Electronic Supplementary Material (ESI) for New Journal of Chemistry.

The role of mono- and dicarboxylic acids in the building of oxomolybdates containing $\{MoO_4\}$, $\{Mo_2O_5\}$, $\{Mo_2O_6\}$, $\{Mo_3O_8\}$, $\{Mo_5O_{17}\}$, $\{Mo_5O_{18}\}$, $\{Mo_8O_{26}\}$, and $\{SiMo_{12}O_{40}\}$ units

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Table S1: 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 15.9 mmol of oxalic and malonic acids

Precursors	HA / mol	pH	Method	Product	Yield /mg
$Na_2MoO_4\cdot 2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Oxalic acid	$1.22\cdot 10^{-3}$	2.0-2.5	R.T.	1	60
			110 °C	2	34
	$2.44\cdot 10^{-3}$	1.0-1.5	R.T.	4 and 5	70 and 15
			110 °C	4	65
$Na_2MoO_4\cdot 2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Oxalic acid	$7.93\cdot 10^{-3}$	0.7-0.9	R.T.	3	70
			110 °C		110
	$1.59\cdot 10^{-2}$	0.7-0.8	R.T.		79
			110 °C		112
$Na_2MoO_4\cdot 2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Malonic acid	$1.22\cdot 10^{-3}$	3.5-4.0	R.T.	6	89
			110 °C		16
	$2.44\cdot 10^{-3}$	About 2.5	R.T.		86
			110 °C		16
$Na_2MoO_4\cdot 2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Malonic acid	$7.93\cdot 10^{-3}$	0.7-0.9	R.T.		12
			110 °C		20
	$1.59\cdot 10^{-2}$	0.7-0.8	R.T.		47
			110 °C		62

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 15.9 mmol of oxalic aned malonic acids

Precursors	HA / mol	pH	Method	Product	Yield / mg
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ + Oxalic acid	$1.22{\cdot}10^{-3}$	2.0-2.5	R.T	1	78
			110 °C		54
	$2.44{\cdot}10^{-3}$	1.0-1.5	R.T.	3	110
			110 °C		114
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ Oxalic acid	$7.93{\cdot}10^{-3}$	0.9-1.0	R.T.	3	98
			110 °C		120
	$1.59{\cdot}10^{-2}$	0.8-0.9	R.T.		116
			110 °C		105
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ Malonic acid	$1.22{\cdot}10^{-3}$	Abot 3	R.T	8	42
			110 °C		70
	$2.44{\cdot}10^{-3}$	About 2.5	R.T.		53
			110 °C		57
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ Malonic acid	$7.93{\cdot}10^{-3}$	1.5-2.0	R.T.	8	30
			110 °C	8 and 9	45 and 16
	$1.59{\cdot}10^{-2}$	1.0-1.5	R.T.		56 and 10
			110 °C	9	75

Table S3: Reactions of $Na_2MoO_4{\cdot}2H_2O$ and $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ or and $[Co(CO_3)(NH_3)_4](NO_3){\cdot}H_2O$ with 1.22, 2.44, 7.93 and 15.9 mmol of formic acid

Precursors	HA / mol	pH	Method	Product	Yield / mg
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ Formic acid	$1.22{\cdot}10^{-3}$	4.0	R.T	8 and 10	92.5
			110 °C		90.7
	$2.44{\cdot}10^{-3}$	3.5	R.T.		87.3
			110 °C		88.6
$Na_2MoO_4{\cdot}2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3){\cdot}H_2O$ Formic acid	$7.93{\cdot}10^{-3}$	2.7	R.T.	8 and 10	104
			110 °C		85
	$1.59{\cdot}10^{-2}$	2.5	R.T.		104.4
			110 °C		88.5
$Na_2MoO_4{\cdot}2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3){\cdot}H_2O$ Formic acid	$1.22{\cdot}10^{-3}$	4.2 - 4.9	R.T.	7	92
			110 °C	Brown powder	15
	$2.44{\cdot}10^{-3}$	3.5 - 3.7	R.T.	7	95.8
			110 °C		42.6
$Na_2MoO_4{\cdot}2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3){\cdot}H_2O$ Formic acid	$7.93{\cdot}10^{-3}$	2.5 – 3.0	R.T.	7	87.9
			110 °C		63
	$1.59{\cdot}10^{-2}$	2.0 - 2.4 2.0 - 2.6	R.T.		78
			110 °C		58

Table S4: Reactions of $Na_2MoO_4\cdot2H_2O$ and $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ or and $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$with 1.22, 2.44, 7.93 and 15.9 mmol of acetic acid

Precursors	HA / mol	pH	Method	Product	Yield / mg
$Na_2MoO_4\cdot2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ Acetic acid	$1.22\cdot10^{-3}$	5.0 - 4.6	R.T	8	113
	$1.22\cdot10^{-3}$	4.5 - 5.0	110 °C		103
	$2.44\cdot10^{-3}$	4.0 - 3.5	R.T.		110
	$2.44\cdot10^{-3}$	4.0 - 4.5	110 °C		82
$Na_2MoO_4\cdot2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ Acetic acid	$7.93\cdot10^{-3}$	3.5 - 3.7	R.T.	8	101
	$7.93\cdot10^{-3}$		110 °C		90
	$1.59\cdot10^{-2}$	3.0 - 3.5	R.T.		105
	$1.59\cdot10^{-2}$		110 °C		92
$Na_2MoO_4\cdot2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Acetic acid	$1.22\cdot10^{-3}$	5.0 - 5.5	R.T.	7	93
	$1.22\cdot10^{-3}$		110 °C	Brown powder	14
	$2.44\cdot10^{-3}$	4.5 - 4.9	R.T.	7	85
	$2.44\cdot10^{-3}$		110 °C	Brown powder	25
$Na_2MoO_4\cdot2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Acetic acid	$7.93\cdot10^{-3}$	3.8	R.T.	7	94
	$7.93\cdot10^{-3}$	3.5 - 4.2	110 °C		18
	$1.59\cdot10^{-2}$	3.0 - 3.8	R.T.		80
	$1.59\cdot10^{-2}$		110 °C		16

Table S5: Reactions of $Na_2MoO_4\cdot2H_2O$ and $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ or and $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ with 1.22, 2.44, 7.93 and 15.9 mmol of propionic acid

Precursors	HA / mol	pH	Method	Product	Yield / mg
$Na_2MoO_4\cdot2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ Propionic acid	$1.22\cdot10^{-3}$	5.5	R.T	10 and 8	102 (mixture)
			110 °C		91 (mixture)
	$2.44\cdot10^{-3}$	4.5	R.T.		89 (mixture)
			110 °C		106 (mixture)
$Na_2MoO_4\cdot2H_2O$ $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ Propionic acid	$7.93\cdot10^{-3}$	3.8 - 4.0	R.T.	10 and 8	98 (mixture)
			110 °C		90 (mixture)
	$1.59\cdot10^{-2}$	3.5 - 3.6	R.T.		107 (mixture)
			110 °C		81.4
$Na_2MoO_4\cdot2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Propionic acid	$1.22\cdot10^{-3}$ $1.22\cdot10^{-3}$	5.5 - 5.5	R.T.	7	82
			110 °C	Brown powder	23
	$2.44\cdot10^{-3}$	4.8 – 5.0	R.T.	7	87
			110 °C	Brown powder	20
$Na_2MoO_4\cdot2H_2O$ $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ Propionic acid	$7.93\cdot10^{-3}$	4.0	R.T.	7	88
			110 °C		74
	$1.59\cdot10^{-2}$	3.5 - 4.0	R.T.		84
			110 °C		69

Procedures for the synthesis of compounds 1–5

Solution based method at room temperature.

General procedure: The aqueous solution (5 mL) of sodium molybdate and oxalic acid was added in aqueous solution (15 mL) of Co(III) complex salt. The resulting reaction mixture was allowed to stand at room temperature.

a*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 1.22 mmol* $C_2O_4^{2-}$ *: 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$ *or* $[Co(CO_3)(NH_3)_4]^+$*.*

The resulting, red solution had pH value around 2.5. After 45 days the red crystals of compound **1** were obtained; the product was collected by filtration, washed with a small amount of cold water and dried to constant weight in a desiccator. The isolated red plate-like crystals of **1** were suitable for single crystal diffraction experiments.

b*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 2.44 mmol* $C_2O_4^{2-}$ *: 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$ *or* $[Co(CO_3)(NH_3)_4]^+$*.*

In the reaction with $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$ the resulting red solution had pH around 1.5. After about 72 hours red crystals of **3** were obtained; the product was collected by filtration, washed with a small amount of cold water and dried to constant weight in a desiccator. The same product was obtained in the reactions with 7.93 or 15.90 mmol of oxalic acid, respectively.

In the reaction with $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ the resulting red solution had pH about 1.5. After about 48 hours red crystalline product of **4** was obtained. Two weeks after isolation of **4**, red crystals of **5** were obtained from the mother liquor; the both products were collected by filtration, washed with a small amount of cold water and dried to constant weight in a desiccator. The crystals of **4** and **5** were suitable for single crystal diffraction experiments.

c*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 7.93 or 15.90 mmol* $C_2O_4^{2-}$ *: 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$ *or* $[Co(CO_3)(NH_3)_4]^+$*.*

In all reactions with both Co(III) precursors red crystals of **3** suitable for single crystal diffraction experiments were obtained.

Hydrothermal synthesis at 110 °C.

b*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 2.44 mmol* $C_2O_4^{2-}$ *: 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$ *or* $[Co(CO_3)(NH_3)_4]^+$*.*

In the reaction with precursor $[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$, the resulting red solution had pH around 1.5. After 72 hours red crystals of **3** were obtained. The crystals were suitable for single crystal diffraction experiments.

In the reaction with precursor $[Co(CO_3)(NH_3)_4](NO_3)\cdot H_2O$ the resulting red solution had pH around 1.5. After 24 hours red crystals of **4**, suitable for single crystal diffraction experiments were obtained.

c*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 7.93 or 15.90 mmol* $C_2O_4^{2-}$ *: 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$ *or* $[Co(CO_3)(NH_3)_4]^+$*.*

The resulting reaction mixtures had pH between 1 and 1.5. In all reactions, the obtained red crystals of **3**, were suitable for single crystal diffraction experiments.

Procedures for the synthesis of compounds 6–10

Solution based method at room temperature.

General procedure: The aqueous solution (5 mL) of sodium molybdate and acid (malonic or formic or acetic or propionic) was added in aqueous solution (15 mL) of Co(III) complex salt. The resulting reaction mixture was allowed to stand at room temperature.

a*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 1.22 (or 2.44 or 7.93 or 15.90) mmol malonic acid : 0.203 mmol* $[Co(CO_3)(NH_3)_4]^+$*.*

Immediately after mixing the solutions, in all reaction mixtures violet powder of **6** was precipitated. The resulting reaction mixture had pH between 1 and 4. The violet product **6** was filtered off, washed with a small amount of cold water and dried to constant weight in a desiccator.

If the violet powder of **6** was allowed to stand in the mother liquor, after six months a small amount of violet crystals of **7** was obtained. The crystals were suitable for single crystal diffraction experiments.

b*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 1.22 mmol acid (formic or acetic or propionic acid) : 0.203 mmol* $[Co(CO_3)(NH_3)_4]^+$*.*

The violet crystalline product **7** was isolated in all reactions with formic, acetic and propionic acid, respectively. The resulting reaction mixtures had pH between 2 and 5. The product **7** was also isolated in reactions with 2.44, 7.93 or 15.90 mmol of acids, respectively.

c*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 1.22 mmol malonic acid : 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$*.*

Immediately after mixing the solutions in all reaction mixtures, mixture of pink powder and red prisms of **8** was obtained. The resulting reaction mixture had pH between 1 and 3. The crystals were mechanically separated, washed with a small amount of cold water and dried to constant weight in a desiccator. If the pink powder (in the mixture with crystals) was allowed to stand in the solution, after two months, it was transformed to unstable red crystals of **8**, suitable for single crystal diffraction experiments. The same results were obtained in the reactions with 2.44 or 7.93 of malonic acid, respectively. In the reaction with 15.90 mmol of malonic acid pink powder transformed to crystalline product **9** after six months.

d*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 1.22 mmol acid (formic or acetic or propionic) : 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$*.*

The mixture of unstable red prisms of **8** and stable red plates of **10** were obtained in all reactions. The same products were also obtained in the reactions with 2.44, 7.93 or 15.90 mmol of acids, respectively. The resulting reaction mixtures had pH between 4 and 2 (formic acid), 4.5 and 3.5 (acetic acid) and 3.5 and 5.5 (propionic acid). The crystals of **8** and **10** were suitable for single crystal diffraction experiments.

Hydrothermal synthesis at 110 ℃.

General procedure: The aqueous solution of sodium molybdate (0.517 mmol in 5 mL) and acid (malonic or formic or acetic or propionic) was added in aqueous solution (15 mL) of 0.203 mmol Co(III) complex salt. The final reaction mixture was heated in a 30 mL Teflon-lined reactor at 110 °C for 1.5 h.

a*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 1.22 (or 2.44 or 7.93 or 15.90) mmol malonic acid : 0.203 mmol* $[Co(CO_3)(NH_3)_4]^+$.

The resulting reaction mixtures had pH between 1 and 4. In all reactions, as a first product violet powder of **6** was isolated and it transforms to violet crystals of **7** by standing in mother liquor at room temperature.

b*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 7.93 or 15.90 mmol malonic acid : 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$.

In the reaction with 7.93 mmol of malonic acid pink powder obtained after cooling of the solution transforms to red crystalline product **9** after seven days while in the reaction with 15.93 mmol of malonic acid the only observable product was **9**. The resulting reaction mixture had pH between 1 and 2. The isolated red crystals of **9** were suitable for single-crystal diffraction experiments.

c*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-} *: 1.22 (or 2.44 or 7.93 or 15.90) mmol acid (formic or acetic or propionic) : 0.203 mmol* $[Co(CO_3)(NH_3)_4]^+$.

In the reactions with 1.22 or 2.44 mmol of formic, acetic and propionic acid, respectively, the final product was unidentified black-brown powder. The resulting reaction mixture had pH between 5 and 5.5.
The violet crystalline product of **7** was isolated in all other reactions with formic, acetic and propionic acid. The resulting reaction mixture had pH between 2 and 4.

d*) Molar ratio of precursors: 0.517 mmol* MoO_4^{2-}*: 1.22 mmol acid (formic, acetic or propionic) : 0.203 mmol* $[Co(C_2O_4)(NH_3)_4]^+$.

The mixture of unstable red prisms of **8** and stable red plates of **10** was obtained in all reactions. The same products were also obtained in reactions with 2.44 or 7.93 or 15.90 mmol of acids, respectively. The resulting reaction mixtures had pH between: 4 and 2 (formic acid); 4.5 and 3.5 (acetic acid); 3.5 and 5.5 (propionic acid). The crystals of **8** and **10** were suitable for single crystal diffraction experiments.

Synthesis of $[Co(C_2O_4)(NH_3)_4]_4[Mo_{12}SiO_{40}]\cdot 6H_2O$ in reactions of $Na_2MoO_4\cdot 2H_2O$, $[Co(C_2O_4)(NH_3)_4]NO_3\cdot H_2O$ and Na_2SiO_3 in presence of:

a) malonic acid

Hydrothermal synthesis:

125 mg of $Na_2MoO_4\cdot 2H_2O$ (0.517 mmol) and 5 mg of Na_2SiO_3 (0.041 mmol) were dissolved in water (5 mL) and added to the aqueous solution (15 mL) of $[Co(C_2O_4)(NH_3)_4]NO_3\cdot H_2O$ (60 mg, 0.203 mmol). The 2.2 mL of concentrated malonic acid solution were added to the mixture. The solution colour turned from dark rose to dark red and the resulting pH value was around 1.5. The reaction mixture was heated in a 30 mL Teflon-lined reactor for 90 minutes at 110°C and then cooled to the room temperature. The resulting light red solution with the

precipitated light red powder was left to stand at room temperature. After two days dark red octahedral crystals started to appear and after two months all the light red powder transformed into dark red crystals which were filtered off, washed with cold water and dried on air (97.5 mg).

b) hydrochloric acid

125 mg of $Na_2MoO_4 \cdot 2H_2O$ (0.517 mmol) and 5 mg of Na_2SiO_3 (0.041 mmol) were dissolved in water (5 mL) and added to the aqueous solution (15 mL) of $[Co(C_2O_4)(NH_3)_4]NO_3 \cdot H_2O$ (60 mg, 0.203 mmol). The pH of solution was adjusted to 1.5 the addition of 2 mol dm^{-3} of hydrochloric acid solution. The colour of the solution turns from dark rose to orange. The solution was then heated in a 30 mL Teflon-lined reactor for 90 minutes at 110°C and then cooled to room temperature. The resulting light red solution with the precipitated light red powder was left to stand at room temperature. After ten days dark red octahedral crystals started to appear and after one month all the light red powder transformed into dark red crystals which were filtered off, washed with cold water and dried on air (100 mg).

a) malonic acid

Synthesis under reflux:

125 mg of $Na_2MoO_4 \cdot 2H_2O$ (0.517 mmol) and 5 mg of Na_2SiO_3 (0.041 mmol) were dissolved in water (5 mL) and added to the aqueous solution (15 mL) of $[Co(C_2O_4)(NH_3)_4]NO_3 \cdot H_2O$ (60 mg, 0.203 mmol). The 2.2 mL of concentrated malonic acid solution were added to the mixture. The solution colour turned from dark rose to dark red and the resulting pH value was around 1.5. The solution was then heated under reflux for 90 minutes. Upon cooling the solution to room temperature, a light pink needle-like crystals started to form. After three months large dark red crystals started to appear.

125 mg of $Na_2MoO_4 \cdot 2H_2O$ (0.517 mmol) and 5 mg of Na_2SiO_3 (0.041 mmol) were dissolved in water (5 mL) and added to the aqueous solution (15 mL) of $[Co(C_2O_4)(NH_3)_4]NO_3 \cdot H_2O$ (60 mg, 0.203 mmol). The pH of solution was adjusted to 1.5 by by addition of 2 mol dm^{-3} hydrochloric acid solution. The solution colour turned from dark rose to orange and light pink precipitate appeared. The mixture was then heated under reflux for 90 minutes. During the reaction, the light pink precipitate was dissolved, and the colour of the solution turned orange red. Upon cooling down the solution to room temperature, a light pink needle-like crystals started to form. After three months the pink crystals transformed into dark red octahedral crystals which were filtered off, washed with cold water and dried on air (35 mg).

	1st	2nd	3rd	4th
1	**3.29 %**	**16.99 %**	**17.38 %**	
	51-104 °C	**165-361 °C**	**379-418 °C**	
2	**8.51 %**	**29.77 %**	**30.11 %**	
	41-126 °C	**127- 268 °C**	**269-336 °C**	
3	**7.34 %**	**44.83 %**	**2.79 %**	
	33-147 °C	**147-360 °C**	**360-402 °C**	
4	**7.53 %**	**38.42 %**	**4.64 %**	
	87-121 °C	**121-382 °C**	**382-420 °C**	
5	**5.32 %**	**48.58 %**	**2.27 %**	
	68-96 °C	**98-387 °C**	**387-441 °C**	
6	**8.26 %**	**14.73 %**	**2.65 %**	**1.85 %**
	33-133 °C	**133-303 °C**	**303-358 °C**	**358-408 °C**
7	**8.74 %**	**10.98 %**	**1.44 %**	
	34-143 °C	**145-340 °C**	**343-421 °C**	
8	**8.46 %**	**19.92 %**	**6.98 %**	
	34-153 °C	**156-301 °C**	**301-389 °C**	
9	**17.29 %**	**8.36 %**		
	163-249 °C	**249-355 °C**		
10	**7.96 %**	**22.44 %**	**5.04 %**	
	36-165 °C	**164-316 °C**	**316-344 °C**	

Table S6: TG data for compounds **1–10.**

Table S7: Crystallographic data of compounds **3**, **4**, **5**, **7**, **8**, **9** and **10**.

	3	**4**	**5**	**7**
Formula	$C_8H_{36}Co_2Mo_2N_8O_{27}$	$C_4H_{16}CoMoN_4NaO_{13}$	$C_{14}H_{62}Co_4Mo_3N_{16}O_{43}$	$Co_2H_{31}Mo_5N_7O_{23}$
M_r	986.19	506.07	1666.33	1094.88
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	$P2_1/c$	P-1	$P2_1/n$
a (Å)	7.4297(2)	8.0975(2)	12.8695(4)	9.3392(4)
b (Å)	10.3770(3)	11.9126(3)	17.6441(5)	28.0114(9)
c (Å)	10.9734(4)	15.0744(4)	25.3842(7)	9.6973(4)
α (°)	66.911(3)	90	103.533(2)	90
β (°)	74.016(3)	100.603(2)	101.392(2)	102.988(4)
γ (°)	87.852(2)	90	106.284(2)	90
V (Å^3)	745.79(4)	1429.28(6)	5160.9(3)	2471.95(17)
Z	1	4	4	4
Reflections unique	23798	9164	44533	26766
Reflections observed [$I > 2\,\sigma(I)$]	3180	2543	12700	5035
Parameters	226	237	1493	351
R_1(obs)	0.0355	0.0220	0.0599	0.0673
wR_2(obs)	0.0919	0.0680	0.1512	0.1488
GooF	1.075	1.077	1.026	1.078

	8	**9**	**10**
Formula	$C_8H_{72}Co_4Mo_8N_{16}O_{54}$	$C_8H_{60}Co_4Mo_{12}N_{16}O_{62}Si$	$C_8H_{68}Co_4Mo_8N_{16}O_{52}$
M_r	2260.05	2787.81	2224.02
Crystal system	triclinic	tetragonal	triclinic
Space group	P-1	$I4_1/a$	P-1
a (Å)	8.51130(10)	16.6637(3)	8.51020(10)
b (Å)	13.7625(2)	16.6637(3)	13.7353(2)
c (Å)	13.9561(2)	23.1974(6)	13.95510(10)
α (°)	93.0160(10)	90	95.0810(10)
β (°)	107.3180(10)	90	107.1720(10)
γ (°)	103.2230(10)	90	102.5790(10)
V (Å^3)	1506.42(4)	6441.4(3)	1500.51(3)
Z	1	4	1
Reflections unique	45721	22807	38779
Reflections observed [$I > 2\,\sigma(I)$]	6014	5493	5998
Parameters	409	245	424
R_1(obs)	0.0662	0.0411	0.0344
wR_2(obs)	0.1799	0.0746	0.0868
GooF	1.060	1.087	1.044

As well as **$[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 10H_2O$ (10)**, **$[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 12H_2O$ (8)** crystallizes in the P-1 space group with one formula unit per unit cell whose contents differs only by the amount of water molecules present. The unit cell parameters are similar for both compounds, unit cell angles being different (α = 93.01°, β = 107.32°, γ = 103.22° for **8** and α

= 95.08°, β = 107.17°, γ = 102.58° for **10**) making the cell volume of **8** larger than cell volume of **10** resulting in larger voids in the overall hydrogen bonded framework of cations and anions that can fit additional water molecules. The three-dimensional network of hydrogen bonded anions and cations in **8** is isostructural with the network found in **10** with N–H···O hydrogen bonds interconnecting anions and cations being approximately the same length in both compounds (around 3 Å).

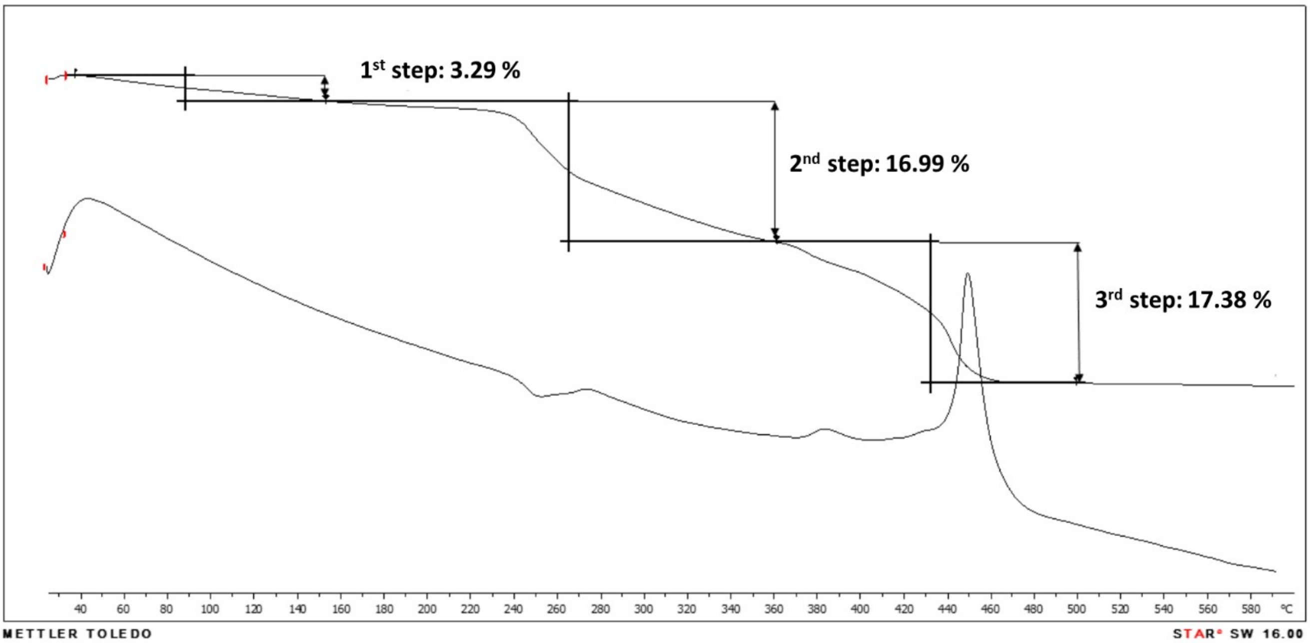


Figure S1: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_2[MoO_4]\cdot H_2O$ (**1**).

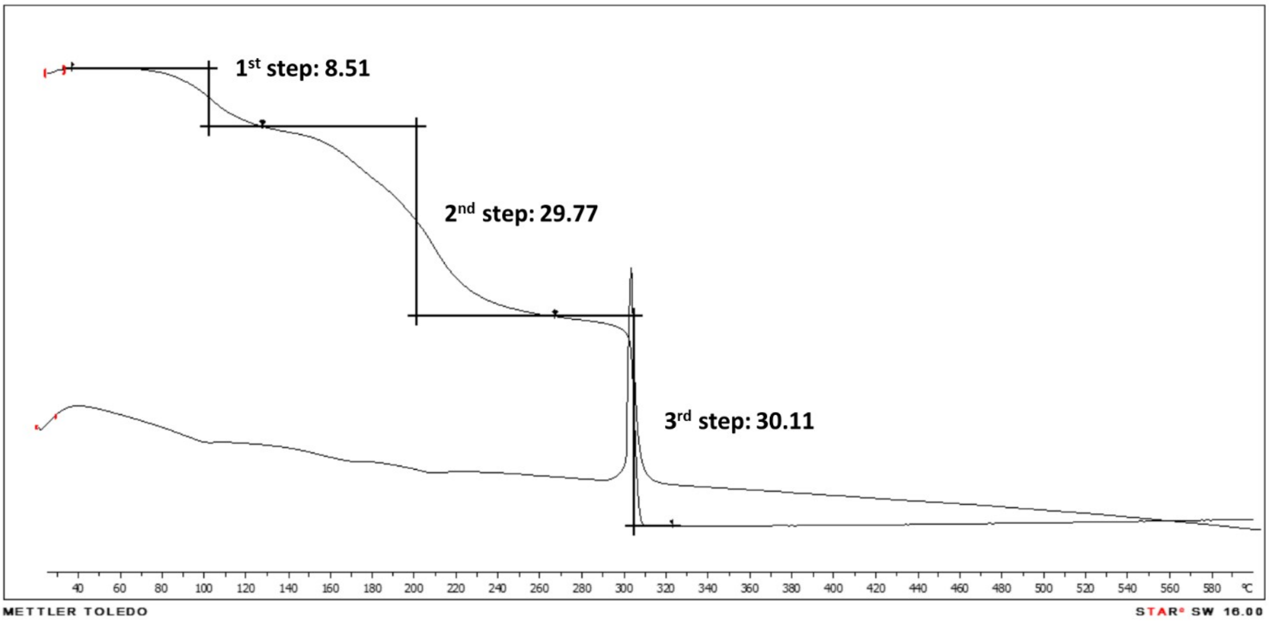


Figure S2: TG/DTA curve of $[Co^{III}(C_2O_4)(NH_3)_4]_2[Co^{II}(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$ (**2**).

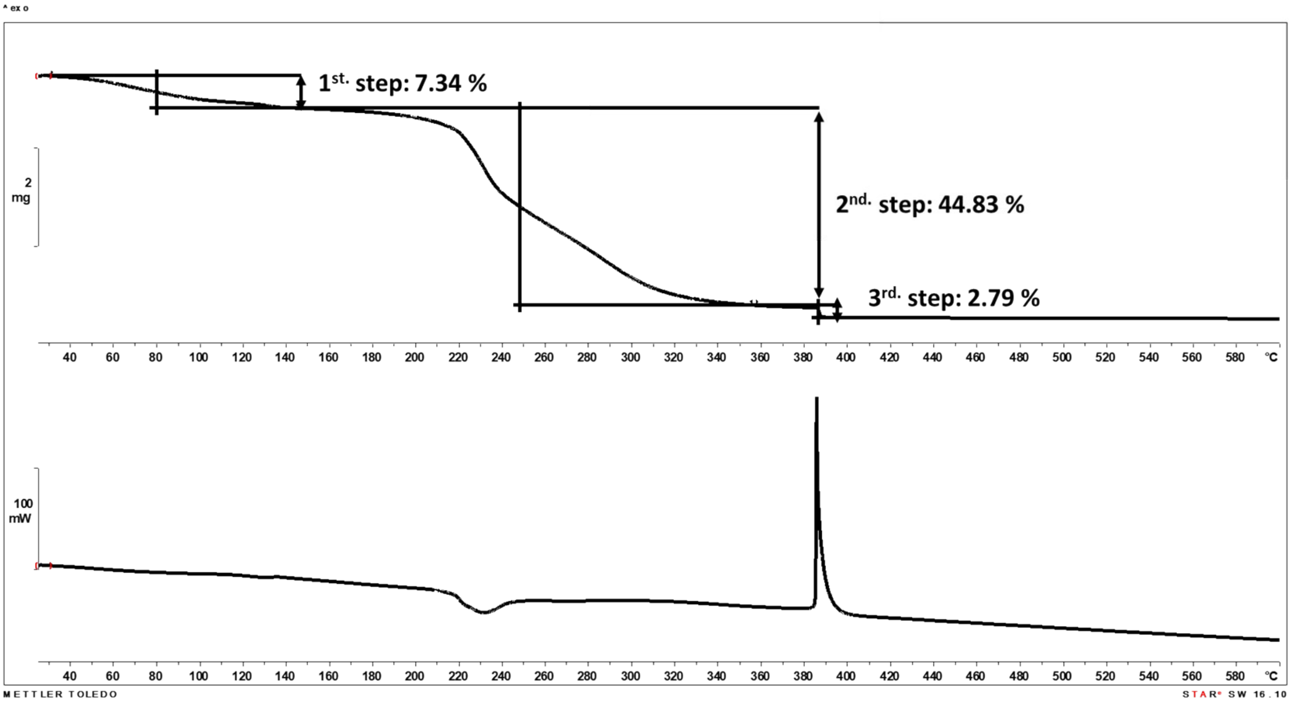


Figure S3: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_2[Mo_2O_4(\mu\text{-}O)(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$ (**3**).

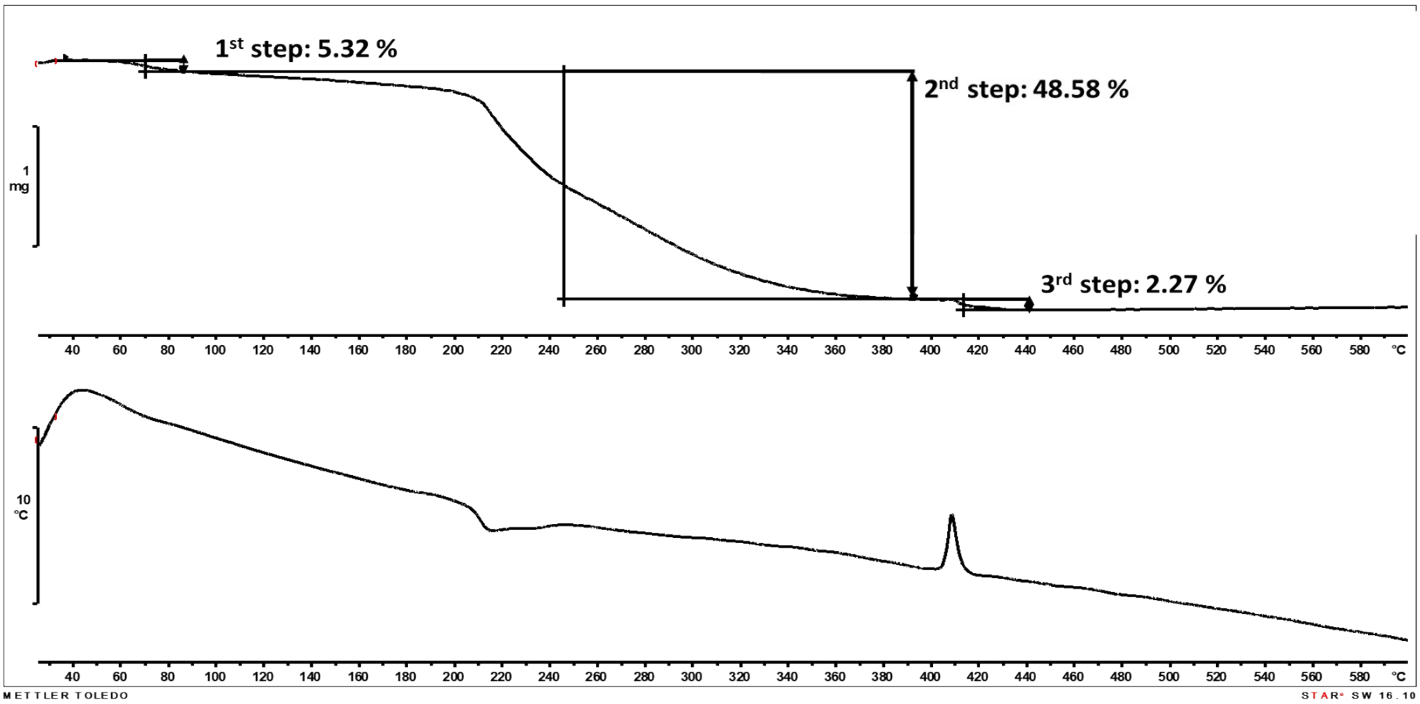


Figure S4: TG/DTA curve of $Na_2[Co(C_2O_4)(NH_3)_4][Mo_2O_4(\mu\text{-}O)_2(C_2O_4)_2]\cdot 4H_2O$ (**4**).

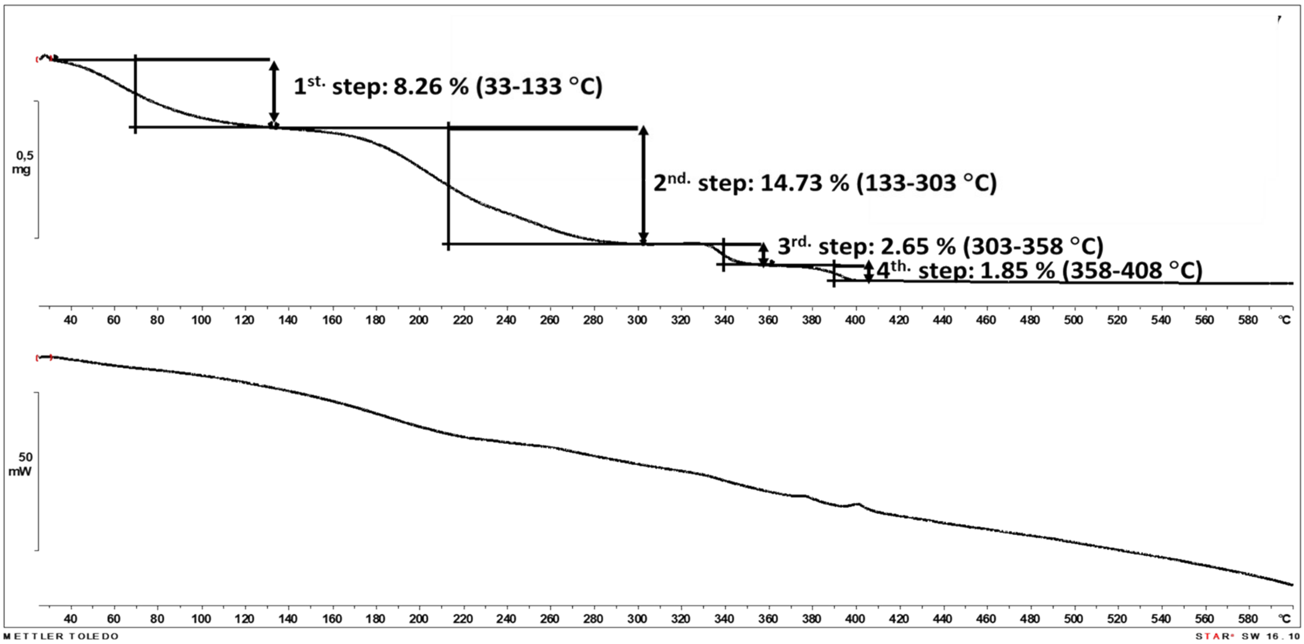


Figure S5: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_4[Mo_3O_6(\mu\text{-}O)_2(C_2O_4)_3(H_2O)_2]\cdot 5H_2O$ (**5**).

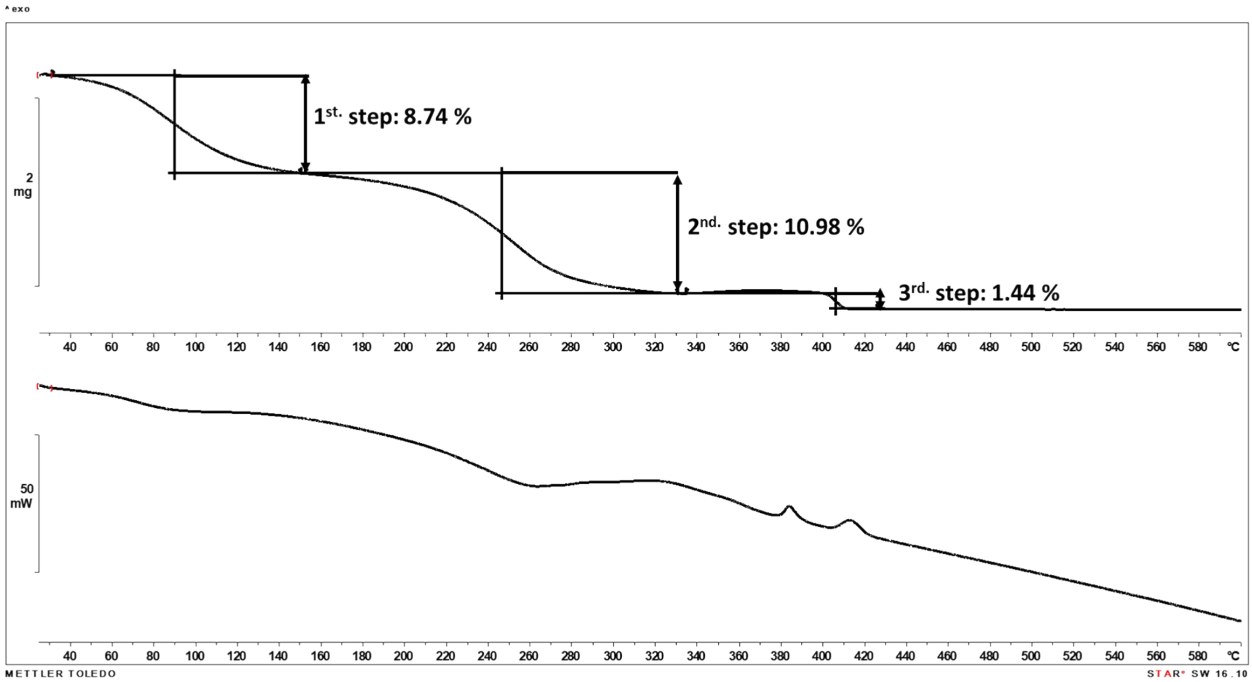


Figure S6: TG/DTA curve of $[Mo_5Co_2O_{17}(HCO_3)(H_2C_3O_4H)(NH_3)_7]\cdot 5H_2O$ (**6**).

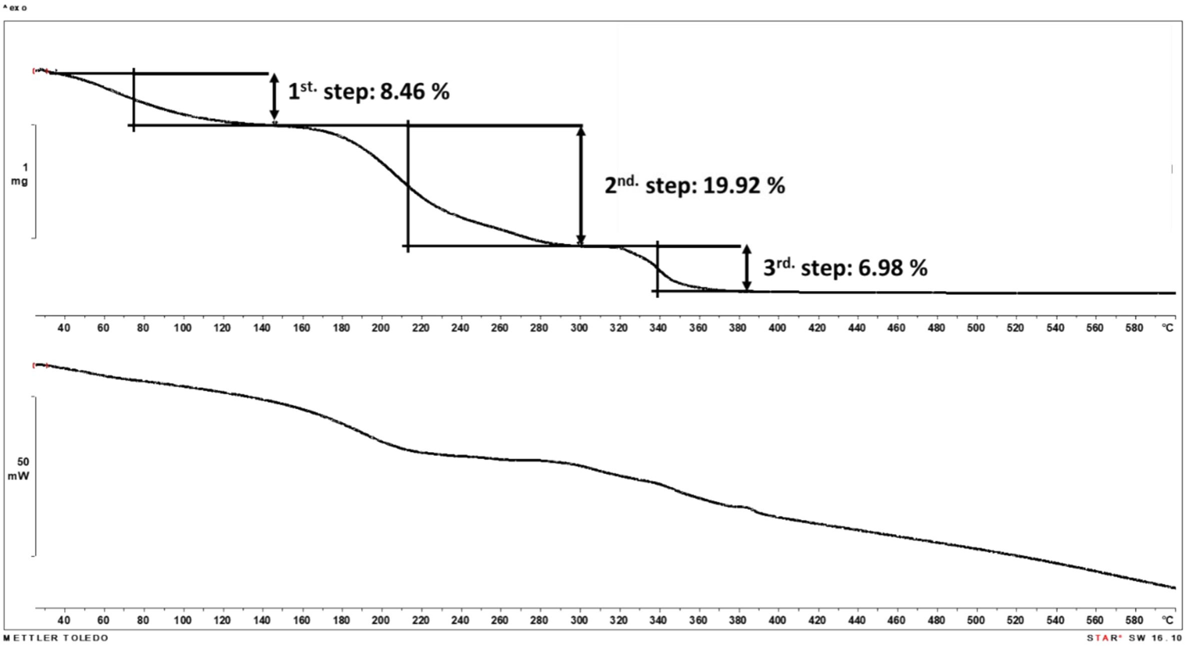


Figure S7: TG/DTA curve of $[Mo_5Co_2O_{18}(NH_3)_7]\cdot5H_2O$ (**7**).

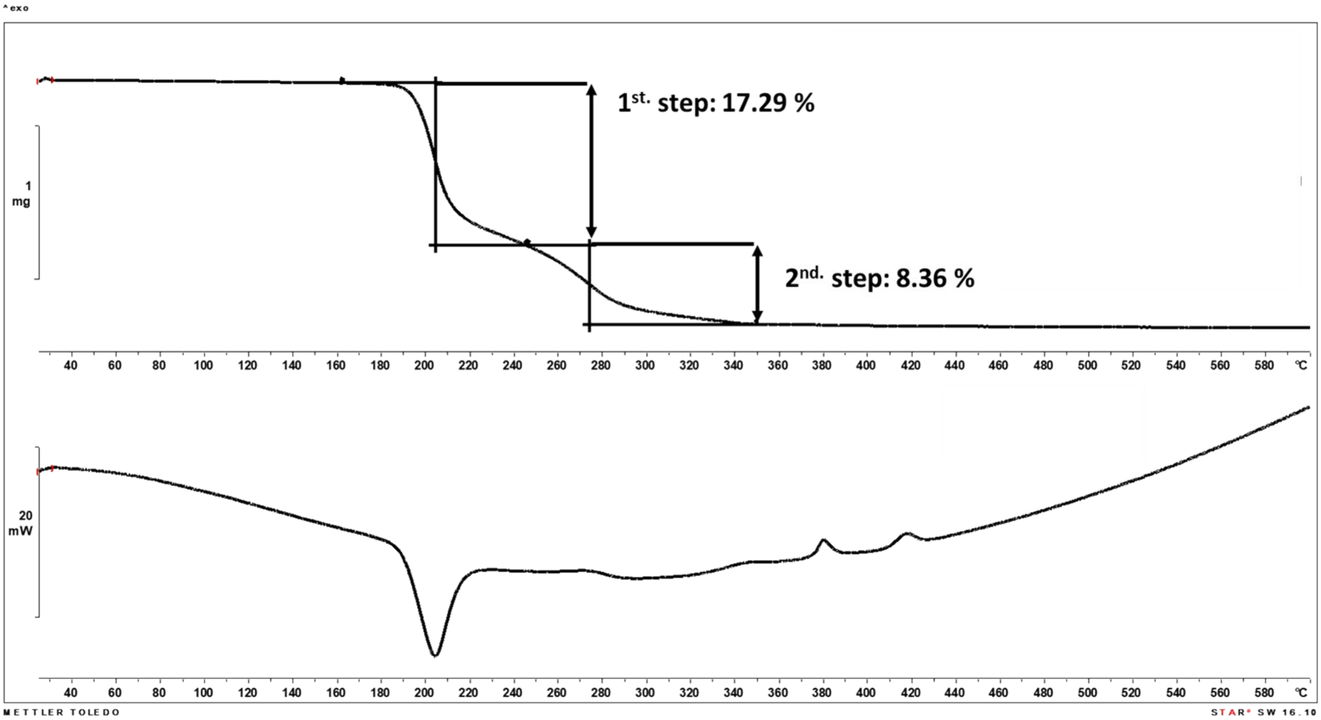


Figure S8: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot12H_2O$ (**8**).

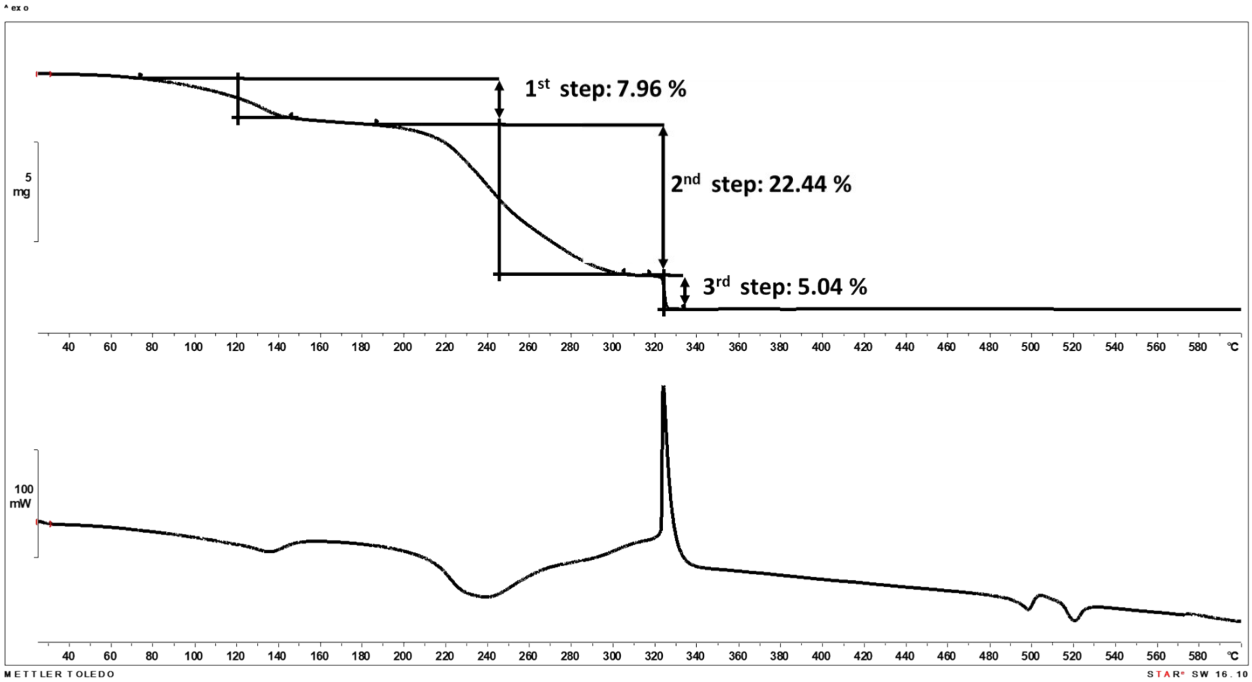


Figure S9: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_4[SiMo_{12}O_{40}]\cdot 6H_2O$ (**9**).

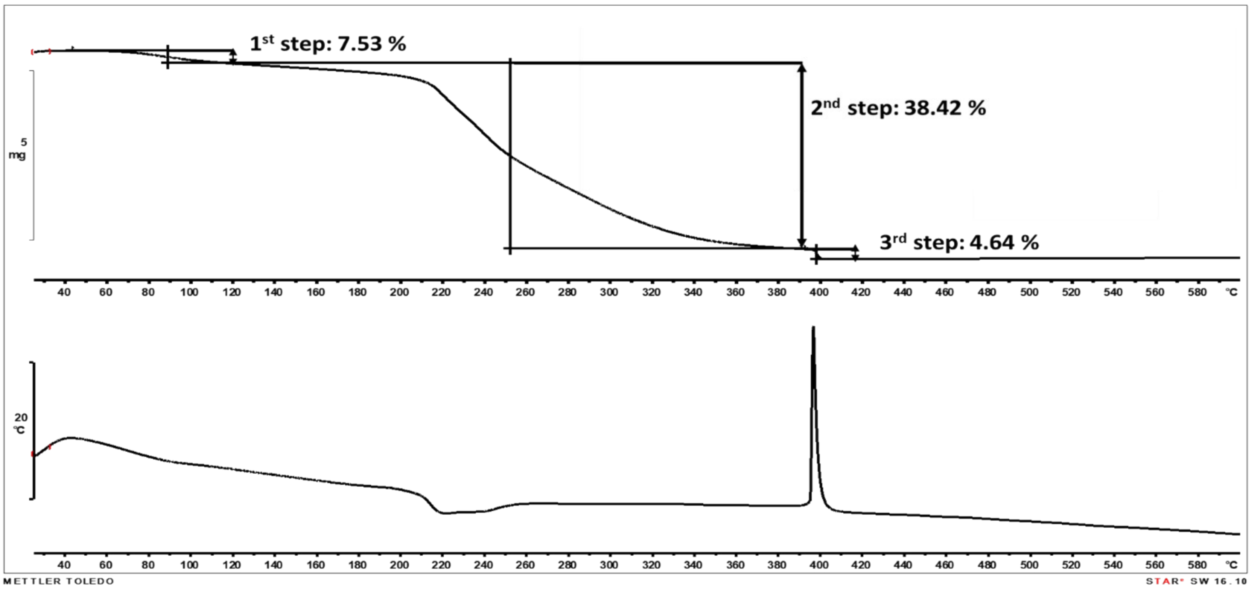


Figure S10: TG/DTA curve of $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 10H_2O$ (**10)**.

Table S8: Characteristic IR vibrations (in cm^{-1}) of isolated products **1**–**10** and used precursors

	ν_s(Mo=O$_t$) + ν_a(Mo=O$_t$)	ν_s(Mo–O–Mo) + ν_a(Mo–O–Mo)	ν(Mo–O in Mo–O–Mo) + ν(Mo–O)	ν_s(N-H) + ν_s(O-H)	δ_s(N-H)	ν_a(C-O)	ν_s(C-O) + ν(C-C)	ν_s(O-H)	ν_s(M-O) + ν(C-C)	δ(O-C=O) + ν(M-O)
$Na_2MoO_4\cdot 2H_2O$	953	797, 741	598							
$[Co(C_2O_4)(NH_3)_4](NO_3)\cdot H_2O$				3180, 3269, 3492	1304, 1278		1632, 1417, 1364			
Oxalic acid						1692,1687	1464, 1377	2954 - 2854		
Malonic acid						1695	1432,1302, 1213, 1167	3026 - 2948		
Acetic acid						1718	1413, 1295	3400 - 2935		
Formic acid						1727, 1722	1338, 1180	3400 - 3200		
Propionic acid						1756, 1716	1290 - 1080	2985 - 2561		
(1) $[Co(C_2O_4)(NH_3)_4]_2[MoO_4]$	955, 900	800, 762	536, 481	3297, 3203, 2927		1705, 1668	1381, 1318			
(2) $[Co^{III}(C_2O_4)(NH_3)_4]_2[Co^{II}(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$				3269, 3179, 3104		1649	1405, 1269		554, 490	819, 796
(3) $Na_3[Co(C_2O_4)(NH_3)_4][Mo_2O_4(\mu\text{-}O)_2(C_2O_4)_2]\cdot 4H_2O$	942, 892	820, 788, 726	533, 484	3293, 3191		1707, 1668	1392, 1313, 1256			
(4) $[Co(C_2O_4)(NH_3)_4]_4[Mo_3O_6(\mu O)_2(C_2O_4)_3(H_2O)_2]\cdot 5H_2O$	942, 890	823, 789, 716	557, 533, 483	3293, 3191		1702, 1665	1387, 1315, 1258			
(5) $[Co(C_2O_4)(NH_3)_4]_2[Mo_2O_4(\mu\text{-}O)(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$	954, 902	796	535, 474	3308, 3198		1704, 1680	1393, 1326, 1249			
(6) $[Mo_5Co_2O_{17}(HCO_3)(H_2C_3O_4H)(NH_3)_7]\cdot 5H_2O$		885, 838	636	3472, 3286, 3181		1603, 1563	1419, 1361, 1306		566, 530	
(7) $[Mo_5O_{18}Co_2(NH_3)_7]\cdot 5H_2O$	884, 841	836, 831	575, 484	3278		1618	1307			
(8) $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 12H_2O$	955 - 905 897 - 868	773 - 688	609, 560	3530 - 3493 3301 - 3181		1699 - 1647	1406 - 1242		570 - 486	
(9) $[Co(C_2O_4)(NH_3)_4]_4[SiMo_{12}O_{40}]\cdot 6H_2O$	991, 948	824, 769	561, 531	3491, 3186		1697 - 1635	1359 - 1252		561, 531	
(10) $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 10H_2O$			525,483	3493 - 3185						

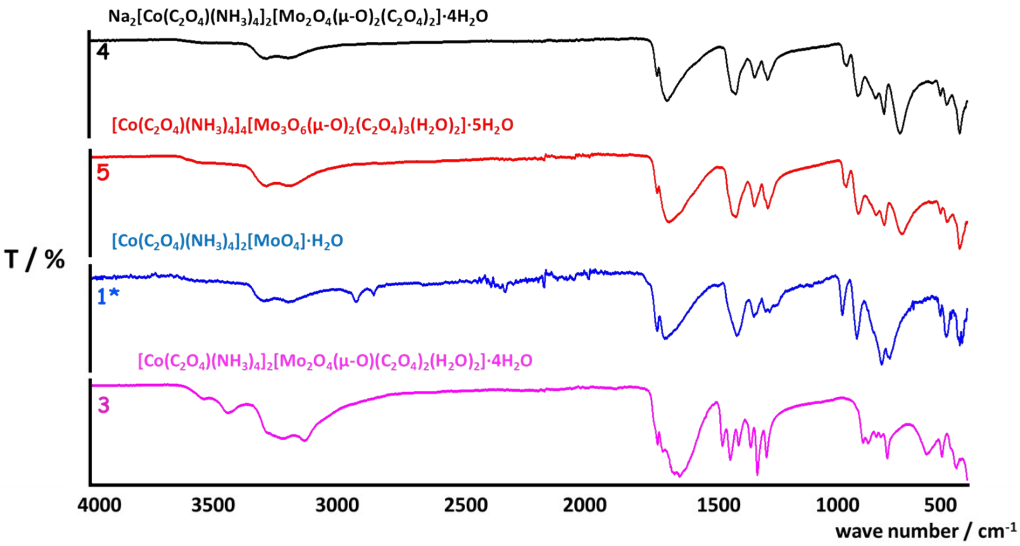


Figure S11: Comparison of IR spectra of $[Co(C_2O_4)(NH_3)_4]_2[MoO_4]\cdot H_2O$ (**1**), $[Co(C_2O_4)(NH_3)_4]_2[Mo_2O_4(\mu\text{-}O)(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$ (**3**), $Na_2[Co(C_2O_4)(NH_3)_4][Mo_2O_4(\mu\text{-}O)_2(C_2O_4)_2]\cdot 4H_2O$ (**4**) and $[Co(C_2O_4)(NH_3)_4]_4[Mo_3O_6(\mu\text{-}O)_2(C_2O_4)_3(H_2O)_2]\cdot 5H_2O$ (**5**).

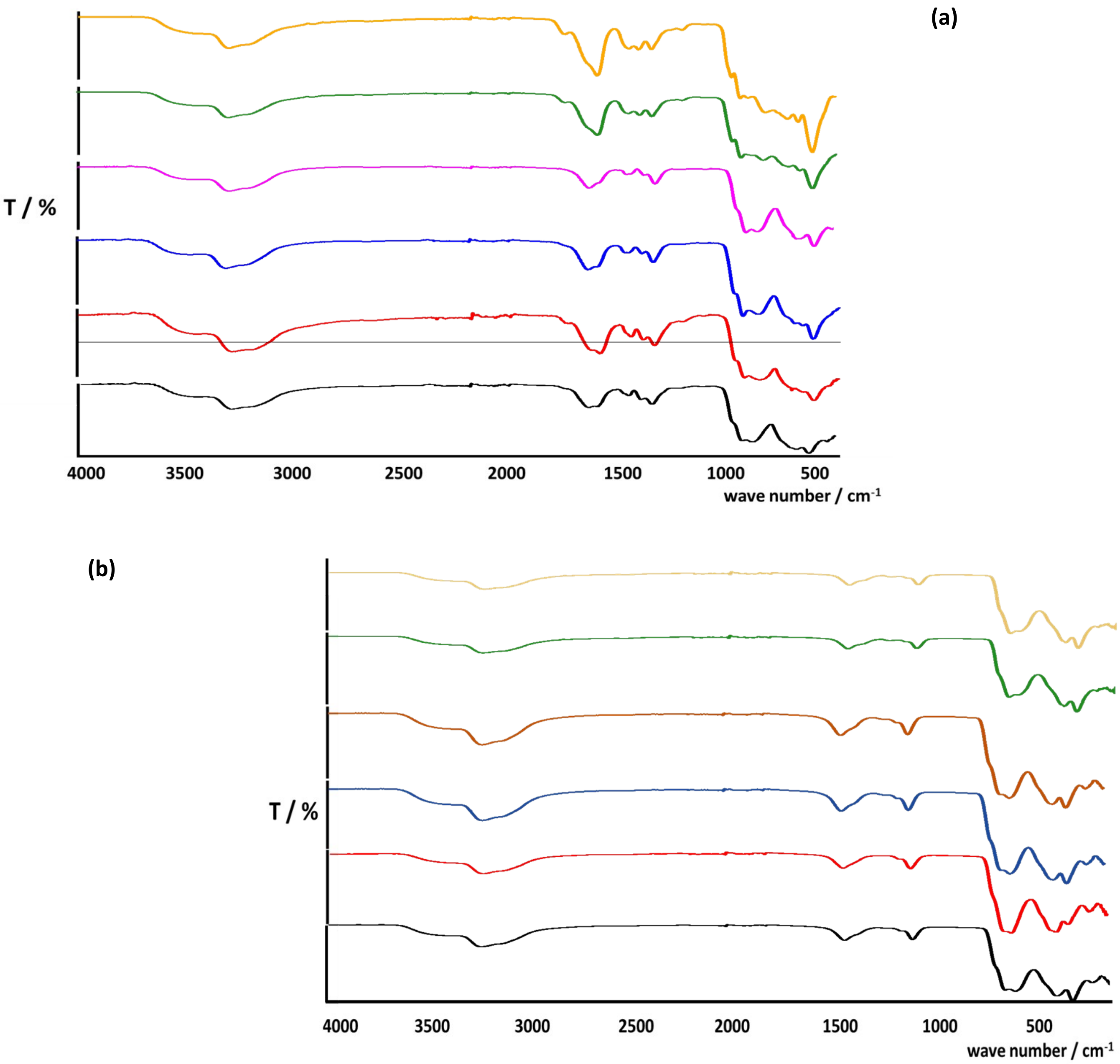
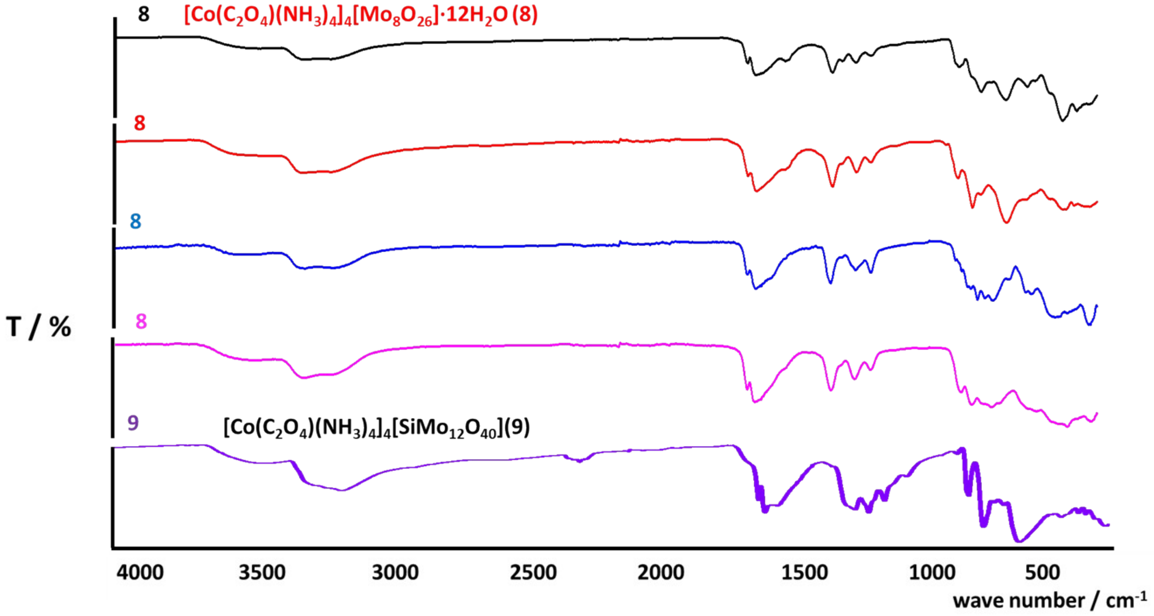
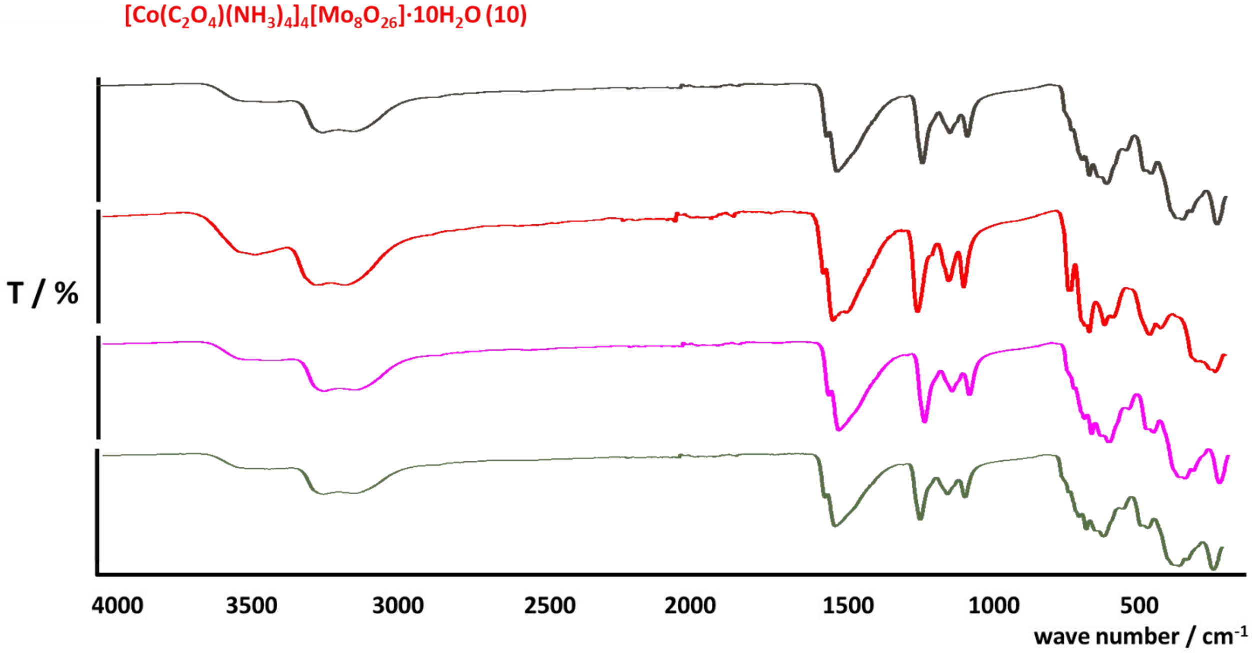


Figure S12: Comparison of selected IR spectra of a) $[Mo_5Co_2O_{17}(HCO_3)(H_2C_3O_4H)(NH_3)_7]\cdot H_2O$ (**6**) and b) $[Mo_5Co_2O_{18}(NH_3)_7]\cdot 5H_2O$ (**7**) obtained in reactions of $[Co(CO_3)(NH_3)_4]^+$ with different concentrations of acids. a) black: in reaction with 1.22 mmol malonic acid (R.T.); red: with 2.44 mmol malonic acid (R.T.); blue: with 15.90 mmol malonic acid (R.T.); pink: 1.22 mmol malonic acid (110 °C); green: 2.44 mmol malonic acid (110 °C); yellow: with 15.90 mmol malonic acid (110 °C); (b) black: with 2.44 mmol malonic acid (R.T.); red: 2.44 mmol formic acid (R.T.); blue: 2.44 mmol acetic acid (R.T); brown: 7.93 mmol formic acid (110 °C); green: 7.93 mmol acetic acid (110 °C); yellow: 7.93 mmol propionic acid (110 °C).



(a)



(b)

Figure S13: Comparison of selected IR spectra of a) $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 12H_2O$ (**8**), $[Co(C_2O_4)(NH_3)_4]_4[SiMo_{12}O_{40}]\cdot 6H_2O$ (**9**) and b) $[Co(C_2O_4)(NH_3)_4]_4[Mo_8O_{26}]\cdot 10H_2O$ (**10**) obtained in reactions of $[Co(C_2O_4)(NH_3)_4]^+$ with different concentrations of acids. (a) violet: 15.9 mmol of malonic acid (110 °C); pink: 2.44 mmol malonic acid (R.T.); blue: 1.22 mmol formic acid (R.T.); red: 1.22 mmol acetic acid (R.T); black: 1.22 mmol propionic acid (b) green: 7.93 mmol formic acid (110 °C); pink: 7.93 acetic acid (110°C); red: 15.90 mmol propionic acid (110 °C); black: 1.22 mmol propionic acid (110 °C).

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. All samples of compounds **6** and **7** were prepared for the NMR investigations in the same way.

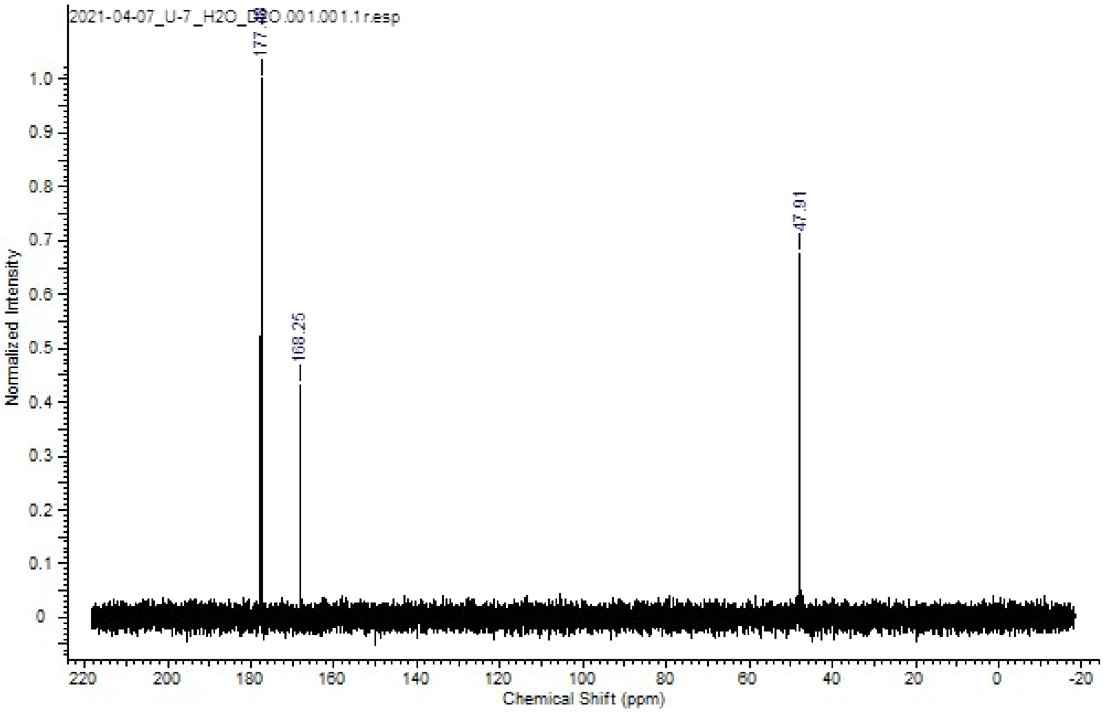
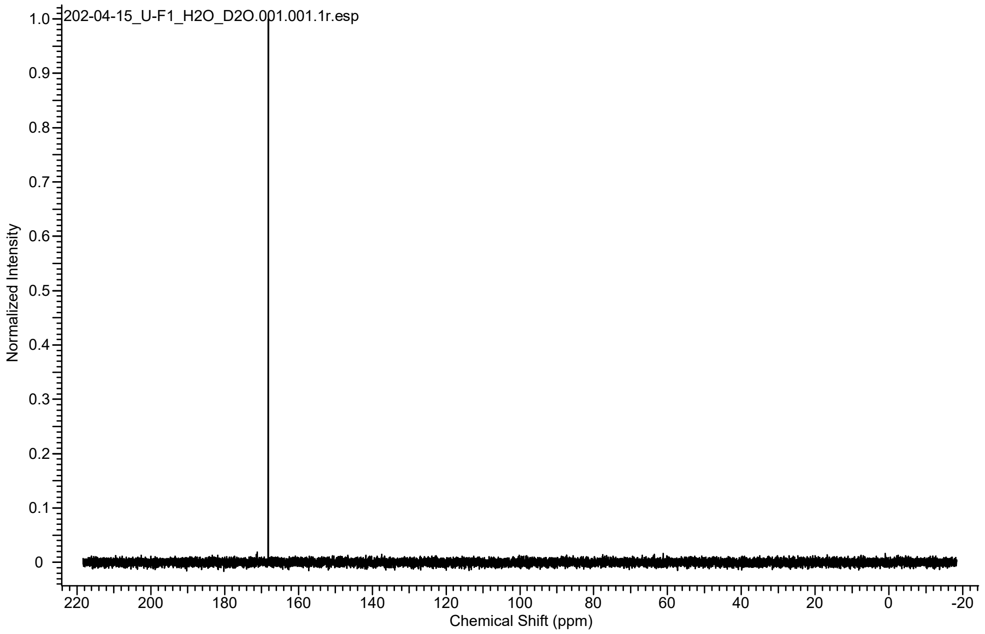
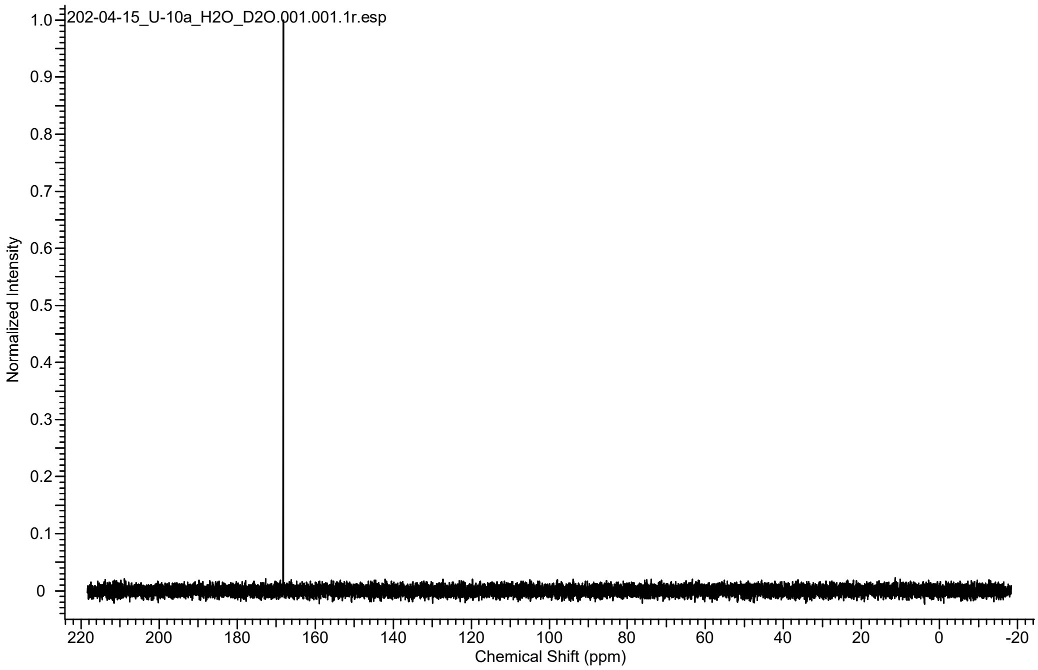


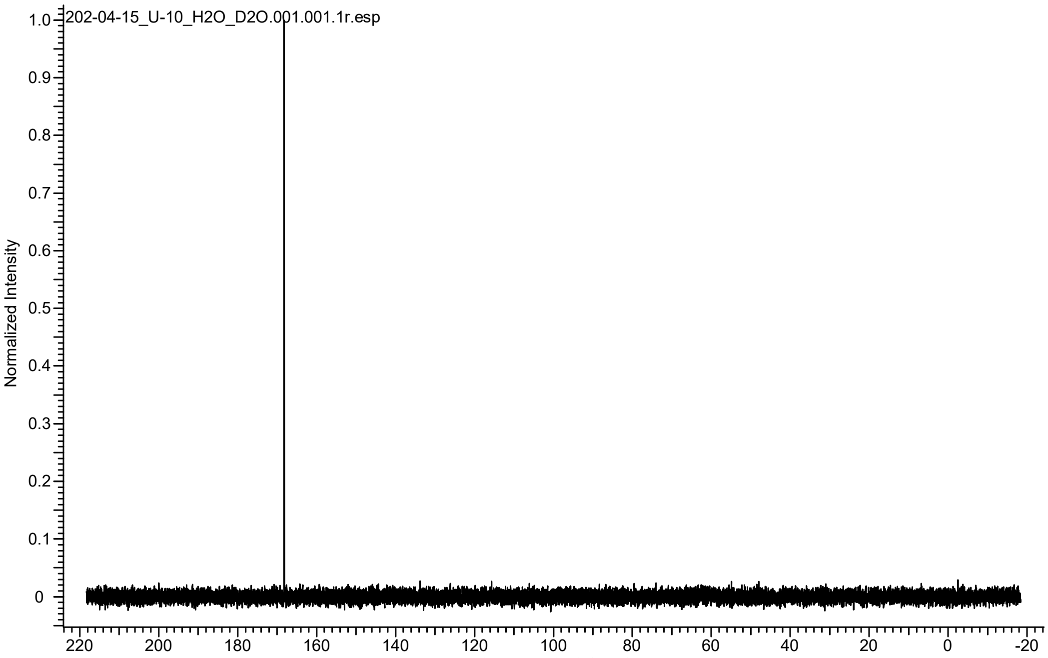
Figure S14: ^{13}C NMR spectrum of $[Mo_5Co_2O_{17}(HCO_3)(H_2C_3O_4H)(NH_3)_7]\cdot H_2O$ (**6**).



(a)



(b)



(c)

Figure S15: Examples of ^{13}C NMR spectra of $[Mo_5Co_2O_{18}(NH_3)_7]\cdot 5H_2O$ (**7**) obtained in reactions with a) formic b) acetic and c) propionic acid.

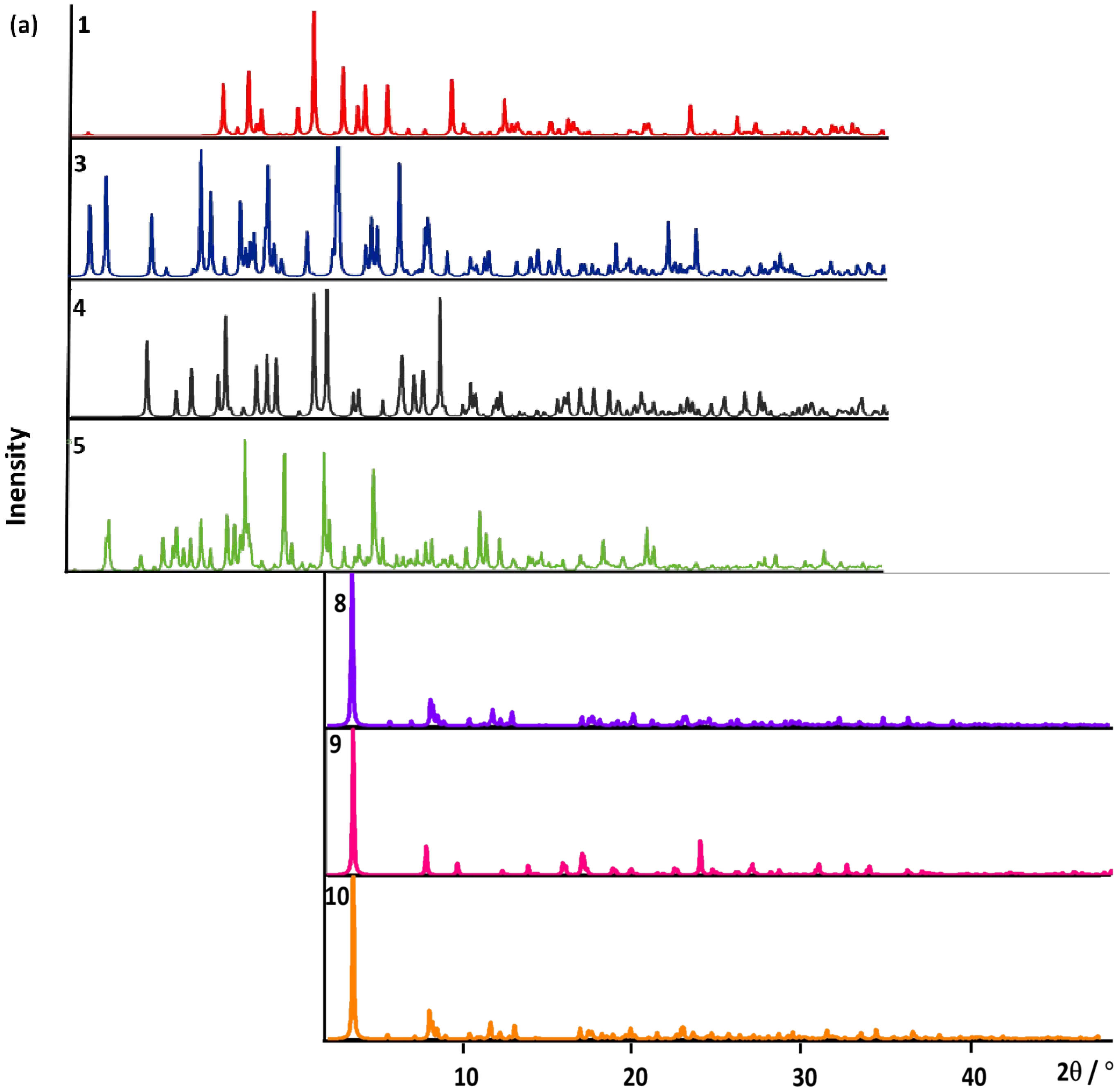


Figure S16: PXRD patterns of prepared oxomolybdate salts: **1** (red), **3** (blue), **4** (black), **5** (green), **8** (violet), **10** (orange) and **9** (pink).

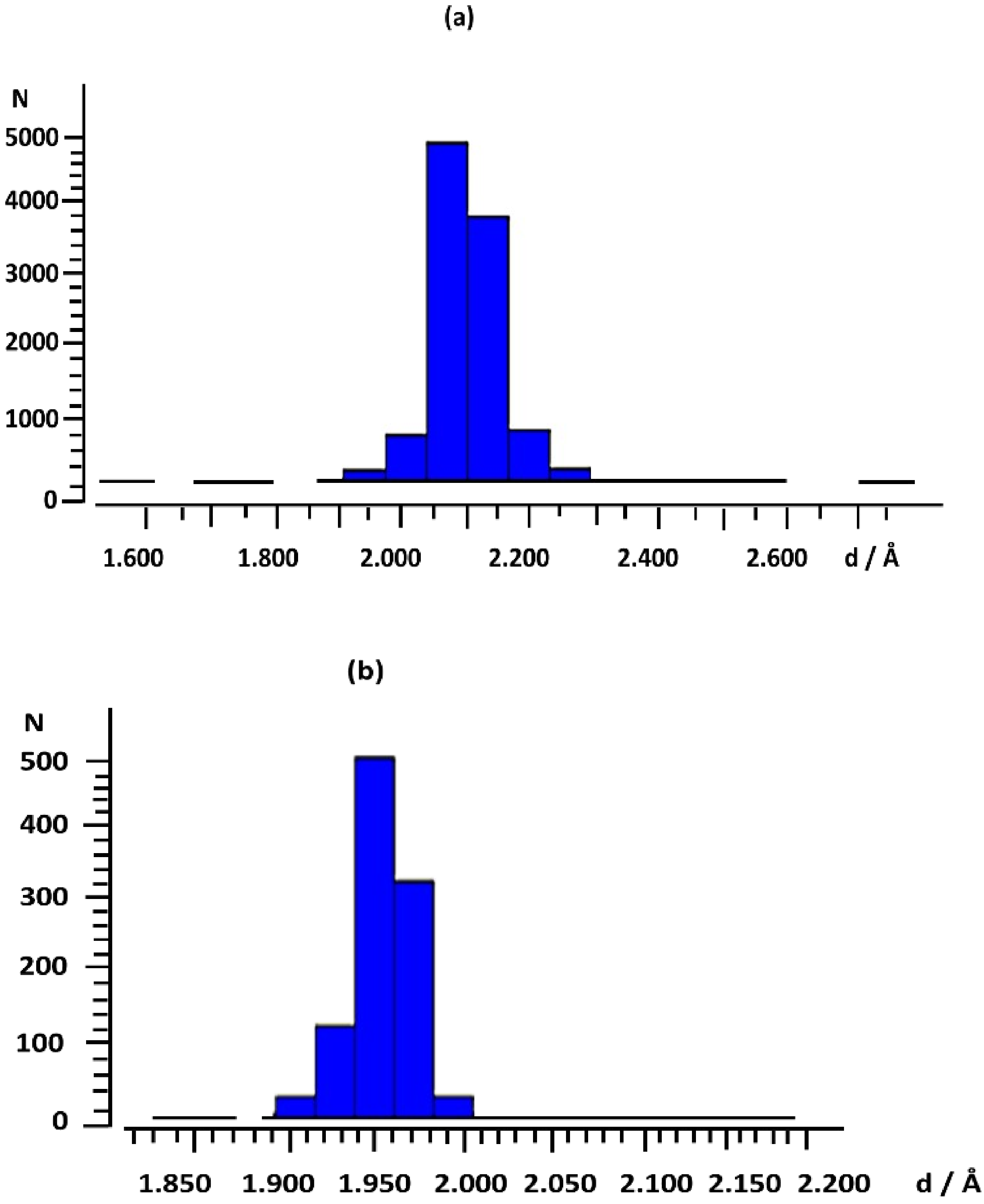


Figure S17. Histogram of the bond length values found in the CSD data base for a) Co–OH_2; b) Co–NH_3.