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# Thermal behaviour of some solid coordination compounds with malic acid as ligand

T.V. Albu[a,*], Ioana Mindru[a], Luminita Patron[a], E. Segal[b], Maria Brezeanu[a]

[a]Institute of Physical Chemistry, Splaiul Independentei 202, Sector 6, Bucharest, Romania
[b]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, B-dul Republicii 13, Sector 1, Bucharest, Romania

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## Abstract

The authors present the results concerning the synthesis and the characterisation of some coordination compounds with malic acid as ligand: $Co(C_4H_4O_5)\cdot 2H_2O$, $[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O$ and $[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$. The heterometallic compound is a precursor of Co-ferrite. The values of the non-isothermal kinetic parameters for the dehydration reactions were determined. These values obtained by three integrals methods are in a satisfactory agreement. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Coordination compounds; Co-ferrite; Decomposition; Kinetics; Non-isothermal

## 1. Introduction

Ferrites represent an important part of advanced materials that enjoy a wide range of applications. Their utilisation extends to ceramic materials and catalysts [1,2], sensors and magnetic ink [3,4] etc.

The chemical and physical properties of oxidic materials with spinel structure depend on the synthesis method and on the treatment that affects the interdispersion of components and the defining of morphology. Therefore considerable efforts have been made to develop synthesis methods that yield precursors with two or more metallic ions included in the same crystalline structure. Such a method seems to be the thermal decomposition of polynuclear coordination compounds.

In this note, an investigation concerning the possibility to obtain $Fe_2^{III}Co^{II}O_4$, by using the thermal decomposition of polynuclear coordination compounds with malic acid as ligand is presented. The choice of malic acid as ligand is justified by our experience concerning some simple and complex systems with this hydroxycarboxylic acid [5,6].

## 2. Experimental

The compounds were separated through a variant of the method used by Melson and Pickering [7]. 24 h after complete precipitation, the coordination compounds were filtered, washed with ethanol and dried in vacuum, in the presence of $P_4O_{10}$ and subsequently characterized by elemental chemical and physico-chemical analysis. The metal content was determined by the atomic absorption spectrophotometry and the C, H content by the normal combustion method.

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[*] Corresponding author.

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The following results were obtained:

$Co(C_4H_4O_5)\cdot 2H_2O$: Calcd/Found: Co%: 25.99/26.03; C%: 21.14/21.54; H%: 3.52/4.08

$[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O$: Calcd/Found: Fe%: 29.19/28.99; C%: 12.50/13.02; H%: 4.16/4.54

$[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$ Calcd/Found: Fe%: 18.33/18.45; Co%: 9.65/9.72; C%: 15.71/16.17; H%: 3.92/4.23

The electronic spectra were recorded on a Specord M-40 spectrophotometer, in the range 50,000–11,000 $cm^{-1}$. The IR spectra were obtained in the range 400–4000 $cm^{-1}$, using an IR Specord type M-80 spectrophotometer.

The heating curves have been recorded using a Paulik-Paulik-Erdey Q 1500 D derivatograph, in static air atmosphere, with $\alpha$-$Al_2O_3$as the inert reference compound, at variously heating rates in the range 1.5–10 K $min^{-1}$ in the temperature range 20–1000°C. The derivatographic data have been used in order to evaluate the decomposition non-isothermal kinetic parameters by three integral methods after Coats–Redfern [8], Flynn–Wall (for constant heating rate) [9] and Urbanovici–Segal [10] who modified Coats–Redfern method. The data were worked out by help of a computer program written by Dragoe and Segal [11]. The program allows to obtained the TG curves in coordinations ($\alpha$, $T^\circ$) using the obtained Coats–Redfern values of the kinetic parameters.

## 3. Results and discussion

In order to establish the optimal conditions of isolation of some coordination compounds, we succeeded in the study of the systems:

$$Co(II) : C_4H_4O_5^{2-} \qquad (I)$$

$$Fe(III) : C_4H_4O_5^{2-} \qquad (II)$$

and

$$2Fe(III) : 1Co(II) : C_4H_4O_5 \qquad (III)$$

where $C_4H_4O_5^{2-}$is the dianion of the malic acid.

The molecular formulae of these coordination compounds were established by correlating the elemental chemical data with the IR and electronic spectra. The following general formuale are proposed:

$$Co(C_4H_4O_5)\cdot 2H_2O$$

$$[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O$$

$$[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$$

The coordination compounds are crystalline powders. Their colour depends on the nature of the metallic ions: pink for the Co(II)-compound, yellow for the Fe(III)-compound and brown-yellow for the mixed one. All of them are strongly water soluble and insoluble in most organic solvents.

Data regarding the coordination of the ligand in the isolated compounds were obtained, by recording IR spectra of these compounds over 400–4000 $cm^{-1}$ range and comparing them with that of malic acid. (Table 1).

The broad band occurring in the 3200–3500 $cm^{-1}$ range in all of these spectra can be assigned to the formation of hydrogen bonds in water or/and ethanol. This band confirms the presence of the water molecules in the molecules of the investigated compounds.

The IR spectra of Fe(III)-malate and of the mixed coordination compounds show an average intensity band at $\sim$3380 $cm^{-1}$ that may be assigned to the OH frequency. This band correlated with those which appeared at $\sim$970 $cm^{-1}$ (assigned to OH deformation ($\delta_{OH}$) for the OH bridge) and at $\sim$530 $cm^{-1}$ (assigned to $\nu_{M-O}$ (M–OH)), respectively, demonstrates the existence of OH bridges. The band at $\sim$1730 $cm^{-1}$ in the vibration spectrum of the malic acid assigned to $\nu_{CO}$ is replaced in all compounds spectra by the bands: $\nu_{as}$(OCO) at $\sim$1570–1550 $cm^{-1}$ and $\nu_s$(OCO) at $\sim$1300 $cm^{-1}$, respectively. The presence of these two bands suggests the coordination of both $COO^-$ groups of the malic acid molecules to their metallic ions.

A sharp and strong band assigned to $\nu_{C-OH}$ was evidenced at $\sim$1120 $cm^{-1}$ in the malic acid spectrum. This band is shifted to the low frequencies in the spectra of coordination compounds ($\sim$1090–1070 $cm^{-1}$), due to the coordination of alcoholic group of malic dianion to the metallic ions.

The electronic spectra recorded over 9000–25,000 $cm^{-1}$ for all of these compounds suggested an octahedral high spin configuration for Fe(III) ($d^5$) and Co(II)($d^7$) ions, respectively. The band positions and assignments are listed in Table 2.

Table 1
IR spectral data of malic acid and mixed malate compound

| Malic acid | $[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$ | Assignment |
|---|---|---|
| ~3400 vs | 3450–3250 br | $\nu_{HO,\ OH}$ |
| 1730 vs | – | $\nu_{CO}$ |
| 1650 m | 1560 vs | $\nu_{OCOasym}$ |
| 1440 m | – | $\nu_{CO} + \delta_{OH}$ |
| 1420 m | – | |
| – | 1370 vs | $\nu_{OCOsym}$ |
| 1295 m | – | |
| 1270 w | 1250 w | |
| 1230 w | – | |
| 1195 m | 1190 w | $\nu_{CCasym}$ |
| 1120 w | 1080 m | $\nu_{C\text{–}OH}$ |
| 1100 w | 1020 w | |
| – | 970 m | $\delta_{OH}$ |
| 960, 935 m | – | |
| – | 860 m | $\nu_{H\ Orock}$ |
| 760 w | – | $\delta_{COOH}$ |
| 670 m | 680 m | |
| – | 580 m | |
| 640, 540 w | – | |
| – | 530 m | $\nu_{MO\ (OH)}$ |

Table 2
d–d electronic transitions of the metal ions present in the coordination compounds

| Compound | Band position ($cm^{-1}$) | | |
|---|---|---|---|
| | $^6A_{1g} \rightarrow {}^4T_{1g}$ | $^4A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ (G) | $^4T_{1g} \rightarrow {}^4T_{1g}$ (P)($\nu_3$) |
| $Co(C_4H_4O_5)\cdot 2H_2O$ | – | – | 18,500 |
| $[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O$ | 11,000 | 23,300 | – |
| $[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$ | 11,200 | 23,800 | 20,000 |

In order to establish if the polynuclear coordination compounds may be used as precursors for Co-ferrites, the thermal decomposition of these compounds was investigated.

### 3.1. Thermal behaviour of $Co(C_4H_4O_5)\cdot 2H_2O$

The decomposition curves obtained for $Co(C_4H_4O_5)\cdot 2H_2O$ are shown in Fig. 1.

According to the derivatographic data, obtained for $\beta = 8.5\ K\ min^{-1}$, the thermal decomposition occurs through the reactions described by the equations:

$$Co(C_4H_4O_5)\cdot 2H_2O(g) \overset{110^\circ C}{\rightarrow} Co(C_4H_4O_5)(s) + 2H_2O(g) \tag{1}$$

$$Co(C_4H_4O_5)(s) \overset{280^\circ C}{\rightarrow} Co(C_3H_2O_4)(s) + \text{gaseous products} \tag{2}$$

$$Co(C_3H_2O_4)(s) + 13/6\ O_2(g) \overset{300^\circ C}{\rightarrow} 1/3\,Co_3O_4(s) + 3Co_2(g) + H_2O(g) \tag{3}$$

The temperatures written above the arrow correspond to the maximum decomposition rate as shown by the DTG curve. The only kinetically workable reaction was the first one (reaction 1) corresponding to the dehydration. The values of the kinetic parameters obtained under non-isothermal conditions are listed in Table 3.

A satisfactory agreement among the values of the kinetic parameters obtained by help of the three

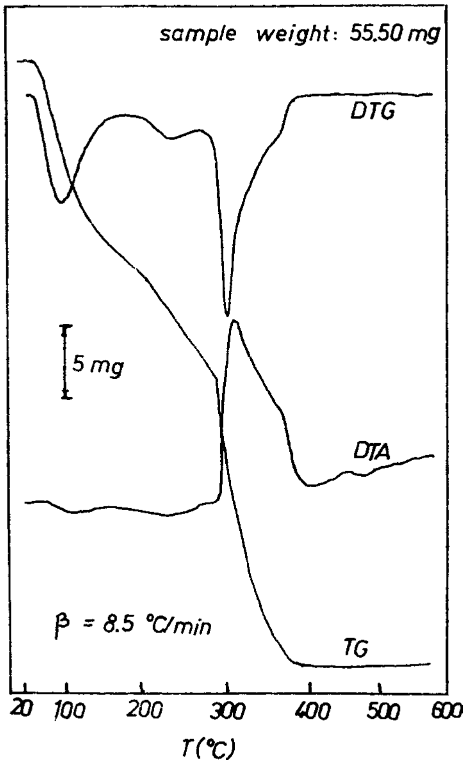

Fig. 1. The derivatogram of $Co(C_4H_4O_5){\cdot}2H_2O$ for $\beta = 8.5\ K\ min^{-1}$.

applied integral methods are to be noticed. Fig. 2 shows the regenerated thermogravimetric curve in coordinates ($\alpha$, $T^0$) and the experimental points which lie practically on it.

### 3.2. Thermal behaviour of $[Fe_2(C_4H_4O_5)(OH)_4]{\cdot}4H_2O$

According to the derivatogram recorded with $\beta = 8.25\ K\ min^{-1}$, in the range 25–700°C, the decomposition of the investigated coordination compound occurs in the following two reactions:

$$[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O(s) \overset{115^\circ C}{\rightarrow} [Fe_2(C_4H_4O_5)(OH)_4](s) + 4H_2O(g) \quad (4)$$

$$[Fe_2(C_4H_4O_5)(OH)_4](s) + 6O_2(g) \overset{220^\circ C}{\rightarrow} Fe_2O_3(s) + 4CO_2(g) + 4H_2O(g) \quad (5)$$

For reaction (4), the only kinetically workable, the values of the non-isothermal kinetic parameters are listed in Table 3. Fig. 3 shows the regenerated curve ($\alpha$, $T^0$) for the same reaction as well as the experimental points on it.

### 3.3. Thermal behaviour of $[Fe_2Co(C_4H_4O_5)_2(OH)_4]{\cdot}6H_2O$

The following two decomposition reactions have been identified at the heating of this compound with a heating rate of $8.2\ K\ min^{-1}$.

$$[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O(s) \overset{115^\circ C}{\rightarrow} [Fe_2Co(C_4H_4O_5)_2(OH)_4](s) + 6H_2O(g) \quad (6)$$

Table 3
Value of the non-isothermal kinetic parameters for reactions (1), (4) and (5)

| | Method | $n$ | $E$ (kJ mol$^{-1}$) | $A$ (s$^{-1}$) | /r/[a] |
|---|---|---|---|---|---|
| Reaction (1), $\beta = 3.5\ K\ min^{-1}$ | Coats–Redfern | 1.9 | 55.5 | $1.1 \times 10^5$ | 0.9923 |
| | Flynn–Wall | 1.8 | 56.6 | $2.3 \times 10^5$ | 0.9939 |
| | C–R modified | 1.8 | 55.0 | $9.9 \times 10^4$ | 0.9920 |
| Reaction (4) $\beta = 3.9\ K\ min^{-1}$ | Coats–Redfern | 1.5 | 57.3 | $1.6 \times 10^5$ | 0.9990 |
| | Flynn–Wall | 1.5 | 60.3 | $6.6 \times 10^5$ | 0.9992 |
| | C–R modified | 1.4 | 56.8 | $1.5 \times 10^5$ | 0.9989 |
| Reaction (5) $\beta = 3.9\ K\ min^{-1}$ | Coats–Redfern | 1.7 | 55.6 | $6.7 \times 10^4$ | 0.9977 |
| | Flynn–Wall | 1.7 | 58.8 | $3.0 \times 10^5$ | 0.9982 |
| | C–R modified | 1.7 | 56.6 | $1.1 \times 10^5$ | 0.9975 |

[a] /r/ is the correlation coefficient of the liniar regression.

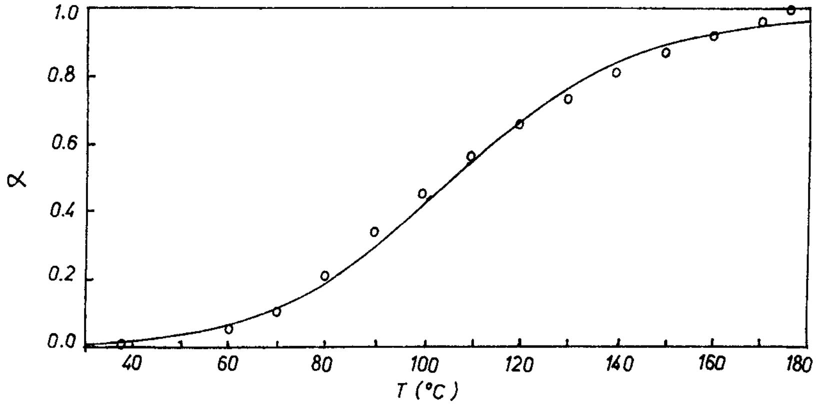

Fig. 2. Regenerated ($\alpha$, $T^0$) curve for the reaction (1) at $\beta = 3.5$ K min$^{-1}$ (———) calculated curve; (o) experimental points.

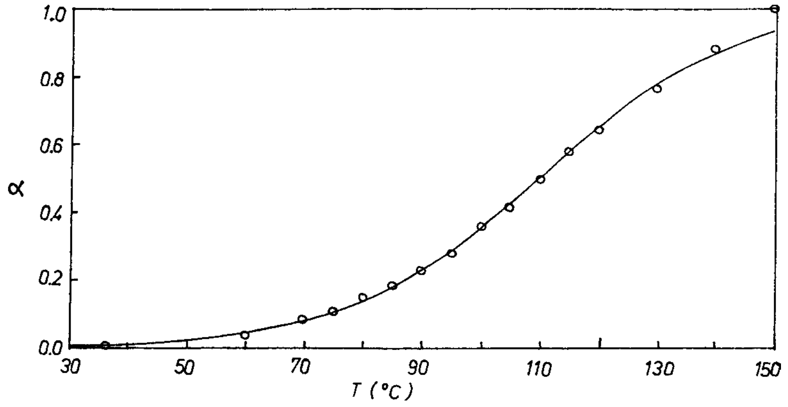

Fig. 3. Regenerated ($\alpha$, $T^0$) curve for the reaction (4) at $\beta = 3.90$K * min$^{-1}$.

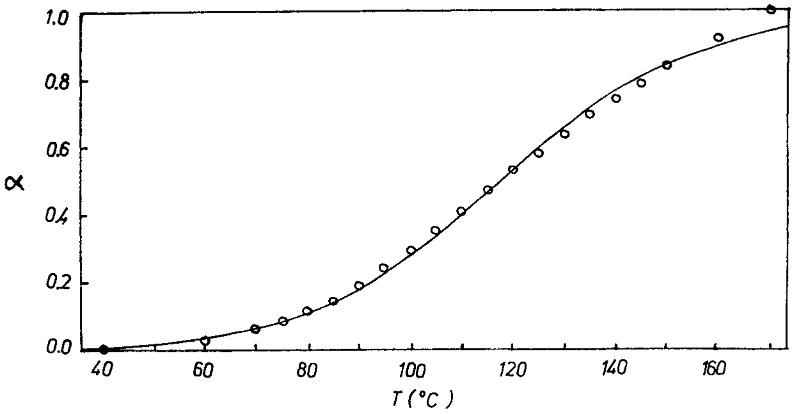

Fig. 4. Regenerated ($\alpha$, $T^0$) curve for the reaction (6) at $\beta = 3.91$ K * min$^{-1}$.

$$[Fe_2Co(C_4H_4O_5)_2(OH)_4](s) + 6O_2(g) \xrightarrow{220^\circ C} [Fe_2CoO_4](s) + 8CO_2(g) + 6H_2O(g) \quad (7)$$

As in the former case only the dehydration reaction (6) is practically workable. The non-isothermal kinetic parameters are also listed in Table 3. One can notice a quite good agreement between the values of the non-isothermal kinetic parameters obtained by help of the applied methods. The regenerated thermogravimetric curve in coordinates ($\alpha$, $T^0$) and the experimental points which lie on it (Fig. 4) show the correctness of the values of the determined non-isothermal kinetic parameters.

The conclusion inferred from the values of the kinetic parameters is that the first decomposition reaction is the same for all these three compounds.

## 4. Conclusions

1. The following three compounds: $Co(C_4H_4O_5)\cdot 2H_2O$ $[Fe_2(C_4H_4O_5)(OH)_4]\cdot 4H_2O$ $[Fe_2Co(C_4H_4O_5)_2(OH)_4]\cdot 6H_2O$ have been synthesized and characterized by IR and electronic spectra.
2. The heating curves of these compounds have been recorded in the temperature range 25–1000°C.
3. The non-isothermal kinetic parameters of the hydration which is the first reaction of the thermal decomposition, for all the investigated compounds, have been determined.

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