

Thermal investigation of solid 2-methoxycinnamylidenepyruvate of some bivalent transition metal ions

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Abstract Solid-state M-2-MeO-CP compounds, where M represents bivalent Mn, Fe, Co, Ni, Cu, Zn and 2-MeO-CP is 2-methoxycinnamylidenepyruvate, were synthesized for the first time. Simultaneous thermogravimetry and differential thermal analysis, differential scanning calorimetry, X-ray powder diffractometry, infrared spectroscopy, TG-FTIR system, elemental analysis and complexometry have been used to characterize and to study the thermal behaviour of the compounds. The dehydration in all the compounds, except for iron occurs in a single step. The thermal decomposition of the anhydrous compounds occurs in two or three steps with the formation of the respective oxides, Mn_3O_4 , Fe_2O_3 , Co_3O_4 , NiO, CuO and ZnO, as final residue. The results also provided information concerning the thermal behaviour and identification of the gaseous products evolved during the heating of these compounds.

Keywords Bivalent transition metals · 2-methoxycinnamylidenepyruvate · Thermal behaviour

Introduction

Synthesis of benzylidenepyruvic acid (HPB) and cinnamylidenepyruvic and (HCP), as well as phenyl-substituted derivatives of these acids, has been reported [1, 2]. These acids are of continuous interest as intermediates in

pharmacological, industrial and chemical syntheses, in the development of enzyme inhibitors and drugs, and in other studies [3–6].

Several metal-ion compounds of phenyl-substituted derivatives of benzylidenepyruvate $C_6H_5(CH)_2COCOO^-$ and cinnamylidenepyruvate, $C_6H_5(CH)_4COCOO^-$, have been investigated in aqueous solutions [7, 8] and in solid state [9–13]. These works report the thermodynamic stability (β_1) and spectroscopic parameters (ϵ_{1max} , λ_{max}) in aqueous solutions associated with 1:1 complex species. In the solid state, the works reported the synthesis and investigation of the compounds by thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry and other methods of analysis. Establishment of the stoichiometry and the details of the thermal behaviour were main purposes of these studies.

In this article, solid-state compounds of bivalent manganese, iron, cobalt, nickel, copper and zinc with 2-methoxycinnamylidenepyruvate, $2-CH_3O-C_6H_4-(CH)_4COCOO^-$, (2-MeO-CP) were prepared. These compounds obtained for the first time were investigated by means of complexometry, elemental analysis, X-ray powder diffractometry, infrared spectroscopy, simultaneous TG and DTA and DSC. The results have allowed obtaining information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

Experimental

The 2-methoxycinnamaldehyde, $(CH_3O-C_6H_4-(CH)_2-CHO)$ 96% pure predominantly trans, was obtained from Aldrich, and the sodium pyruvate ($H_3C-CO-COONa$) 99% pure was obtained from Sigma.

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Sodium 2-methoxycinnamylidenepyruvate (Na-2-MeO-CP) and its corresponding acid were both synthesized following the same procedure as well as described in literature [14].

Aqueous solution of Na-2MeO-CP 0.1 mol L^{-1} was prepared from 2-MeO-HCP suspension by treatment with sodium hydroxide 0.1 mol L^{-1} ; whose pH was adjusted around 8 using a pH-meter with a glass electrode. Aqueous solutions of the bivalent metal ions were prepared by dissolving the respective chlorides.

The solid-state compounds were prepared by adding slowly, with continuous stirring, the ligand solution to the respective metal-chloride solutions until total precipitation of the metal ions.

The precipitates were washed with distilled water until chloride ions were eliminated, filtered through and dried on Whatman n° 42 filter paper and kept in a desiccator over anhydrous calcium chloride.

To avoid oxidation of Mn(II) and Fe(II), all their solutions, as well as the water employed for washing their precipitates were purged with nitrogen gas.

In the solid-state compounds, metal ions, water and 2-MeO-CP contents were determined from TG curves. The metal ions were also determined by complexometric titration with standard EDTA solution [15, 16] after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution.

X-ray powder patterns were obtained with a Siemens D-5000 X-ray diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and setting of 40 kV and 20 mA.

Infrared spectra for Na-2-MeO-CP and for its metal-ion compounds were run on a Nicolet model Impact 400 FTIR instrument within the $4000\text{--}400 \text{ cm}^{-1}$ range. The solid samples were pressed into KBr pellets.

Carbon and hydrogen microanalysis were performed using elemental analyser (EA) 1110 CHNS-O Elemental Analyzer (CE instruments.)

Simultaneous TG-DTA and DSC curves were obtained with two thermal analysis systems, model SDT 2960 and

DSC Q10, both from TA Instruments. The purge gas was an air flow of 100 mL min^{-1} for the TG-DTA and 50 mL min^{-1} for the DSC. A heating rate of 20 K min^{-1} for the TG-DTA and 40 K min^{-1} (this heating rate was adopted because it was the condition which presented the best resolution of these curves) for the DSC was adopted, with samples weighing 7.00 mg for the TG-DTA and 5.00 mg for the DSC. Alumina and aluminium crucibles, the latter with perforated cover, were used for TG-DTA and DSC, respectively.

The monitoring of the gaseous products was carried out using a Thermogravimetric Analyzer Mettler TG-DTA coupled to a Fourier-transform infrared (FTIR) Nicolet iS10 spectrometer with gas cell and DTGS KBr detector. The furnace and the heated gas cell (523 K) were coupled through a heated ($T = 473 \text{ K}$) 120 cm stainless steel line transfer with diameter of 2 mm, both purged with dry nitrogen (50 mL min^{-1}). The FTIR spectra were recorded with 32 scans per spectrum at a resolution of 4 cm^{-1} .

Results and discussion

The analytical and thermoanalytical (TG) results of the synthesized compounds are shown in Table 1. These results permitted to establish the stoichiometry of the compounds, which is in agreement with the general formula $\text{M}(2\text{-MeO-CP})_2 \cdot n\text{H}_2\text{O}$, where M represents Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), 2-MeO-CP is 2-methoxycinnamylidenepyruvate and $n = 1,5$ (Fe), 2 (Mn, Co, Cu, Zn) and 3 (Ni).

FTIR of the compounds

In 2-MeO-CP (sodium salt) strong band at 1581 cm^{-1} and a medium intensity band located at 1402 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [17, 18], the band centred at 1668 cm^{-1} is typical of a conjugated ketonic

Table 1 Analytical and thermoanalytical (TG) data of the $\text{M}(\text{L})_2 \cdot n\text{H}_2\text{O}$ compounds; M metal; L 2-methoxycinnamylidenepyruvate

Compounds	Oxide/%			Ligand lost/%		Water/%		Carbon/%		Hydrogen/%		Residue
	Calcd.	EDTA	TG	Calcd.	TG	Calcd.	TG	Calcd.	Elemental analysis	Calcd.	Elemental analysis	
Mn(L) ₂ ·2H ₂ O	13.79	13.47	13.80	79.71	79.56	6.51	6.63	56.42	56.31	4.01	3.85	Mn ₃ O ₄
Fe(L) ₂ ·1.5H ₂ O	14.64	14.23	14.42	80.40	80.58	4.96	5.00	57.26	57.39	4.07	4.29	Fe ₂ O ₃
Co(L) ₂ ·2H ₂ O	14.40	13.96	14.18	79.13	79.10	6.47	6.72	56.02	55.90	3.99	3.80	Co ₃ O ₄
Ni(L) ₂ ·3H ₂ O	12.99	12.73	12.79	77.61	77.91	9.40	9.30	54.28	54.49	3.86	3.97	NiO
Cu(L) ₂ ·2H ₂ O	14.15	14.33	13.94	79.44	79.71	6.41	6.34	55.56	55.85	3.95	4.00	CuO
Zn(L) ₂ ·2H ₂ O	14.43	14.14	14.20	79.18	79.30	6.39	6.50	55.38	55.46	3.94	3.70	ZnO

Table 2 Spectroscopic data for sodium 2-methoxycinnamylidenepyruvate and compounds with some bivalent metal ions

Compounds	Anti-symmetrical vibrations of the COO ⁻ group $\nu_{\text{asym}}(\text{COO}^-)/(\text{cm}^{-1})$ S = strong	Symmetrical vibrations of the COO ⁻ group $\nu_{\text{asym}}(\text{COO}^-)$ m = medium	Vasym (COO ⁻) (NaL)-(C=O) (metal compounds) $\Delta\nu(\text{COO}^-)/(\text{cm}^{-1})$	$\nu\text{C=O}$: ketonic carbonyl stretching frequency $\nu(\text{C=O}^-)/(\text{cm}^{-1})$	$\Delta\nu(\text{C=O})$ (NaL)- $\nu(\text{C=O})$ (metal compounds) $\Delta\nu(\text{C=O}^-)$
Na L	1581 s	1402 m	–	1668	–
Mn(L) ₂ ·2H ₂ O	1545 s	1392 m	36	1630	38
Fe(L) ₂ ·1.5H ₂ O	1541 s	1394 m	40	1626	42
Co(L) ₂ ·2H ₂ O	1541 s	1393 m	40	1630	38
Ni(L) ₂ ·3H ₂ O	1541 s	1391 m	40	1630	38
Cu(L) ₂ ·2H ₂ O	1551 s	1391 m	40	1620	48
Zn(L) ₂ ·2H ₂ O	1543 s	1393 m	38	1632	36

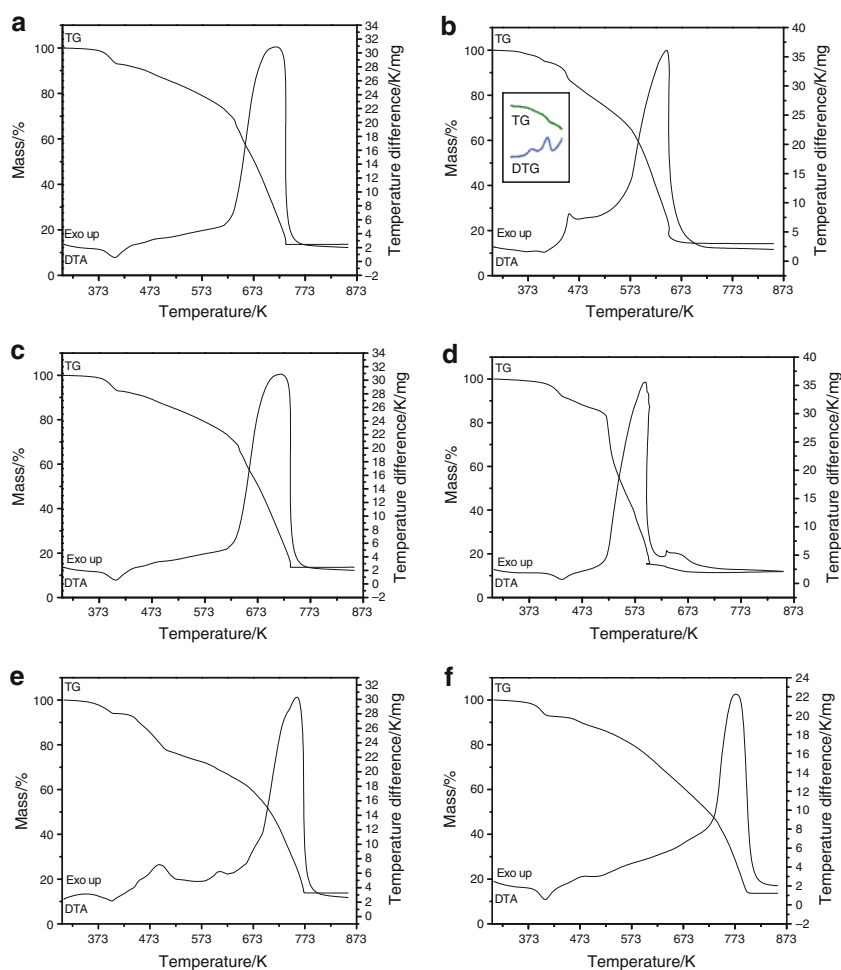
carbonyl group [17, 19]. For all the compounds the bands assigned to the anti-symmetrical stretching frequencies of the carboxylate groups, as well as that assigned to the ketonic carbonyl are shifted to lower values relative to the corresponding frequencies in 2-MeO-CP itself (sodium salt). This behaviour indicates that both groups act as coordination centres in the metal compounds [19, 20] and in agreement with the other metal-ion compounds of

phenyl-substituted derivatives of benzylidene and cinnamylidenepyruvate [21, 22]. The data displayed in Table 2 show that these shifts are dependent on the metal ions.

TG–DTA and DSC

Simultaneous TG–DTA and DSC curves of the compounds are shown in Figs. 1 and 2, respectively. The TG–DTA

Fig. 1 TG–DTA curves of the compounds: **a** Mn(L)₂·2H₂O (m = 7.16 mg), **b** Fe(L)₂·1.5H₂O (m = 7.18 mg), **c** Co(L)₂·2H₂O (m = 7.18 mg), **d** Ni(L)₂·3H₂O (m = 7.12 mg), **e** Cu(L)₂·2H₂O (m = 6.70 mg) and **f** Zn(L)₂·2H₂O (m = 7.13 mg); L 2-methoxycinnamylidenepyruvate



curves show mass losses in three or four steps, corresponding to endothermic peaks due to dehydration and exothermic peaks attributed to the oxidation of the organic matter. The DSC curves also show endothermic and exothermic peaks, corresponding to the mass losses displayed by the TG curves. The thermal stability of the anhydrous compounds (I), as well as the final temperature of thermal decomposition (II) as shown by the TG–DTA curves, depends on the nature of the metal ion which follow the order:

(I) Ni = Co > Zn > Cu > Fe = Mn

(II) Zn > Cu > Mn > Co > Fe = Ni

In our previous study, the TG–DTA curves also showed that as much (I) as (II) depends on the nature of the ligand, as observed for other compounds with those metal ions, where the order were not the same [23, 24].

The thermal behaviour of the compounds is dependent on the nature of the metal ion, and so the features of each of these compounds are individually discussed.

Manganese compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1a and 2a, respectively. The first mass loss observed between 323 and 413 K (TG), corresponding to an endothermic peak at 403 K (DTA) and 413 K (DSC) is due to dehydration which occurs in a single step, with loss of 2H₂O (Calc. = 6.51%, TG = 6.63%). The thermal decomposition of the anhydrous compound occurs in two overlapping steps between 413–633 K and 633–738 K, with losses of 24.89 and 54.67%, respectively, corresponding to exothermic peak at 713 K (DTA) or the exothermic peak at 483 K and broad exotherms between 613 and >873 K (DSC) which are attributed to oxidation of the organic matter. No thermal event is observed in the DTA curve corresponding to the mass loss between 413–633 K, probably due to heat evolved in this step is not enough to produce the thermal event. The total mass loss up to 873 K is in agreement with the Mn₃O₄ as final residue. (Calc. = 86.22%, TG = 86.19%).

Iron compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1(b) and 2(b), respectively. The mass loss observed up to 413 K (TG), with evidence of two consecutive steps, corresponding to an endothermic peak at 408 K (DTA) or 413 K (DSC), is due to dehydration with loss of 1.5 H₂O (Calc. = 4.96%, TG = 5.00%). A closer examination of the dehydration process is shown in the Fig. 1b with an enlarged detail of the TG curve and its respective DTG

curve, which shows two peaks in the DTG curve related to the two mass losses between 303 and 423 K, confirming that the dehydration occurs in two steps: between 323–383 K and 383–413 K, respectively. Immediately after the dehydration, the anhydrous compound shows mass losses in three overlapping steps: between 413 and 463 K (6.32%), 463 and 573 K (22.13%) and 573 and 683 K (52.13%) corresponding to the exothermic peaks at 453 K and 643 K (DTA) or the exothermic peak at 453 K and broad exotherms between 523 and >873 K (DSC), attributed to the oxidation of Fe(II)–Fe(III) of the organic matter. The total mass loss up to 683 K is in agreement with the Fe₂O₃ as final residue (Calc. = 85.36%, TG = 85.58%).

Cobalt compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1c and 2c, respectively. The first mass loss that occurs between 323 and 438 K (TG), corresponding to endothermic peak at 428 K (DTA) or 438 K (DSC), is due to dehydration with loss of 2H₂O (Calc. = 6.47%, TG = 6.72%). The thermal decomposition of the anhydrous compound occurs in two steps: between 438–623 K and 623–703 K, with losses of 32.54 and 46.56%, respectively, corresponding to exothermic peak at 688 K (DTA) or the broad exotherms between 643 and >873 K, attributed to the oxidation of the organic matter. No thermal event is observed in the DTA and DSC curves corresponding to the mass losses between 438 and 623 K, as already observed in the manganese compound. The total mass loss up to 703 K is in agreement with the Co₃O₄ as final residue. (Calc. = 85.60%, TG = 85.82%).

Nickel compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1d and 2d, respectively. The mass loss that occurs between 323 and 438 K (TG), corresponding to endothermic peak at 433 K (DTA) or 438 K (DSC), is due to dehydration with loss of 3H₂O (Calc. = 9.40%, TG = 9.30%). The thermal decomposition of the anhydrous compound occurs in three steps: between 438–518, 518–603 and 603–683 K, with losses of 5.70, 69.85 and 2.36%, respectively. These mass losses correspond to exothermic peaks at 593 and 633 K (DTA) or the broad exotherms between 498 and >873 K (DSC), attributed to the oxidation of the organic matter. The total mass loss up to 683 K is in agreement with the NiO as final residue (Calc. = 87.01%, TG = 87.21%). The small mass gain in the 670–800 K range is attributed to the oxidation of Ni to NiO caused by the organic matter decomposition, during the previous step.

Copper compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1e and 2e, respectively. The mass loss observed between 323 and 403 K (TG), corresponding to endothermic peak at 398 K (DTA) or 403 K (DSC), is due to dehydration with loss of 2H₂O (Calcd. = 6.41%, TG = 6.34%). The anhydrous compound is stable up to 423 K and above this temperature the thermal decomposition occurs in three steps with losses of 17.26% (423–503 K), 16.10% (503–623 K) and 46.35% (623–773 K). These mass losses corresponding to the exothermic peaks at 493, 608 and 758 K (DTA) or to the exothermic peaks at 443, 483, 350 and 623 K and a large exotherm between 653 and 853 K (DSC), attributed to the oxidation of the organic matter. The total mass loss up to 773 K is in agreement

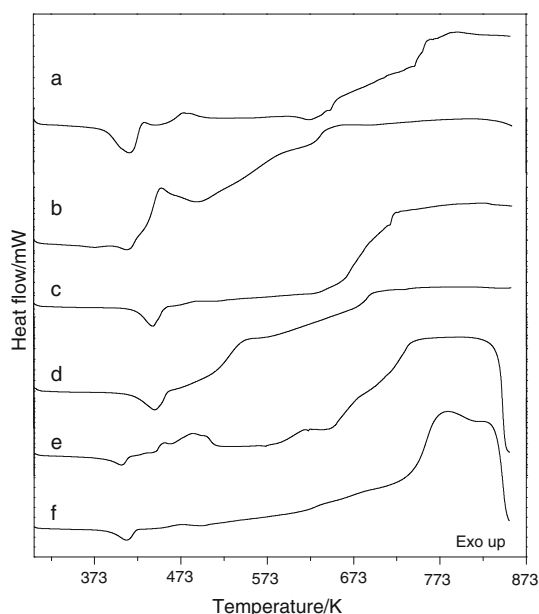
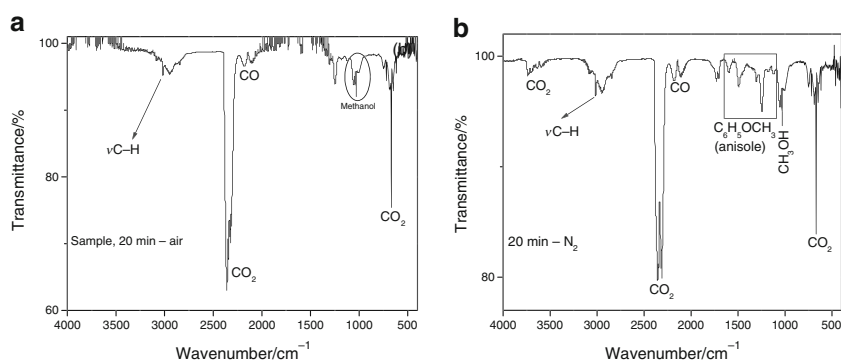


Fig. 2 DSC curves of the compounds: *a* Mn(L)₂·2H₂O (*m* = 4.94 mg), *b* Fe(L)₂·1.5H₂O (*m* = 4.99 mg), *c* Co(L)₂·2H₂O (*m* = 4.99 mg), *d* Ni(L)₂·3H₂O (*m* = 5.00 mg), *e* Cu(L)₂·2H₂O (*m* = 3.08 mg) and *f* Zn(L)₂·2H₂O (*m* = 3.19 mg); *L* 2-methoxycinnamylidene-pyruvate

Fig. 3 FTIR spectra of gaseous products released during the decomposition of the Co(L)₂·2H₂O. **a** Air atmosphere; **b** N₂ atmosphere



with the CuO as final residue (Calcd. = 85.85%, TG = 86.14%).

Zinc compound

The TG–DTA and DSC curves of the compound are shown in Figs. 1f and 2f, respectively. The mass loss observed between 323 and 413 K (TG), corresponding to endothermic peak at 403 K (DTA) or 408 K (DSC), is due to the dehydration with loss of 2H₂O (Calcd. = 6.39%, TG = 6.50%). The anhydrous compound is stable up to 428 K, and above this temperature the thermal decomposition occurs in three steps with losses of 5.20% (428–493 K), 43.10% (493–733 K) and 32.20% (733–803 K), corresponding to the exothermic peaks at 473 and 773 K (DTA) or to the exotherms between 623 and 853 K (DSC), attributed to oxidation of the organic matter. The total mass loss up to 803 K is in agreement with the formation of ZnO as final residue (Calcd. = 85.57%, TG = 85.80%).

The differences observed concerning to the peak temperatures, as well as the DTA and DSC profiles are undoubtedly due to the perforated cover used to obtain the DSC curves, whilst the TG–DTA ones are obtained without cover.

The dehydration enthalpies found for the Mn, Fe, Co, Ni, Cu and Zn compounds from the DSC curves were: 118.8, 51.9, 111.3, 117.2, 55.8 and 98.6 kJ mol⁻¹, respectively.

Monitoring of gaseous products by FTIR

The gaseous products evolved during the thermal decomposition of these compounds in dynamic air and nitrogen atmospheres were monitored by FTIR. The FTIR spectra of the gaseous products released during the thermal decomposition of Co-2-MeO-CP in air and N₂ atmospheres, as representative of all the compounds studied in this study are shown in Fig. 3. In air atmosphere, Fig. 3a shows carbon dioxide as majority product (anti-symmetrical stretching at 2360, 2345 and scissoring (degenerated) at

666 cm^{-1}), besides methanol [three characteristic peaks (triplet) in fingerprint region 1060, 1032 and 1005 cm^{-1}]. For the N_2 atmosphere, Fig. 3b also shows carbon dioxide as the main product evolved, besides methanol and anisole, the latter (phenyl alkyl ether) has characteristic peaks at 1250 and 1040 cm^{-1} related to the axial asymmetric and symmetric deformation C–O–C, respectively, and two peaks at 1594 and 1491 cm^{-1} , related to C=C of the ring.

Conclusions

From TG curve, elemental analysis and complexometry results, a general formula could be established to these compounds in the solid state.

The infrared spectroscopic data of the compounds suggest that the 2-MeO-CP acts as a bidentate ligand to the metal ions considered in this study.

This study has also showed that the gaseous products evolved during the thermal decomposition of these compounds were: CO_2 , CO, methanol, anisole and fragments of carbonic chain due to the presence of the peak at 720 cm^{-1} .

The thermal stability of the anhydrous compounds, as well as the final temperature of thermal decomposition, as shown by the TG–DTA curves, depends on the nature of the metal ion.

The TG–DTA and DSC curves provided previously unreported information concerning the thermal behaviour and thermal decomposition of these compounds.

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