(10)	102.5790(10)	96.451(2)
V/Å^3	1506.42(4)	1500.51(3)	1470.20(7)
Z	1	1	1
Reflections unique	45721	38779	18029
Reflections observed [$I>=2\sigma(I)$]	6014	5998	5951
Parameters	427	424	443
R_1(obs)	0.0613	0.0326	0.0355
wR_2(obs)	0.1710	0.0857	0.0995
GooF	1.067	1.044	1.073

b/Å	12.5652(2)	20.6814(3)	13.3673(2)
c/Å	20.6823(4)	13.4605(2)	14.0305(2)
α/°	91.8640(10)	90	84.2600(10)
β/°	101.574(2)	95.0550(10)	73.105(2)
γ/°	99.735(2)	90	71.519(2)
V/Å^3	2949.84(11)	2772.33(6)	1443.65(5)
Z	1	2	1
Reflections unique	43082	21943	34979
Reflections observed [$I>=2\sigma(I)$]	12083	5636	5921
Parameters	765	395	422
R_1(obs)	0.0595	0.0553	0.0316.
wR_2(obs)	0.1742	0.1561	0.0902
GooF	1.038	1.057	1.075

	7	**8**	**9**
Formula	$C_8H_{76}Co_4Mo_8N_{16}O_{56}$	$C_8H_{34}Co_2Mo_4N_8O_{27}$	$C_8H_{66}Co_4Mo_8N_{16}O_{51}$
M_r	2296.01	1176.05	2206.00
Crystal system	triclinic	monoclinic	triclinic

Space group	*P*–1	*I*2/*a*	*P*–1
a/Å	11.5181(3)	27.0622(3)	7.9160(2)
b/Å	12.4156(3)	7.36240(10)	12.5833(3)
c/Å	12.6190(2)	33.9652(4)	15.4115(3)
α/°	89.522(2)	90	108.216(2)
β/°	65.036(2)	92.8440(10)	94.540(2)
γ/°	70.301(2)	90	103.045(2)
V/Å^3	1521.15(7)	6758.98(14)	1401.85(6)
Z	1	8	1
Reflections unique	18953	89140	44530
Reflections observed [$I>=2\sigma(I)$]	6151	7091	5969
Parameters	454	459	406
R_1(obs)	0.0414	0.0523	0.0555
wR_2(obs)	0.1113	0.1464	0.1546
GooF	1.032	1.050	1.116

	11	**12**	**13**
Formula	$Co_2H_{31}Mo_5N_7O_{23}$	$C_6H_{57}Co_3Mo_8N_{12}Na_2O_{62.5}V_5$	$C_6H_{60}CoMo_2N_6Na_3O_{45}V_7$
M_r	1094.83	2542.63	1612.95
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	P-1
a/Å	9.3392(4)	13.2251(3)	12.1225(2)
b/Å	28.0114(9)	15.9667(3)	13.4878(2)
c/Å	9.6973(4)	16.2567(5)	14.4274(2)
α/°	90	86.364(2)	92.9430(10)
β/°	102.988(4)	81.442(2)	97.9090(10)
γ/°	90	88.936(2)	91.0120(10)
V/Å^3	2471.95(17)	3387.59(15)	2332.71(6)
Z	4	2	2
Reflections unique	26766		
Reflections observed [$I>=2\sigma(I)$]	5035		
Parameters	351		
R_1(obs)	0.0623		
wR_2(obs)	0.1458		
GooF	1.078		

Table S10. Hydrogen bonds in the compound **4**

Eleven hydrogen bonds formed between β-octamolybdate and $[Co(C_2O_4)(NH_3)_4]^+$ in 4	
N1–H1A···O6[a]	3.056(11) Å
N1–H1B···O7[b]	3.087(11) Å
N4–H4A···O10[c]	2.988(11) Å
N5–H5A···O2[b]	2.952(10) Å
N5–H5C···O9[b]	2.873(10) Å
N10–H10A···O1[d]	3.204(11) Å
N15–H15B···O8[e]	3.062(10) Å
N15–H15A···O12[e]	3.011(11) Å
N15–H15C···O7[d]	3.133(11) Å
N16–H16A···O4[c]	3.033(10) Å
N16–H16A···O12[e]	3.320(11) Å

a = -*x*,2-*y*,-*z*; b = *x*,*y*,*z*; c = -1+*x*,*y*,*z*; d = *x*,-1+*y*,*z*; e = -*x*,1-*y*,-*z*;

Eleven hydrogen bonds formed between γ-octamolybdate and $[Co(C_2O_4)(NH_3)_4]^+$ in 4	
N2–H2C···O26[a]	3.003(12) Å
N6–H6C···O17[b]	3.032(11) Å
N7–H7B···O23[a]	3.181(11) Å
N7–H7C···O23[b]	3.099(11) Å
N7–H7C···O20[c]	3.260(10) Å
N8–H8C···O23[b]	3.223(10) Å
N8–H8C···O23[b]	3.069(11) Å
N11–H11B···O19[a]	3.380(10) Å
N11–H11C···O24[a]	3.089(10) Å
N12–H12C···O15[d]	3.185(10) Å
N13–H13B···O15[d]	2.831(11) Å

a = 1-*x*,1-*y*,1-*z*; b = *x*,1+*y*,*z*; c = 1-*x*,2-*y*,1-*z*; d = *x*,*y*,*z*

Table S11. Hydrogen bonds in the compound **8**

Eleven hydrogen bonds formed between γ-octamolybdate and $[Co(C_2O_4)(NH_3)_4]^+$ in 8	
N1–H1C···O2[a]	3.002(9) Å
N1–H1A···O8[a]	3.089(9) Å
N3–H3B···O16[b]	2.992(9) Å
N4–H4C···O16[b]	3.004(9) Å
N5–H5B···O2[c]	3.129(7) Å
N5–H5B···O4[c]	3.033(7) Å
N6–H6C···O2[c]	3.139(7) Å
N7–H7A···O14[b]	3.041(7) Å
N7–H7B···O10[d]	3.184(7) Å
N7–H7C···O4[c]	2.993(7) Å
N8–H8A···O16[b]	3.319(7) Å

a = *x*,1+*y*,*z*; b =-1/2+*x*,1-*y*,*z*; c = 1-*x*,1/2+*y*,3/2-*z*; d = 1-*x*,3/2+*y*,3/2-*z*

Table S12. Hydrogen bonds in the compound **9**

Eleven hydrogen bonds formed between $\{Mo_8O_{24}\}$ and $[Co(C_2O_4)(NH_3)_4]^+$ in 9	
N1–H1A···O12[a]	3.156(9) Å
N1–H1C···O9[b]	3.079(10) Å
N2–H2A···O2[c]	2.857(10) Å
N2–H2B···O7[b]	2.983(9) Å
N3–H3A···O5[c]	3.075(9) Å
N5–H5B···O9[d]	3.277(10) Å
N6–H6C···O13[e]	3.163(10) Å
N7–H7A···O9[d]	2.995(11) Å
N7–H7B···O13[e]	3.064(11) Å
N8–H8A···O4[f]	2.977(10) Å
N8–H8B···O2[g]	3.328(10) Å

a = 2-*x*,1-*y*,-*z*; b = *x*,*y*,*z*; c = -1+*x*,*y*,*z*; d = 3-*x*,1-*y*,1-*z*; e = -*x*,*y*,1+*z*; f = 3-*x*,2-*y*,1-*z*; g = 4-*x*,2-*y*,1-*z*

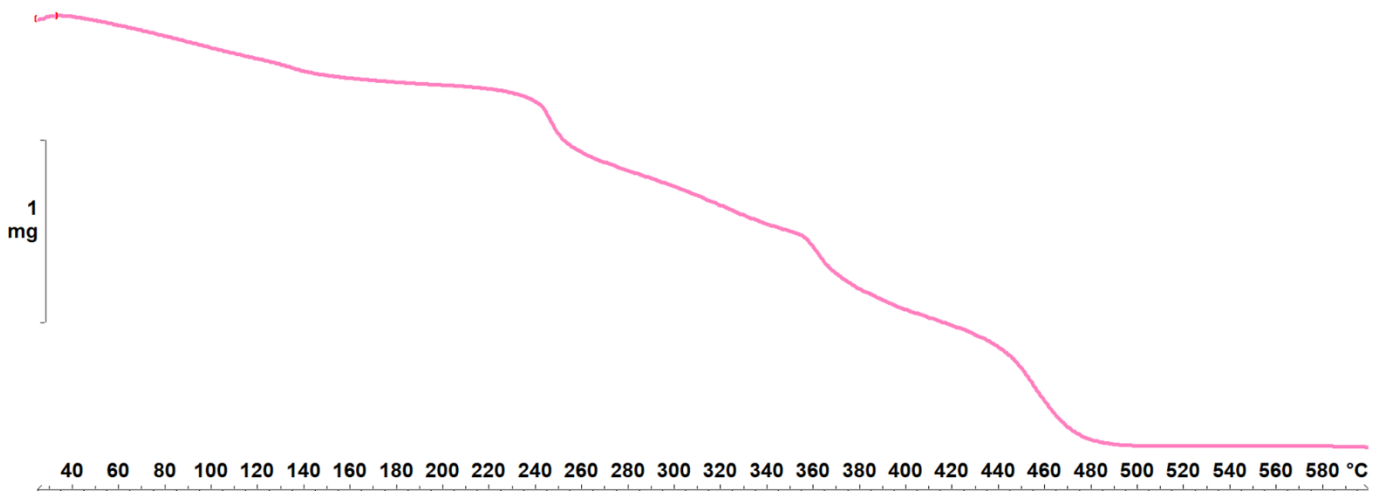


Figure S1. TG curve of $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 10H_2O$ (**1**)

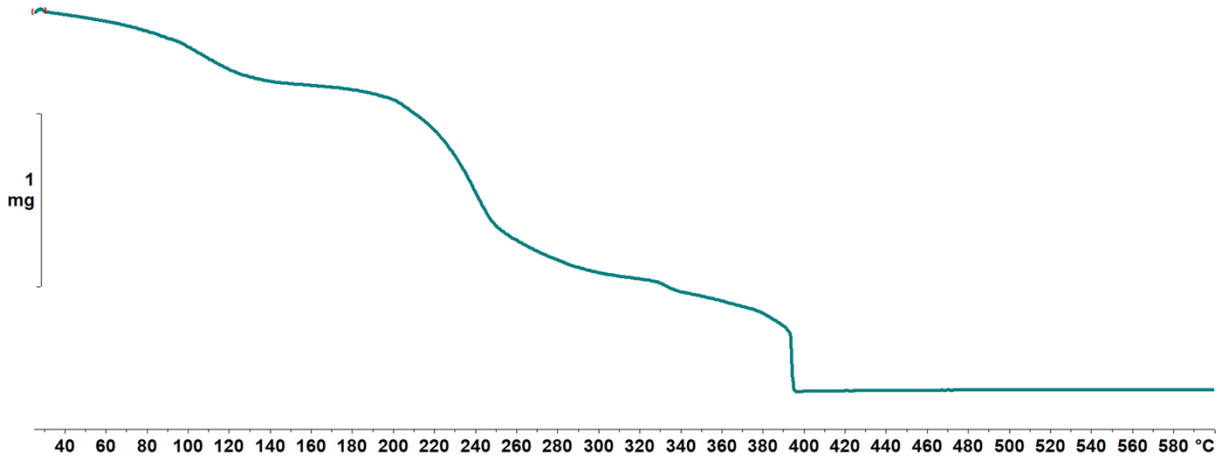


Figure S2. TG curve of $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}]\cdot 12H_2O$ (**2**)

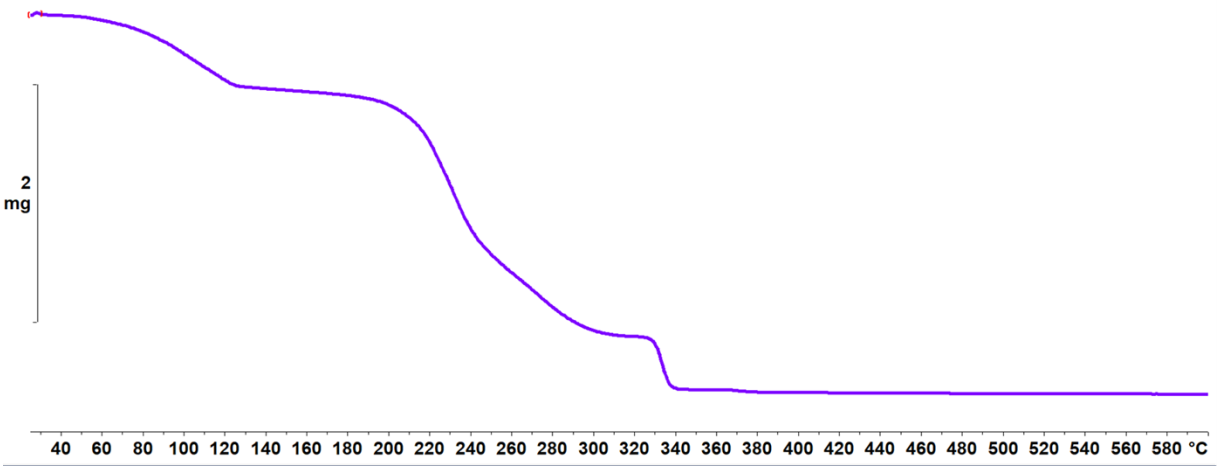


Figure S3. TG curve of $[Co(C_2O_4)(NH_3)_4]_{4n}[Na_2Mo_8O_{29}(H_2O)_4]_n \cdot 6nH_2O$ (**3**)

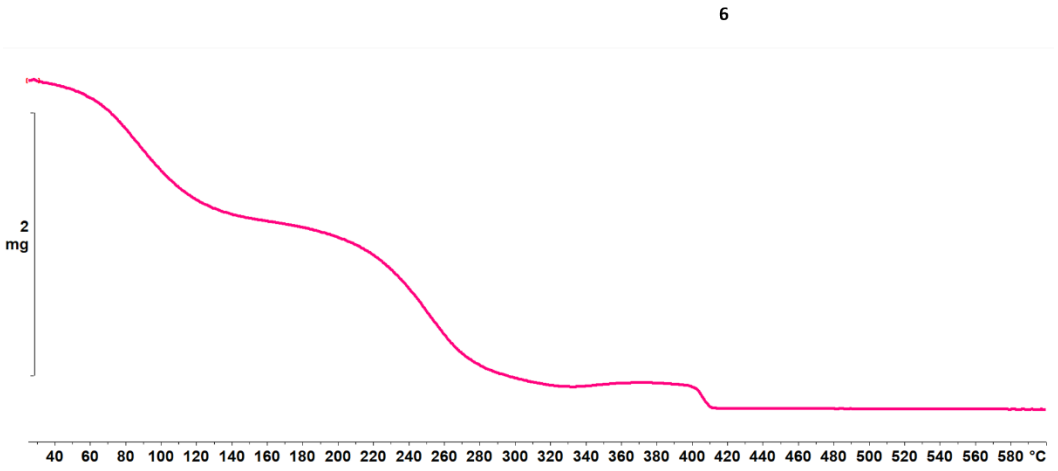


Figure S4. TG curve of $[Co(C_2O_4)(NH_3)_4]_4[\beta\text{-}Mo_8O_{26}] \cdot 4H_2O \cdot C_4H_6O_4$ (**6**)

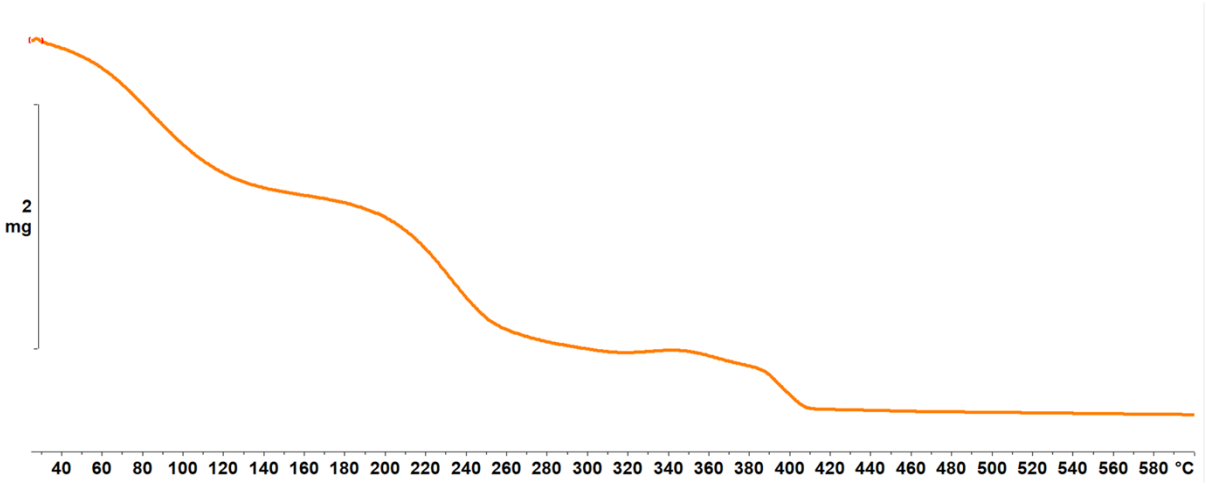


Figure S5. TG curve of $[Co(C_2O_4)(NH_3)_4]_{2n}[Mo_4O_{12}(H_4C_4O_4)]_n \cdot 3nH_2O$ (**8**)

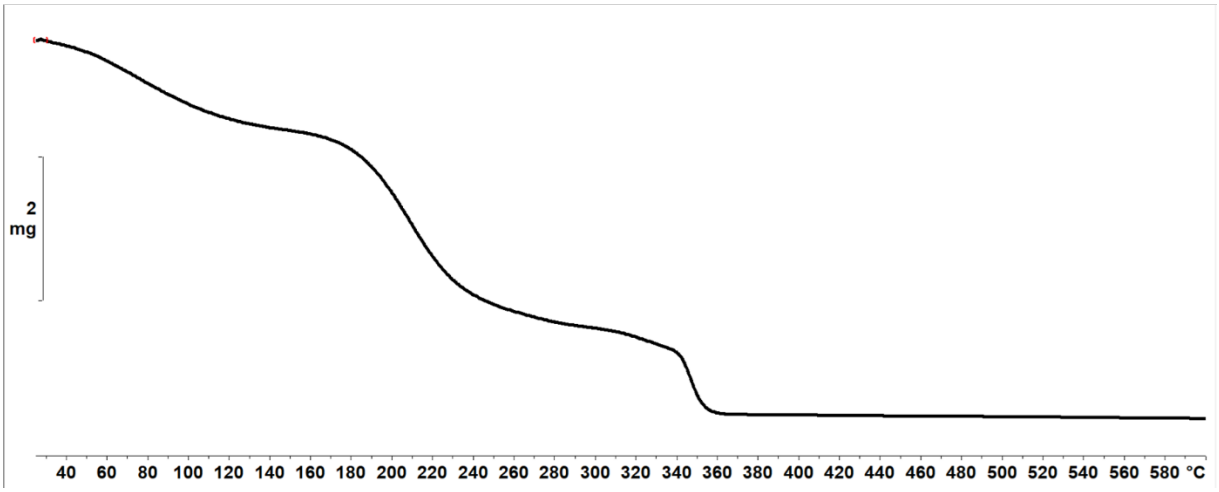


Figure S6. TG curve of $[Mo_5Co_2O_{17}(HCO_3)(H_4C_4O_4H)(NH_3)_7] \cdot 5H_2O$ (**10**)

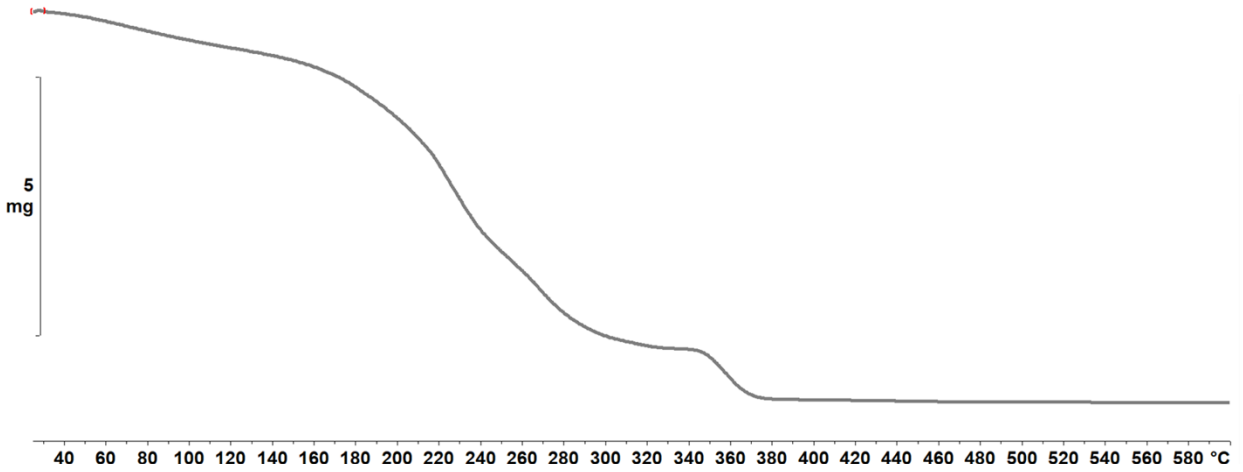


Figure S7: TG curve of $[Mo_7Co_2O_{18}(NH_3)_7]\cdot 5H_2O$ (**11**)

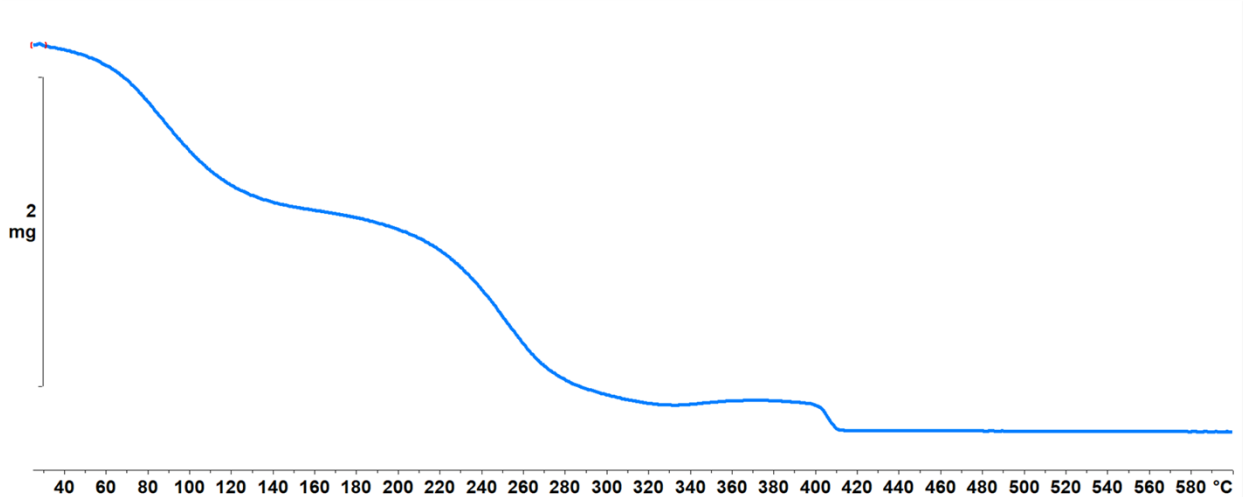


Figure S8. TG curve of $[Co(C_2O_4)(NH_3)_4]_2[H_2Mo_8V_5O_{40}Na_2(H_2O)_8]\cdot xH_2O$ (**12**)

The sample for the NMR experiments was prepared by dissolving it in NaOH solution in D_2O. The resulting dark brown Co_2O_3 oxide precipitated and the remaining solution was taken for the ^{13}C NMR measurements.

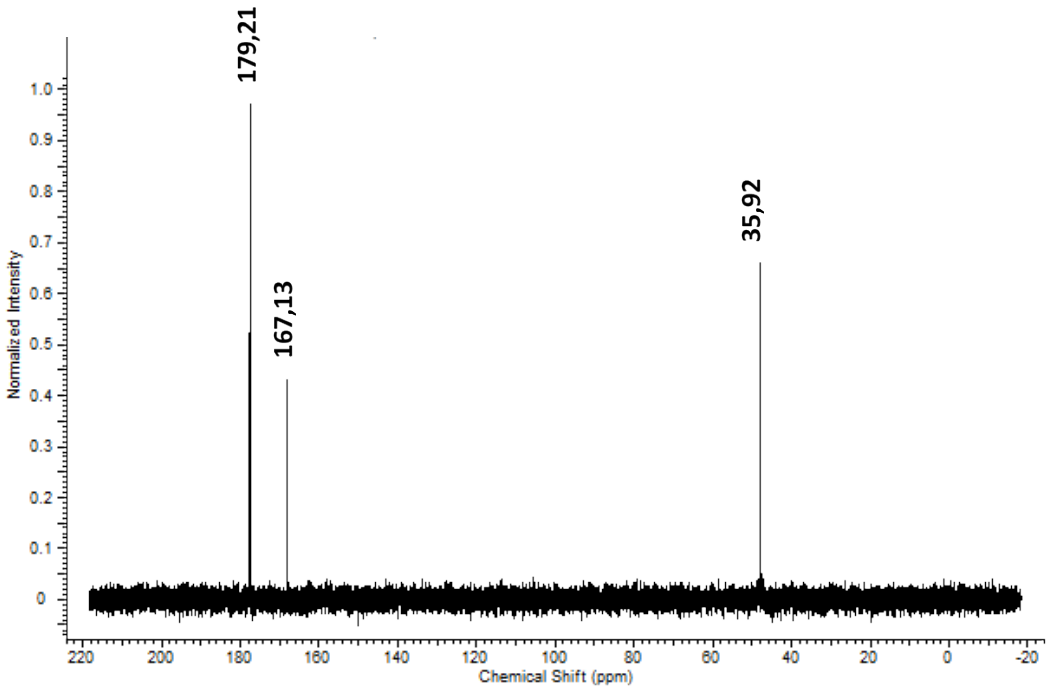


Figure S9. ^{13}C NMR spectrum of $[Mo_5Co_2O_{17}(HCO_3)(H_4C_4O_4H)(NH_3)_7]\cdot 5H_2O$ (**10**)

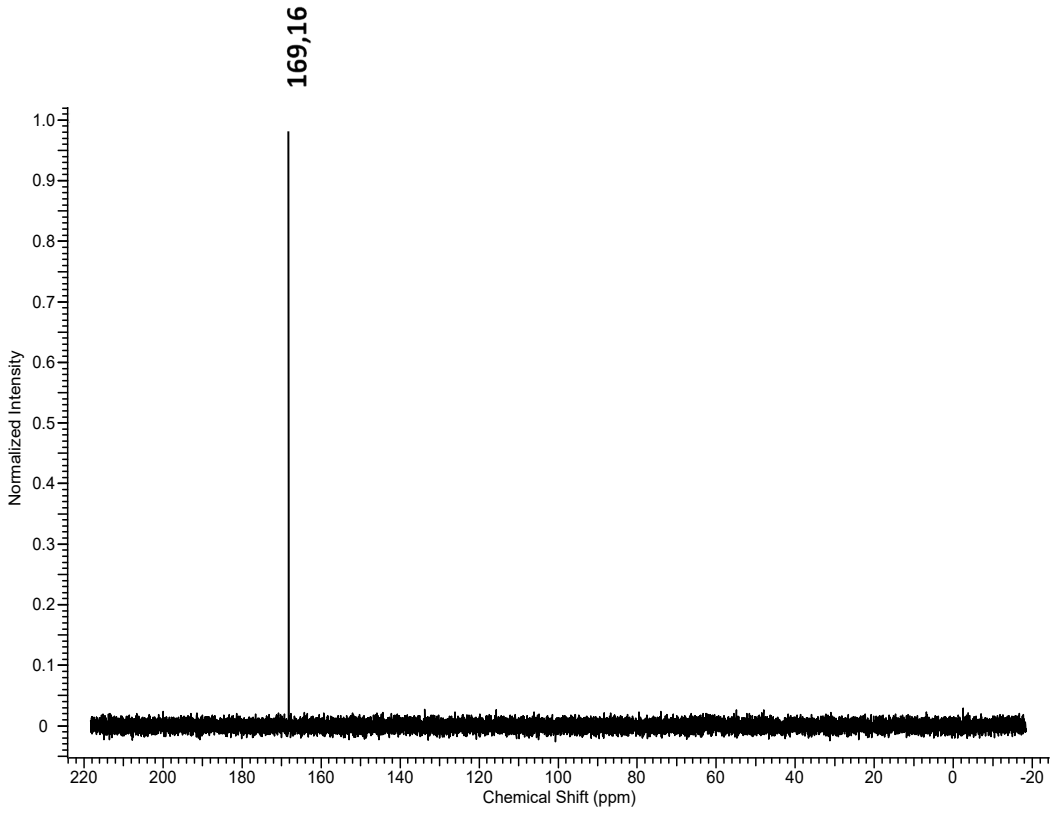


Figure S10. Example of ^{13}C NMR spectra of $[Mo_5Co_2O_{18}(NH_3)_7]\cdot 5H_2O$ (**11**) obtained in reactions with succinic acid

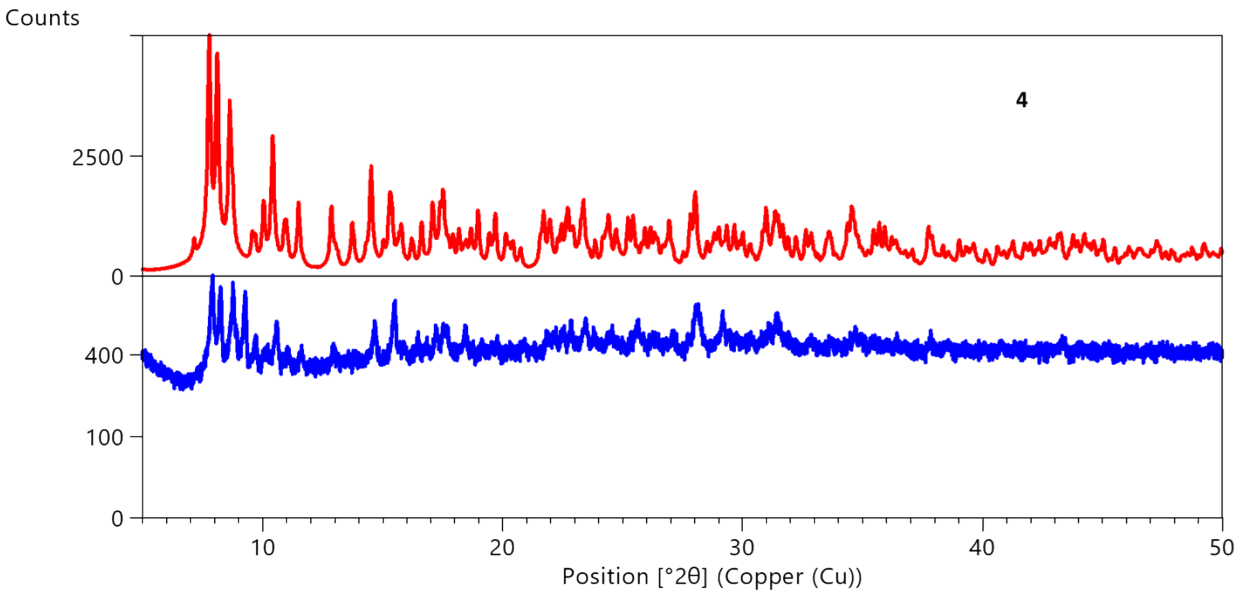


Figure S11. PXRD patterns of compound **4** (red-simulated pattern, blue-experimental pattern)

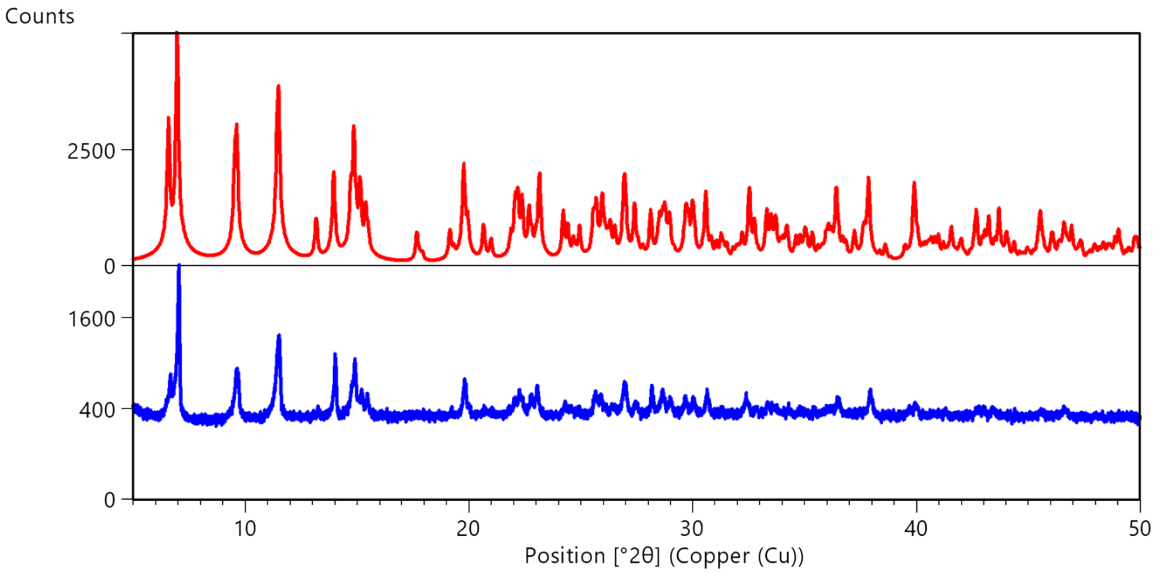


Figure S12. PXRD patterns of compound **6** (red-simulated pattern, blue-experimental pattern)

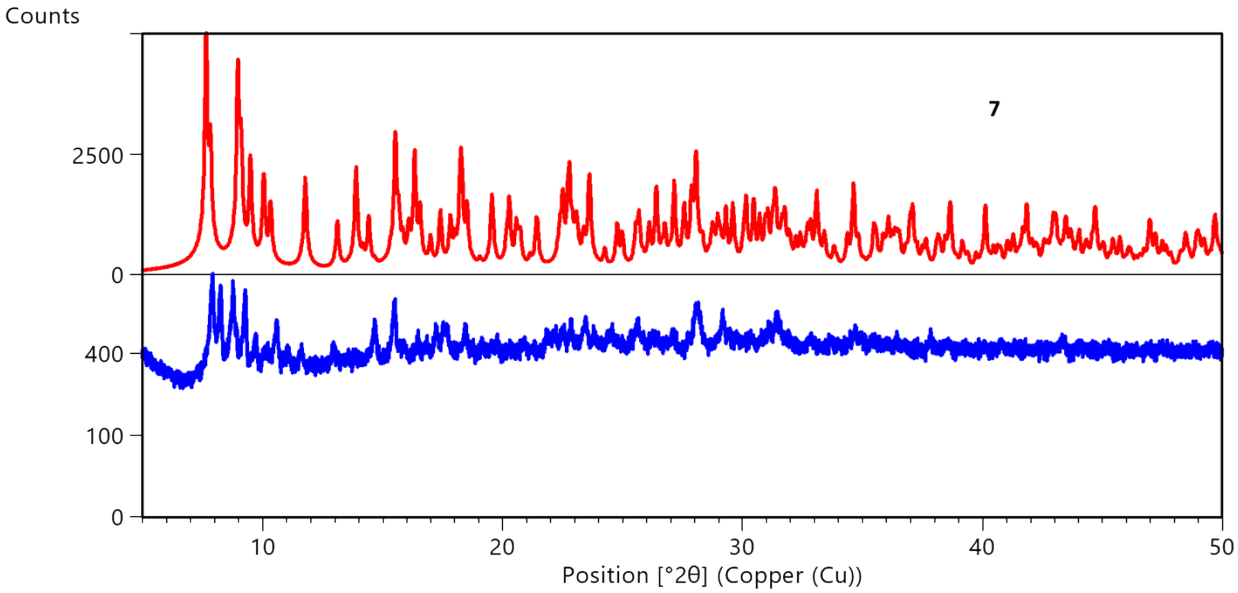


Figure S13. PXRD patterns of compound **7** (red-simulated pattern, blue-experimental pattern)

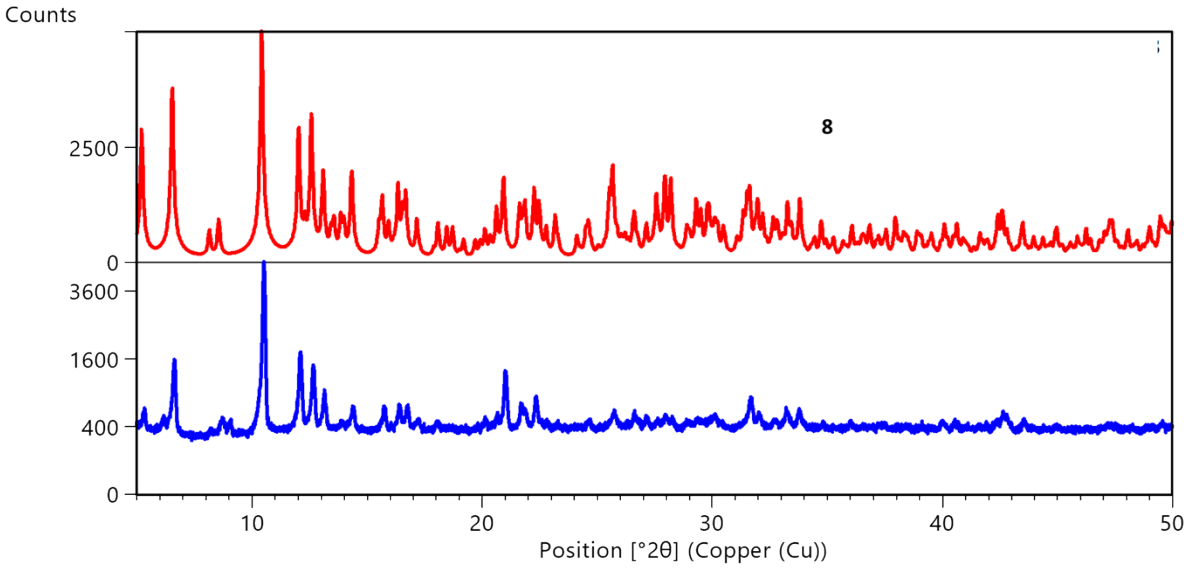
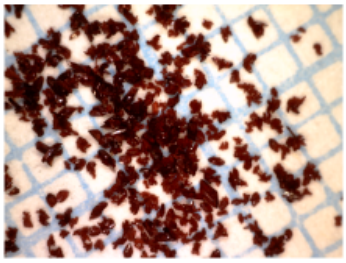
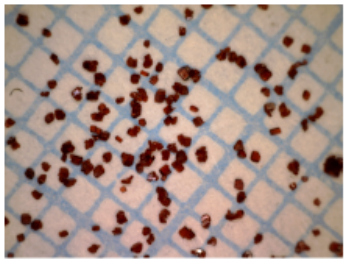


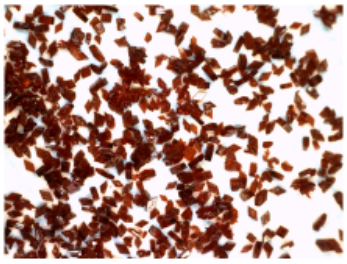
Figure S14. PXRD patterns of compound **8** (red-simulated pattern, blue-experimental pattern)



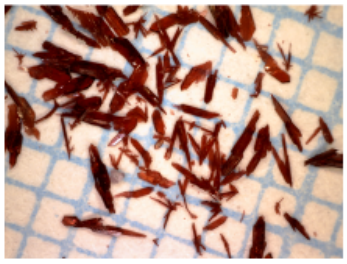
3 – pink plates



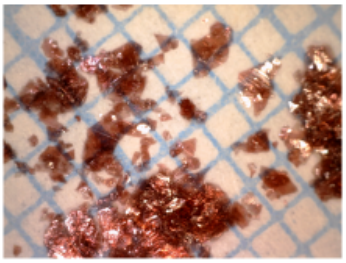
5 – pink prisms



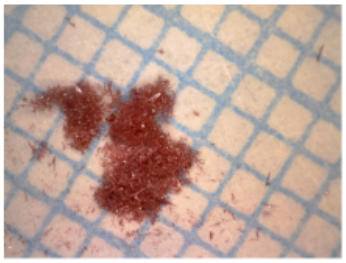
4 – pink prisms



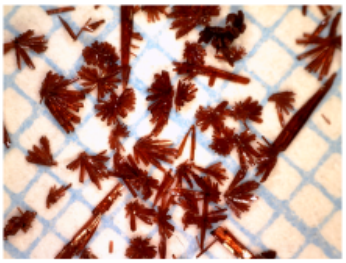
6 – pink prisms



7 – light pink plates



8 – light pink needles



9 – pink rods

Figure S15. Crystals of compounds **3-9**