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# IRON, NICKEL AND ZINC MALATES COORDINATION COMPOUNDS

## Synthesis, characterization and thermal behaviour

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## Abstract

The coordinations compounds $(NH_4)[Fe(C_4H_4O_5)(OH)_2]\cdot 0.5H_2O$, $[Ni(C_4H_4O_5)]\cdot 3H_2O$ and $[Zn(C_4H_4O_5)]\cdot 5H_2O$ were synthesized by a precipitation method and characterized by chemical analysis, spectral (IR, UV-VIS) and magnetical investigations. In the range 50–600°C stepped thermal decompositions occur with formation of anhydrous malates, malonates, oxoacetates (iron and nickel compounds) and hydroxocarbonate (Zn compound) as intermediates observed by FT-IR spectroscopy. $\alpha$-$Fe_2O_3$, NiO and ZnO constitute the final decomposition products.

**Keywords:** iron-, nickel-, zinc-malate coordination compound, non-isothermal analysis

## Introduction

Due to their capacity in chelating metallic ions and low decomposition temperatures with evolving nontoxic compounds (CO, $CO_2$, $H_2O$), ligands belonging to carboxylic acids class are suited for obtaining precursor systems of transition metal oxides [1–8]. Although detailed investigations has been made concerning the obtaining of the simple/mixed oxides through thermal decomposition of formates, acetates, tartrates precursors, a similar interest for complex malates is relative lacking [9–12].

The paper reports the synthesis, characterization and thermal behaviour of Fe, Ni and Zn malates coordination compounds. From practical point of view the undertaken investigations permit to determine a new route of simple oxide synthesis. From the theoretical one, it represents a first but necessary step in elucidation the solid state pathway of mixed oxides formation.

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# Experimental

## *Precursors preparation*

As starting materials, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(CH_3COO)_2$ and malic acid of reagent grade quality were used. The compounds and some of their thermal decomposition intermediates were characterized by elemental chemical analysis: the metal content was determined by atomic absorption technique; the carbon, nitrogen and hydrogen content were obtained by microcombustion technique.

$(NH_4)[Fe(C_4H_4O_5)(OH)_2] \cdot 0.5H_2O$ and $[Ni(C_4H_4O_5)] \cdot 3H_2O$ – metallic salts (2 mmol (0.808 g) of $Fe(NO_3)_3 \cdot 9H_2O$ and 2 mmol (0.58 g) of $Ni(NO_3)_2 \cdot 6H_2O$) and malic acid (6 mmol (0.804 g), 4 mmol (0.536 g)) in molar ratios $Fe^{3+}$: malic acid=1:3 and $Ni^{2+}$: malic acid=1:2, were dissolved in a minimum amount of distilled water (50 mL) and mixed. Subsequently, ethanol was added under stirring till the reaction medium is 1:1=aqueous/ethanolic. For a complete precipitation, the pH was adjusted to 4.5–5 with a $NH_4OH$ 25% : ethanol 1:1 solution. Yellow brown iron containing compound and pale green containing zinc one were obtained. Afterward, the precipitates were aged for 24 h at 4°C. Next, they were filtered, washed with ethanol and vacuum dried. $FeC_4H_{11}NO_{7.5}$ calcd./found Fe%: 22.4/21.78; C%: 19.28/19.43; H%: 4.42/4.50; N%: 5.62/5.74. $NiC_4H_{14}O_{10}$ calcd./found Ni%: 20.89/21.40; C%: 17.10/17.00; H%: 4.98/5.08. $NiC_3H_2O_4$ (reaction intermediate) calcd./found Ni%: 36.50/37.40; C%: 22.41/20.90; H%: 1.24/0.85.

$[Zn(C_4H_4O_5)] \cdot 5H_2O$ – to the reaction mixture prepared by mixing stoichiometric quantities of aqueous solutions of 2 mmol $Zn(CH_3COO)_2$ (0.438 g) and 4 mmol malic acid (0.536 g), molar ratio $Zn^{2+}$: malic acid=1:2, ethanol was added under stirring till the reaction medium is 1:1 aqueous/ethanolic. A white compound was formed. After 24 h at 4°C aging, the compound was filtered, washed with ethanol and dried in vacuum. $ZnC_4H_{12}O_9$ calcd./found Zn%: 24.27/23.89; C%: 17.81/18.04; H%: 4.45/4.55. $ZnC_3H_2O_4$ (reaction intermediate) calcd./found Zn%: 39.06/40.19; C%: 21.50/19.47; H%: 1.19/0.82.

## *Characterization*

The UV-VIS reflectance spectra (11 000–54 000 $cm^{-1}$) were recorded with a JASCO V550 spectrophotometer using MgO as standard. IR spectra (400–4000 $cm^{-1}$) were recorded with a BIO-RAD FTIR 125 type device, in KBr pellets. The thermal measurements were performed using a Q–1500 D derivatograph in a static air atmosphere, with $\alpha$-$Al_2O_3$ as the reference compound, at a heating rate of 5 K $min^{-1}$. The magnetic susceptibility at room temperature were determined using a Faraday balance with Ni as calibrant.

## Results and discussion

### *Synthesis and physico-chemical characterization of precursors*

From the system $M^{2+}$/or $M^{3+}$-malic acid the following coordination compounds were isolated: $(NH_4)[Fe(C_4H_4O_5)(OH)_2]\cdot 0.5H_2O$; $[Ni(C_4H_4O_5)]\cdot 5H_2O$; $[Zn(C_4H_4O_5)]\cdot 4H_2O$.

Analyzing the three IR spectra (Figs 1–3 (a)) the following features may be pointed out:

- the broad bands in the region 3600–2700 $cm^{-1}$ are due to the symmetric and asymmetric stretching frequencies of the weakly bonded crystallization water molecules and hydroxyl groups;
- the water presence is confirmed also by the shoulder at ~1650 $cm^{-1}$ characteristic for its bending mode;
- the free vibration of C=O from 1730 $cm^{-1}$ is split into two very strong bands characteristic for coordinated carboxylic group, respective $\nu_{as(OCO)}$ vibration at 1590–1550 $cm^{-1}$ and $\nu_{s(OCO)}$ one at 1401–1382 $cm^{-1}$;
- in the range 1092–1083 $cm^{-1}$ a medium absorption band assigned to the stretching vibration of alcoholic hydroxyl is also present [13]. The shift of $\nu_{(C–OH)}$ toward lower frequencies indicates a possible coordination of this group to the metallic ions;
- the bands which appear in the range 563–500 $cm^{-1}$ are assigned to M–O stretching vibrations.

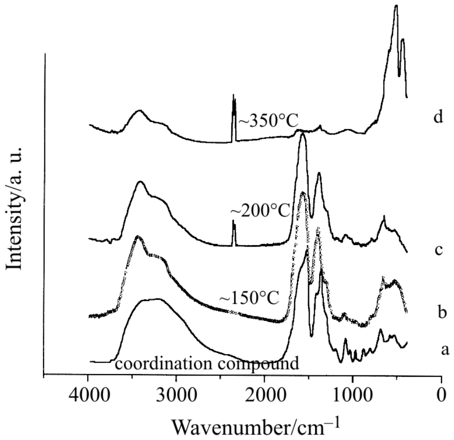

**Fig. 1** IR spectra of the $(NH_4)[Fe(C_4H_4O_5)(OH)_2]\cdot 0.5H_2O$ coordination compound and its solid reaction

On the basis of spectroscopic criteria, the magnitude of separation $\Delta\nu=\nu_{asym}-\nu_{sym}$ may represent an indication of the different coordination modes of the carboxylate ions. So, $\Delta\nu$ values included in the range 140–160 $cm^{-1}$, lower than those observed for ionic compounds ($\Delta Na_2(C_4H_4O_5)$=180 $cm^{-1}$), suggest a bridging bidentate bonding. On the

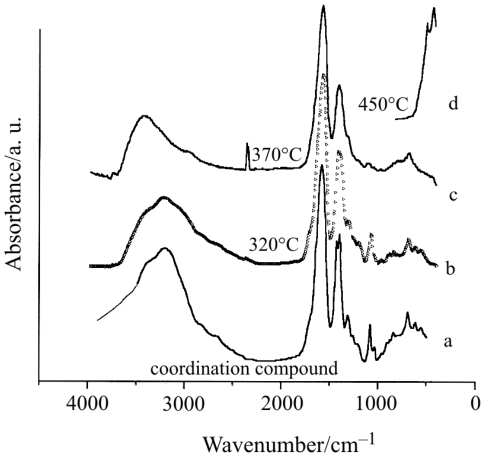

**Fig. 2** IR spectra of the $[Ni(C_4H_4O_5)]\cdot 5H_2O$ coordination compound and its solid reaction decomposition intermediates

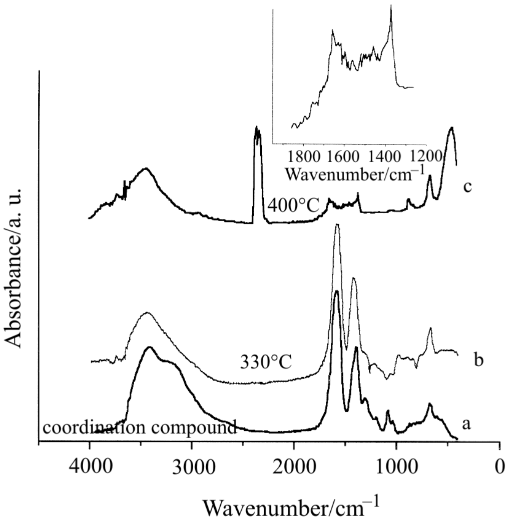

**Fig. 3** IR spectra of the $[Zn(C_4H_4O_5)]\cdot 4H_2O$ coordination compound and its solid reaction decomposition intermediates

other hand, values of $\Delta\nu > 180$ cm$^{-1}$ are characteristic for unidentate coordination compounds.

Concerning our three compounds the following conclusions may be marked:

– the $\Delta\nu$ value of 190 cm$^{-1}$ observed for zinc coordination compound suggests a monodentate bonding of the carboxylate group. Such a linkage conduct to a polymer structure of the compound similar with other transitional metal carboxylate compounds;

– the splitting into two components of the $\nu_{symm}$ vibration detected for nickel coordination compound, leading to $\Delta\nu_1=163$ and $\Delta\nu_2=189$ cm$^{-1}$ values, suggest two different bonding of COO$^-$ group: a bidentate one (corresponding to $\Delta\nu_1$ value) and a monodentate one (corresponding to $\Delta\nu_2$ value);

–for iron coordination compound the splitting of the band localized in 1440–1380 cm$^{-1}$ range is due to the bridging bidentate bond ($\Delta\nu=168$ cm$^{-1}$) and the presence of $NH_4^+$ ion (~1430 cm$^{-1}$).

At room temperature, the effective magnetic moments of nickel and iron compound was found to be $\mu=3.39$ and $\mu=6.12$ BM in agreement with an octahedral configuration of $Ni^{2+}$ and $Fe^{3+}$ high spin [14]. The value obtained for nickel compound which is higher than that corresponding to the spin value ($\mu=2.83$ BM) could be explained through the coupling spin–orbit, which is also found in the slight splitting in the electron spectrum of band $\nu_2$.

The octahedral environments of the two metallic ions are evidenced also by UV-VIS reflectance investigations.

### *Thermal decompositions of the three coordination compounds*

A stepped thermal decompositions of the coordination compounds occur in the range 50–600°C. In order to determine the stages involved in the thermal processes, the decomposition intermediates were identified by means of elemental chemical analysis and IR spectroscopy.

#### $(NH_4)[Fe(C_4H_4O_5)(OH)_2]\cdot 0.5H_2O$ coordination compound

The results of thermal analysis revealed five distinct steps of mass loss (Fig. 4). The experimental total mass loss recorded by TG measurements is 67.82% in comparison with the theoretical value of 67.91% assuming the solid residue to be $\alpha$-$Fe_2O_3$.

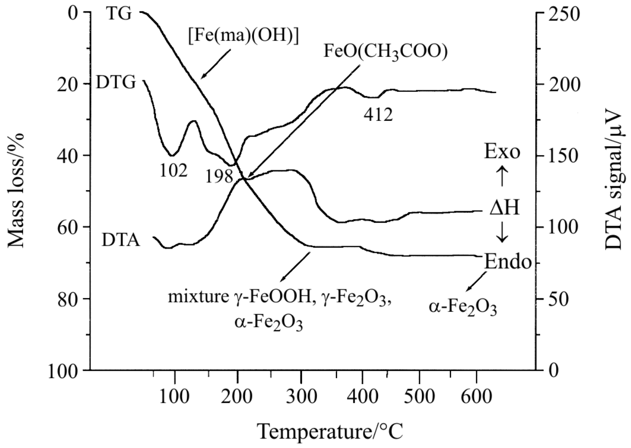

**Fig. 4** Thermoanalytical curves of $(NH_4)[Fe(C_4H_4O_5)(OH)_2]\cdot 0.5H_2O$ coordination compound (initial mass 51.09 mg, heating rate 5°C min$^{-1}$, static air)

The first step (42–138°C) represents the endothermic evolving of 0.5 water and one $NH_4OH$ molecules (calcd./found 17.99/17.68%). The anhydrous malate compound is converted into a malonic one (138–178°C) due to the anion degradation (calcd./found 12.76/12.05%). The next decomposition step (178–225°C) assigned to the formation of an iron oxoacetate $FeO(CH_3COO)$ (calcd./found 17.89/18.08%) which decomposes further (225–331°C), leading to a mixture of iron oxide and oxohydroxides. Subsequently, a well-defined decomposition step (401–448°C), assigned to water releasing from oxohydroxides generated in the reaction medium occurs.

In the IR spectra of the decomposition intermediates, the presence of malonates (Fig. 1 b) is identified by the disappearance of the band assigned to $HO^-$ group (1040 $cm^{-1}$), the formation of an acetate compound by the bands characteristic to $-CH_3$ group at 1100–1000 $cm^{-1}$ and shoulder at ~ 1360 $cm^{-1}$ (Fig. 1 c) [15]. At 350°C the IR spectrum (Fig. 1 d) shows a mixture of lepidocrite ($\gamma$-FeOOH, band at 1022 $cm^{-1}$, shoulder at 750 $cm^{-1}$), maghemite (shoulder at ~600 $cm^{-1}$) and $\alpha$-$Fe_2O_3$ (bands at 543 and 470 $cm^{-1}$). The band evidenced at 2362 $cm^{-1}$ for the intermediates obtained at 200 and 350 $cm^{-1}$ is due to the $\nu(CO_2)$, suggesting its presence in a trapped state within the solid matrix.

### $[Ni(C_4H_4O_5)]\cdot 5H_2O$ coordination compound

For this compound five decomposition mass losses followed by a mass gain are evidenced (Fig. 5). The experimental and theoretical mass losses assuming NiO formation are close (calcd./found 73.40/74.20%).

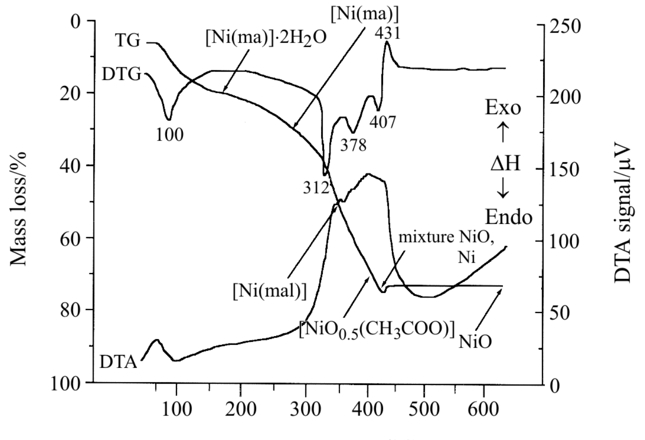

**Fig. 5** Thermoanalytical curves of $[Ni(C_4H_4O_5)]\cdot 5H_2O$ coordination compound (initial mass 49.56 mg, heating rate 5°C $min^{-1}$, static air)

The decomposition starts with two endothermic processes (70–298°C) which can be attributed to water evolving. The first one (70–190°C) represents the elimination of three crystallization water molecules (calcd./found 19.23/20.23%), while the second which occur at higher temperatures (190–298°C), of two water molecules coordinated bonded to the metallic ion (calcd./found 12.83/13.40%). The next step (298–338°C) is assigned to the oxidative fragmentation of the malate ion with formation of a malonate intermediate (calcd./found 10.69/10.02%). The malonate intermediate is identified by chemical analysis and by IR investigations through the disappearance of the bands assigned to OH group (1032 $cm^{-1}$, Fig. 2 b).

On further heating (338–425°C) the malonate intermediate decomposition occurs via an oxoacetate intermediate (338–360°C, calcd./found 17.89/18.08%, Fig. 2 c). The shoulder at ~1300 $cm^{-1}$ and the weak band at ~1050 $cm^{-1}$ are characteristic for $CH_3$ group.

A mass gain (1.26%) may be detected at the end of thermal decomposition (425–445°C). It is known that NiO promotes oxidation of carbon containing materials. Thus, it is reasonable to suppose that the carbonaceous moieties are oxidized on the NiO surface, with a concomitant reduction NiO→Ni. Since the process is conducted in air, the metal undergoes a rapid reoxidation. NiO is identified by the absorption at 495 and 435 $cm^{-1}$ (Fig. 2 d).

### $[ZnC_4H_4O_5]\cdot 4H_2O$ coordination compound

The coordination compound undergoes a stepwise decomposition in four distinct stages of mass loss (Fig. 6). The observed mass loss (67.12%) is in good agreement with the calculated one (67.27%) considering as residue ZnO.

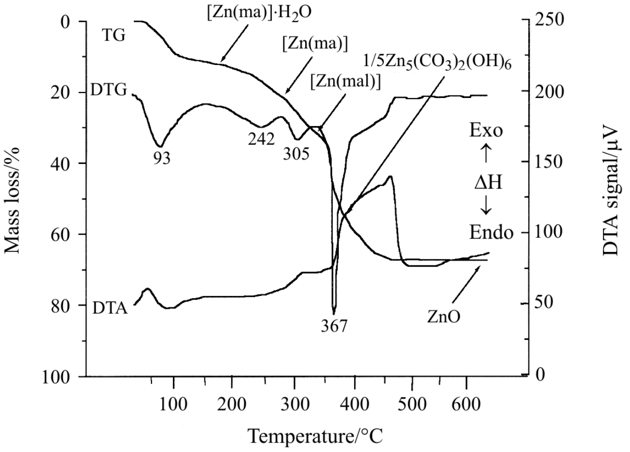

**Fig. 6** Thermoanalytical curves of $[Zn(C_4H_4O_5)]\cdot 4H_2O$ coordination compound (initial mass 49.13 mg, heating rate 5°C $min^{-1}$, static air)

The decomposition starts with two endothermic steps (55–275°C) corresponding to release of two (calcd./found 13.00/13.98%) and respectively one (calcd./found 7.16./7.88%) water molecules. The next decomposition step (275–350°C) represent the oxidative fragmentation of malate anion with formation of the malonic intermediate (calcd./found 11.93/11.42%), identified by chemical analysis and IR spectroscopy (Fig. 3 curve b). On further heating, this compound decompose with formation of hydrozincite [$Zn_5(CO_3)_2\cdot 6(OH)$]. At this stage the absorptions at 1380, 877 and 675 $cm^{-1}$ indicates de formation of $CO_3^{2-}$, while the weak band from 3710 $cm^{-1}$ and the shoulder from 1737 $cm^{-1}$ evidence the presence of $HO^-$ group (Fig. 3 c).

Solid state mechanism

By means of thermoanalytical, chemical analysis and IR measurements the following thermal decomposition steps of the coordination compounds compound may be assumed:

$$\begin{gathered}(NH_4)[Fe(ma)(OH)_2]\cdot 5H_2O \xrightarrow{42-138\,°C} [Fe(ma)(OH)] \\ \xrightarrow{138-178\,°C} [Fe(mal)(OH)] \xrightarrow{178-225\,°C} FeO(CH_3COO) \\ \xrightarrow{225-331\,°C} \text{mixture } \gamma\text{-FeOOH, } \gamma\text{-}Fe_2O_3 \text{ and } \alpha\text{-}Fe_2O_3 \xrightarrow{401-448\,°C} 0.5\alpha\text{-}Fe_2O_3\end{gathered} \tag{1}$$

$$\begin{gathered}[Ni(ma)]\cdot 5H_2O \xrightarrow{70-190\,°C} [Ni(ma)]\cdot 2H_2O \xrightarrow{190-298\,°C} [Ni(ma)] \xrightarrow{298-338\,°C} [Ni(mal)] \\ \xrightarrow{338-360\,°C} NiO_{0.5}(CH_3COO) \xrightarrow{360-425\,°C} \text{mixture NiO and Ni} \xrightarrow{425-445\,°C} NiO\end{gathered} \tag{2}$$

$$\begin{gathered}[Zn(ma)]\cdot 4H_2O \xrightarrow{55-180\,°C} [Zn(ma)]\cdot H_2O \xrightarrow{180-275\,°C} [Zn(ma)] \xrightarrow{275-350\,°C} [Zn(mal)] \\ \xrightarrow{350-374\,°C} 1/5Zn_5(CO_3)_2(OH)_6 \xrightarrow{374-471\,°C} ZnO\end{gathered} \tag{3}$$

where *ma*, *mal* represent the dianions of malic and malonic acids.

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