Synthesis and Structure of Malato Molybdenum(VI) Complexes: Δ-[Co(en)$_3$][MoO$_3$(L-mal)] × H$_2$O and Δ-[Co(en)$_3$]$_n$[Mo$_4$O$_{11}$(L-mal)$_2$(H$_2$O)$_2$Na]$_n$ × 4 n H$_2$O

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THIS PAPER IS DEDICATED TO THE LATE PROFESSOR TOMISLAV CVITAŠ

Abstract: Two Δ-[Co(en)$_3$]$^{3+}$ salts with oxomolybdate anions coordinated with malato ligand, Δ-[Co(en)$_3$][MoO$_3$(L-mal)] × H$_2$O (**1**) and Δ-[Co(en)$_3$]$_n$[Mo$_4$O$_{11}$(L-mal)$_2$(H$_2$O)$_2$Na]$_n$ × 4 n H$_2$O (**2**) were obtained as products of the reaction between *tris*(ethylenediamine)cobalt(III) chloride and sodium molybdate in the presence of L-malic acid. In the reactions of Na$_2$MoO$_4$ and Δ-[Co(en)$_3$]Cl$_3$ with formic, maleic or adipic acid, respectively, as the only product heptamolybdate, Δ-[Co(en)$_3$]$_2$(H$_3$O)[Mo$_7$O$_{24}$]Cl × 9 H$_2$O (**3**) was isolated. All the reactions were conducted by using different synthetic approaches, namely solution-based methods performed at room temperature, under reflux or hydrothermally at 110 °C, along with mechanochemically accelerated (hand grinding or liquid-assisted ball milling) vapour-assisted aging. The isolation of these different oxomolybdate species, depending on the nature of applied dicarboxylic acid, revealed the role of used dicarboxylic acids not solely as ligands, but also as structure-directing agents in the polyoxoanion self-assembly processes. All the products were characterized in the solid state by infrared spectroscopy, thermogravimetric and elemental analysis as well as single-crystal and powder X-ray diffraction.

Keywords: characterization, single crystal X-ray diffraction method, mechanochemical synthesis, vapour-assisted aging, solution-based syntheses, polyoxomolybdates.

INTRODUCTION

COORDINATION compounds of biogenic elements such as Mo with carboxylic acids are of both theoretical and practical interest because many of the processes occurring in biological systems involve the interaction of metal ions with acids.[1,2] Molybdenum ion is an integral component of the multinuclear metal center of nitrogenase enzyme and the mononuclear active site of oxygen transferases.[3] It is believed that molybdenum is taken up by organisms as MoO$_4^{2-}$[4] and therefore oxomolybdate chemistry is of interest to scientists, especially the exploration of the molybdenum-α-hydroxycarboxylic acid interactions.[5,6] It's known that the interaction between molybdenum and *R*-homocitrate in the FeMo-cofactor of nitrogenases takes place through a bidentate coordination of homocitrate and

was considered to be biologically important in the mobilization and the early biosynthesis of FeMo-Co in nitrogenases.[7,8] Nitrogenases that contain citrate or malate instead of homocitrate prevent strong binding of the enzyme and thus prevent the effective reduction of N$_2$, while the process of acetylene and proton reduction takes place unhindered.[9–11] One of the biologically important α-hydroxycarboxylic acid is L-malic acid, intermediate of the citric acid cycle, central metabolic hub that connects the metabolism of carbohydrates, lipids and amino acids. L-Malic acid as α-hydroxydicarboxylic acid possesses one –OH functional group at α-carbon atom and has the ability to act as multidentate ligand towards M^{n+} ions. It can form a large variety of complexes using several possible types of chelation in which the donating oxygen atoms may be either from –OH or one of the present –COOH groups. The

L-malic acid and their corresponding ionized forms (depending on its protonation status) can bind to metal centre through the α-hydroxyl or α-alkoxide group and two carboxyl (or carboxylate) groups in two manners: through the β-carboxyl(ate) group that is coordinated to the same metal centre as the α-hydroxy(alkoxide)carboxyl(ate) group when the ligand acts as tridentate chelating ligand or it can act bidentate towards one metal and use the β-carboxyl(ate) group as a bridge to bind the another metal centre. Reactions of Mo(VI) with malic acid have been studied in different pH ranges and by different methods, e.g. polarimetry, potentiometry, spectrophotometry and NMR spectroscopy.[12–14]

A. Bertlan's polarimetric studies[12] of Mo(VI) and malic acid at different pH indicated the existence of six different complexes in solution, with $\{MoO_4\}$, $\{MoO_2\}$, $\{Mo_4O_{11}\}$ and $\{Mo_7O_{24}\}$ molybdate units. The first spectroscopically and structurally characterized complex with 1 : 1 ratio of molybdenum and malic acid was the binuclear $K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(s\text{-mal})_2] \times 4\ H_2O$ reported by R-H. Zhang.[15] The malate ligand coordinates tridentately with the Mo atom *via* its α-hydroxyl, and α- and β-carboxyl group. The similar complexes $(NH_4)_4[Mo_4O_{11}(s\text{-mal})_2] \times 6\ H_2O$,[15–17] $(NH_4)_4[Mo_4O_{11}(R\text{-mal})_2] \times 6\ H_2O$,[18] $K_3[MoO_2H(s\text{-mal})_2] \times H_2O$ or $Na_3[MoO_2H(s\text{-mal})_2]$,[19] $Cs_2[MoO_2(s\text{-Hmal})_2] \times H_2O$,[20] $(NH_4)_4[MoO_2(s\text{-mal})_2][MoO_2(R\text{-mal})_2]$,[21] and $(Him)_2K_6[(MoO_2)_4O_3(R\text{-mal})_2][(MoO_2)_4O_3(s\text{-mal})_2] \times 8\ H_2O$[22] are also structurally characterized and described in the literature.

As continuation of our previous research on the synthetic route influence on the reactivity of *tris*(ethylenediamine)cobalt(III) ion and molybdate ion in the presence of succinic and malonic acids,[23–25] in this work we decided to explore the influence of the applied synthetic procedure and reaction conditions, along with the used succinic acid homologue or derivative, on the polyoxoanion self-assembly process. By applying solution-based and solid-state methods promoted by mechanochemically accelerated vapour-assisted aging, herein we examined the formation of oxomolybdate species in the reaction systems containing $\Delta\text{-}[Co(en)_3]^{3+}$ cation and $[MoO_4]^{2-}$ anion, and L-malic, adipic, maleic or fumaric acid, respectively. All the above mentioned dicarboxylic acids are somehow structurally related to succinic acid, adipic acid as its higher homologue, and fumaric and maleic acid as its oxidation products. In addition, stereospecific addition of water on double bond of geometrical *cis/trans*-isomers produces D- or L-malic acid, respectively (Scheme 1.).

In the course of our investigations on oxomolybdenum(VI) complexes with malic acid, as α-hydroxycarboxylic acid, we prepared and characterized two oxomolybdate compounds of different nuclearity, $\Delta\text{-}[Co(en)_3][MoO_3(\text{L-mal})] \times H_2O$ (**1**) and
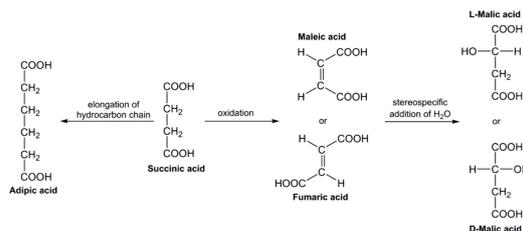
Scheme 1. Succinic acid homologue and its derivatives.
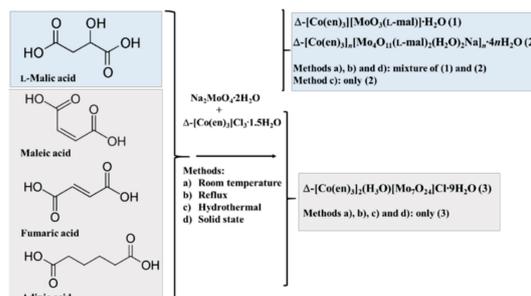
Scheme 2. Reaction pathways for compounds **1**, **2** and **3**.

$\Delta\text{-}[Co(en)_3]_n[Mo_4O_{11}(\text{L-mal})_2(H_2O)_2Na]_n \times 4\ n\ H_2O$ (**2**). All the reactions with adipic, maleic or fumaric acid yielded heptamolybdate $\Delta\text{-}[Co(en)_3]_2(H_3O)[Mo_7O_{24}]Cl \times 9\ H_2O$ (**3**), known from the literature,[25] as the only product (Scheme 2.).

EXPERIMENTAL

Materials and Methods

The starting cobalt(III) complex salt $\Delta\text{-}[Co(en)_3]Cl_3 \times 1.5\ H_2O$ was prepared as described in the literature,[26] while $Na_2MoO_4 \times 2\ H_2O$, L-malic, adipic, maleic and fumaric acids were commercially available and used as received without further purification.

Elemental analyses were provided by the Analytical Services Laboratory of the Ruđer Bošković Institute, Zagreb. Infrared spectra were recorded on a PerkinElmer Spectrum RXI FTIR-ATR spectrometer in a 4000–400 cm^{-1} range. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/DSC 3+ STARe Systems instrument using aluminium oxide crucibles under oxygen stream with the heating rate of 10 °C min^{-1}. In all experiments the temperature was ranged from 25 to 600 °C. The results were processed with the Mettler STARe 9.01 software.

The solid-state reactions, i.e. liquid-assisted grinding (LAG), were carried out using a Retsch MM200 ball mill.

Powder X-ray diffraction patterns were collected using a Malvern Panalytical Aeris powder diffractometer using CuKα radiation in Bragg-Brentano geometry, equipped with a PIXcel^{1D} detector. The sample was

contained on a Si sample holder. Patterns were collected in the range of 2q = 5°–50° with the step size of 0.043° and at 7.14 s per step. The data was collected and visualized using the Malvern Panalytical HighScore Software Suite.[27] FT-infrared spectra, TGA-curves and powder diffraction patterns for **1**, **2** and **3** are given in ESI (Table S1 and S2, Figure S1 and S2).

The crystal and molecular structure of **1** and **2** (Table S3) were determined by single crystal Xray diffraction. Single crystal diffraction data for compound **1** was collected at 170 K using a XtaLAB Synergy-S diffractometer with Cu$K\alpha$ (λ = 1.54184 Å) radiation. The data for compound **2** was collected using an Oxford Diffraction Xcalibur3 CCD diffractometer with graphite-monochromated Mo$K\alpha$ (0.71073 Å) radiation at room temperature. Data collection, reduction and cell refinment was performed using the CrysAlis software package.[28,29] Both structures were solved and refined using the SHELX program suite[30] integrated in the OLEX2[31] system. The structural refinement was performed on F^2 using all data. The hydrogen atoms bonded were placed at calculated positions and treated as riding on their parent atoms. All geometrical calculations and structure visualization were performed using PLATON[32] and Mercury programs[33]. Crystallographic information files are available from the Cambridge Crystallographic Data Centre (CCDC) upon request (http://www.ccdc.cam.ac.uk, CCDC deposition numbers 2337842-2337843).

Synthesis

SOLUTION-BASED METHODS:
a) AT ROOM TEMPERATURE, b) UNDER REFLUX AND
c) HYDROTHERMAL SYNTHESIS AT 110 °C

Δ-[Co(en)₃][MoO₃(ʟ-mal)] × H₂O (1) and
Δ-[Co(en)₃]ₙ[Mo₄O₁₁(ʟ-mal)₂(H₂O)₂Na]ₙ × 4 n H₂O (2)

Equal amounts of $Na_2MoO_4 \times 2\,H_2O$ (0.50 mmol) and ʟ-malic acid, $C_4H_6O_5$ (0.50 mmol) were dissolved in water (10 mL). The addition of the aqueous solution (10 mL) containing equal amount of Δ-[Co(en)₃]Cl₃ × 1.5 H₂O (0.50 mmol) to the solution of sodium molybdate and ʟ-malic acid resulted in instantaneous precipitation of a yellow voluminous product. The pH value of reaction mixture was around 4.

a) The resulting reaction mixture was allowed to stand at room temperature. After one month, the yellow voluminous product was completely transformed into the mixture of yellow needle-like crystals of **1** and orange cube-like crystals of **2**. The crystalline precipitate was filtered off, washed with a small amount of cold water, and dried to constant weight in a desiccator (46.2 mg). The products were separated mechanically (**1**: 32.5 mg; **2**: 13.7 mg). The both isolated crystals of **1** and **2** were suitable for single-crystal diffraction experiments.

b) The final mixture was refluxed for 1 h. During the heating of the reaction mixture, the yellow voluminous product was obtained. The reaction mixture was then left to stand at room temperature. After about two weeks, the yellow voluminous product transformed to the yellow needle-like crystals of **1**. The mixture was left to stand at room temperature additionally two weeks and within that period orange cube-like crystals of **2** appeared. The crystals of **1** and **2** were filtered off (53 mg), washed with a small amount of cold water, and dried in a desiccator to a constant mass. The products were separated mechanically (**1**: 28 mg; **2**: 25 mg). The both crystals of **1** and **2** were suitable for single-crystal diffraction experiments.

c) The final reaction mixture was heated at 110 °C for 7 h in a 30 mL Teflon-lined reactor. By cooling the orange cube-like crystals of **2** were obtained. The crystals of **2** were filtered off, washed with a small amount of cold water, and dried in a desiccator to a constant mass (66.2 mg). The isolated crystals of **2** were suitable for single-crystal diffraction experiments.

HAND GRINDING OR LIQUID-ASSISTED BALL MILLING FOLLOWED BY VAPOUR-ASSISTED AGING

d) $Na_2MoO_4 \times 2\,H_2O$ (0.125 mmol), ʟ-malic acid, $C_4H_6O_5$, (0.125 mmol) and Δ-[Co(en)₃]Cl₃ × 1.5 H₂O (0.125 mmol) were ground together in an agate mortar for 10 min, affording a homogeneous mixture, or were placed in a 5 mL stainless steel jar with an addition of acetone (25 μL) and reactants were milled for 1 h at a frequency of 25 Hz. The resulting light yellow-orange inhomogeneous powder solid mixture obtained in both reactions, respectively, was exposed to 100 % humidity at room temperature. After one day mixture of the orange polycrystalline product and yellow needle-like crystals of **1** were observed. After one month the yellow needle-like crystals and the orange polycrystalline product were completely transformed into the orange cube-like crystals of **2**. The product was washed with a small amount of cold water and dried to constant weight in a desiccator (15 mg). The isolated crystals of **2** were suitable for single-crystal diffraction experiments.

Selected IR data (cm⁻¹) for **1** = 3384(w, b), 3102(m, b), 2969(m), 1635(sh), 1580(s), 1460(m), 1373(s), 1169(m), 1117(s), 1056(s), 1020(m), 958(w), 863(m), 845(sh),792(vs), 687(s), 505(vs); elemental analysis calcd. (%) for $C_{10}H_{29}CoMoN_6O_9$: C 22.56, H 5.49, Co 11.07, Mo 18.03, N 15.80; found: C 22.67, H 5.30, Co 10.98, Mo 18.36, N 15.67.

Selected IR data (cm⁻¹) for **2** = 3240(m, b), 3110(sh, b), 1647(m), 1578(s), 1466(m), 1417(sh, s), 1389(s), 1296(w), 1161(m), 1058(m), 925(sh), 912(vs), 879(s, sh), 848(m), 791(m), 704(vs), 636(vs), 561(vs); elemental analysis calcd. (%) for $C_{14}H_{42}CoMo_4N_6NaO_{27}$: C 14.10, H 3.55, Co 4.94, Mo 32.19, N 7.05, Na 1.93; found: C 14.01, H 3.57, Co 4.79, Mo 31.92, N 6.83, Na 1.88.

REACTIONS WITH ADIPIC, FUMARIC AND MALEIC ACIDS

In the identical experiments described under a), b), c) and d) but with adipic, maleic or fumaric acid, respectively, as the only product heptamolybdate **3**, described in the literature was observed.[25]

Crystallography

The unit cell of Δ-[Co(en)$_3$][MoO$_3$(L-mal)] × H$_2$O (**1**) contains one complex cobalt(III) cation and a monomeric malatomolybdate anion, to the best of our knowledge the first example of a (O,O',O''-malato)trioxomolybdate(VI) anion (Figure 1). The molybdenum atom in [MoO$_3$(L-mal)]$^{3-}$ is octahedrally coordinated by six oxygen atoms – three from oxo ligands, and three from the tridentate malate ligand. The coordination of triply deprotonated malate anion to a molybdenum is consistent with those in the previously reported crystal structures.[34]

Each anion is surrounded by altogether four cations and two water molecules forming an extensive network of hydrogen bonds (data are given in Table S4). Two hydrogen bonds between oxygen atoms of the malate deprotonated carboxylate groups and water molecules form a one–dimensional chain along the crystallographic a–axis (Figure 2a). These chains are further interconnected by H-bonds with the [Co(en)$_3$]$^{3+}$ cations forming a three-dimensional supramolecular framework (Figure 2b).
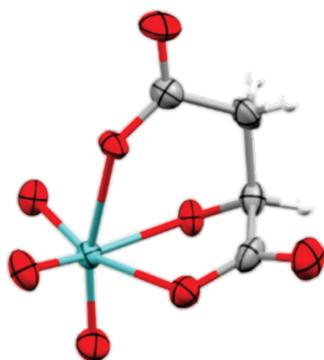
Tetranuclear compound Δ-[Co(en)$_3$]n[Mo$_4$O$_{11}$(L-mal)$_2$(H$_2$O)$_2$Na]$_n$ × 4 n H$_2$O (**2**) is a coordination polymer consisting of Co(III) cations and infinite chains of malato-coordinated tetramolybdate anions bridged by sodium cations and water molecules. The coordination sphere around each of the molybdenum atom is octahedral, with one oxo ligand, two bridging oxygen atoms (one bridging molybdenum atoms, one bridging a molybdenum and a sodium atom) and three being the oxygen atoms from the malate ligand. β-carboxylate groups of the malate ligand acts as a bridging ligand between three molybdenum atoms (Figure 3a). The sodium atom is surrounded by six oxygen atoms, two are oxo ligands bridging the sodium with two molybdenum atoms, one is from the alkoxide group of the malate ligand bridging the sodium and molybdenum as well, one is an oxygen belonging to the carboxylate group of another molybdate anion, and two are from coordinated water molecules. Tetranuclear molybdate compounds with coordinated malate anions have previously been reported in the literature,[17,34] but this is the first example of such anions forming infinite chains by coordinating to sodium cations (Figure 3b). The oxygen atoms on the polyanion chain act as acceptors, with nitrogen atoms of the ethylenediamine ligands being the hydrogen bond donors which together with water molecules form a vast three dimensional supramolecular framework (Figure 4). The list of hydrogen bonds presents in **2** are given in Table S5.

Figure 1. Structure of [MoO$_3$(L-mal)]$^{3-}$ anion in **1**.

(a)   **(b)**
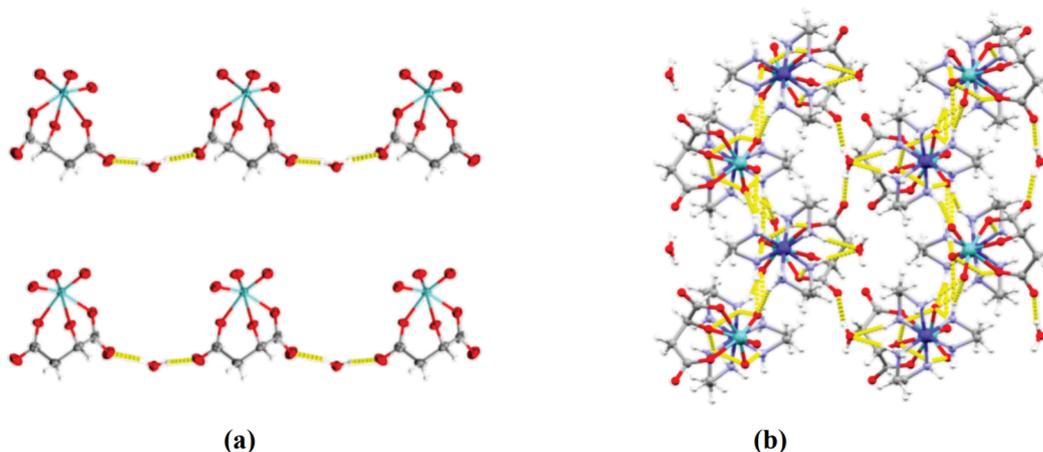
Figure 2. Structure of **1**: (a) one-dimensional chains parallel to the crystallographic a–axis formed by anions and water molecules; (b) crystal packing viewed along the crystallographic b–axis with a supramolecular network of hydrogen bonds.
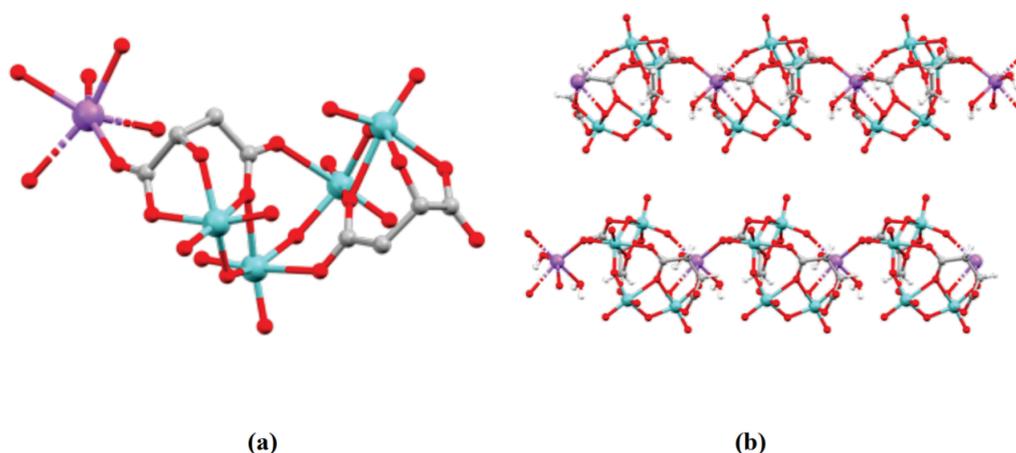
Figure 3. Structure of **2**: (a) subunit of the $[Mo_4O_{11}(\text{L-mal})_2(H_2O)_2Na]^{3-}$ anion; hydrogen atoms are omitted for better clarity; (b) one-dimensional coordination polymer chains parallel to the crystallographic *a*–axis.
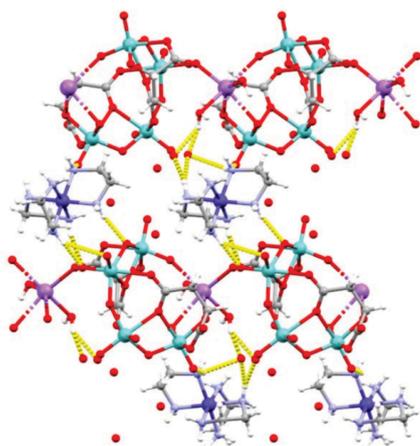
Figure 4. Structure of **2**: crystal packing viewed along the crystallographic *c*–axis with the hydrogen-bonded supra-molecular network.

RESULTS AND DISCUSSION

In the reactions with L-malic acid, as the only substituted α-hydroxycarboxylic acid used in this study, we isolated oxomolybdate species with monomeric {MoO₃(L-mal)} and tetrameric {(MoO₂)₄O₃(L-mal)₂} units as building blocks. The reactions were carried out by using equal amounts of reactants (sodium molybdate, Δ-*tris*(ethylenediamine) cobalt(III) chloride and L-malic acid) and in aqueous medium at room temperature or under reflux, solvothermally at 110 °C or in solid-state by employing mechanochemically accelerated (hand grinding or liquid-assisted ball milling) vapour-assisted aging. All solution-based reactions were initiated by instantaneous formation of the yellow voluminous product, at pH between 3.5 and 5. In the reaction at room temperature and under reflux the

yellow voluminous product transformed after one month to yellow needle-like crystals of **1** and orange cube-like crystals of **2**. L-Malic acid is coordinated in two different manners in oxomolybdates **1** and **2**: in **1** acts as tridentate chelating ligand *via* the carboxylate groups and deprotonated hydroxy group, and in **2** acts as a chelating bidentate ligand with one of the carboxylate group and α-alkoxide group towards one metal centre, and with the β-carboxylate group acts as bridging ligand that monodentately coordinates another metal centre. In **2** β-carboxylate groups of the malate ligand acts as a bridging ligand between three molybdenum atoms. The FT-infrared spectra of the isolated compounds (Figure 5) reflect the above-described structural features and can serve to distinguish modes of coordination. In the ν(Mo-O) region (900–700 cm⁻¹) of monomeric $[MoO_3(\text{L-mal})]^{3-}$ strong separated broad band with several shoulders is observed unlike in the spectrum of coordination polymer **2** where several very strong bands, originated from ν(Mo-O_t) and ν(Mo₂O_b) stretchings, appear. These observations are in accordance to the literature data.[15]
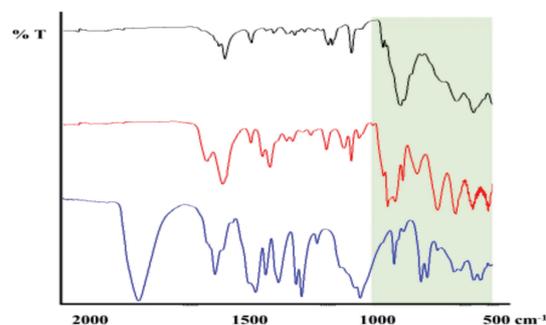
Figure 5. Characteristic bands in FT-infrared spectra of **1** (black), **2** (red) and L-malic acid (blue).

In addition, the FT-infrared spectral characteristics of **1** and **2** display characteristic features of coordinated malate ligand. The antisymmetric stretching carboxy vibrations $v_{as}(COO)$ of the complexes all are shifted to lower frequencies when compared to those of free malic acid.

The corresponding symmetric stretching vibrations $v_s(COO)$ appear at $1460 \sim 1374$ cm^{-1} and $1417 \sim 1322$ cm^{-1} for **1** and **2**, respectively.

The formation of product **2**, as the only product, was driven in solution at elevated temperature and pressure while the aging of the solid reaction mixtures formed by the mechanochemical approach occurs *via* the yellow needle-like crystals of **1** as intermediates.

The absence of coordination of adipic, maleic and fumaric acids to molybdenum is in accordance with the results obtained in reactions with succinic or malonic acid.[23,25] We postulated that the reaction conditions and the interplay between the hydrogen-bond donating and accepting capacity of the used dicarboxylic acids, and their potential function as a chelating or bridging ligand promotes and facilitates formation of the observed diverse (poly)oxomolybdates from the {MoO$_4$} units.

CONCLUSIONS

The temperature is the most important factor in the self-assembly process of oxomolybdate units and formation of coordination polymer Δ-[Co(en)$_3$]$_n$[Mo$_4$O$_{11}$(L-mal)$_2$(H$_2$O)$_2$Na]$_n$ $\times 4\,n$ H$_2$O. During mechanochemically accelerated aging, the formation of monomeric Δ-[Co(en)$_3$][MoO$_3$(L-mal)] was observed and confirmed the assumption that it is one of the intermediate products formed during the condensation of oxomolybdate units. The final product in described reaction conditions was Δ-[Co(en)$_3$]$_n$[Mo$_4$O$_{11}$(L-mal)$_2$(H$_2$O)$_2$Na]$_n \times 4\,n$ H$_2$O.

Supplementary Information. Supporting information to the paper is attached to the electronic version of the article at: https://doi.org/10.5562/cca4086.

PDF files with attached documents are best viewed with Adobe Acrobat Reader which is free and can be downloaded from Adobe's web site.

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