

SOLID-STATE COMPOUNDS OF 2-METHOXYBENZYLIDENEPYRUVATE WITH SOME BIVALENT METAL IONS

Synthesis, characterization and thermal behavior studies

M. Kobelnik¹, E. Schnitzler² and M. Ionashiro^{1*}

¹Instituto de Química, Universidade Estadual Paulista, Araraquara, São Paulo, C P. 355, CEP 14801-970, Brazil

²Departamento de Química, Universidade Estadual de Ponta Grossa, Ponta Grossa, Paraná, Brazil

Solid-state M–2-MeO-BP compounds, where *M* represents bivalent Mn, Fe, Co, Ni, Cu, Zn and 2-MeO-BP is 2-methoxybenzylidenepyruvate have been synthesized. Simultaneous thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy, elemental analysis and complexometry were used to characterize and to study the thermal stability and thermal decomposition of these compounds. The results led to information about the composition, dehydration, crystallinity and thermal decomposition of the isolated compounds.

Keywords: bivalent transition metals, characterization, 2-methoxybenzylidenepyruvate, thermal behavior

Introduction

Several metal-ion complexes with five phenyl-substituted derivatives of benzylidenepyruvate, $C_6H_5-CH=CH-COOCO^-$ (BP), i.e., 4-dimethylamino (4-DM-BP), 4-methoxy (4-MeO-BP), 2-methoxy (2-MeO-BP), 4-chloro (4-Cl-BP) and 4-methyl (4-Me-BP) have been investigated in aqueous solutions and in solid-state. In aqueous solutions these works reported the thermodynamic stability (β_1), and spectroscopic parameters ($\epsilon_{1\max}$, λ_{\max}) associated to 1:1 complex species, as well as analytical applications of Na-4DM-BP for gravimetric determination of Cu (II), or as indicator in the complexometric titrations of Th(IV), Al(III) with EDTA [1–5].

In the solid-state, the works reported the synthesis and investigation of the compounds by means of thermogravimetry, derivative thermogravimetry (TG/DTG), differential thermal analysis (DTA), X-ray powder diffractometry and complexometry. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies [6–19].

In the present paper, solid-state compounds of bivalent Mn, Fe, Co, Ni, Cu and Zn with 2-methoxybenzylidenepyruvate (2-MeO-BP) were prepared. These compounds were investigated by complexometry, simultaneous TG-DTA, DSC, infrared spectroscopy and X-ray powder diffractometry. The obtained data provide information on the composition, thermal stability and thermal decomposition of these compounds in the solid-state.

Experimental

The sodium salt of 2-methoxybenzylidenepyruvic acid (2-MeO-BP) was prepared as described in the literature [18, 20]. Aqueous solutions of the bivalent metal ions were prepared by dissolving the corresponding chlorides, except for iron, where the sulphate was used.

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

The precipitates were washed until elimination of chloride (or sulphate) ions, filtered through and dried on Whatman No. 42 filter paper and kept in a desiccator over anhydrous calcium chloride.

In case of the solid compounds, metal ion, water and 2-MeO-BP contents were determined from TG curves. The metal ion content was also determined by complexometry with standard EDTA solution [21]. However, to avoid the interference of 2-methoxybenzylidenepyruvate, i.e. to behave as metallic indicator during titration with EDTA, the organometal complexes had been burnt to their respective oxides and then resulted oxides were dissolved in hydrochloric acid solution and then were titrated with EDTA.

Simultaneous TG-DTA and DSC curves were obtained using models SDT 2960 and DSCQ 10, both from TA Instruments. The purge gas was a dynamic air flow at a flow rate of 100 mL min^{-1} . $20^\circ\text{C min}^{-1}$

* Author for correspondence: massaoi@iq.unesp.br

heating rate was applied, with samples weighing about 7 mg. Alumina and aluminum crucibles, the latter with perforated covers were used for TG-DTA and DSC, respectively.

X-ray powder pattern were recorded by Siemens D-5000 X-ray diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda=1.544 \text{ \AA}$) and settings of 40 kV and 20 mA.

Infrared spectra for 2-MeO-BP (sodium salt) as well as for its metal-ion compounds were obtained using a Nicolet model Impact 400 FT-IR instrument in the $4000\text{--}400 \text{ cm}^{-1}$ range. The solid samples were pressed to KBr pellets.

Carbon and hydrogen contents were determined by microanalytical procedure, with an EA 1110 CHNS-O Elemental Analyser from CE Instruments.

Results and discussion

The data of analysis and the thermogravimetric results are collected in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the $\text{ML}_2 \cdot n\text{H}_2\text{O}$ general formula, where M represents bivalent Mn, Fe, Co, Ni, Cu or Zn, 2-MeO-BP is 2-methoxybenzylidenepyruvate and $n=1$ (Fe, Cu), 1.5 (Mn), 2 (Ni, Zn) or 2.5 (Co).

The X-ray powder diffraction patterns showed that the manganese and cobalt compounds have crystalline structure while the other compounds were in their amorphous state.

Infrared spectroscopic data on 2-methoxybenzylidenepyruvate (sodium salt) and its compounds with the metal ions considered in this work are shown

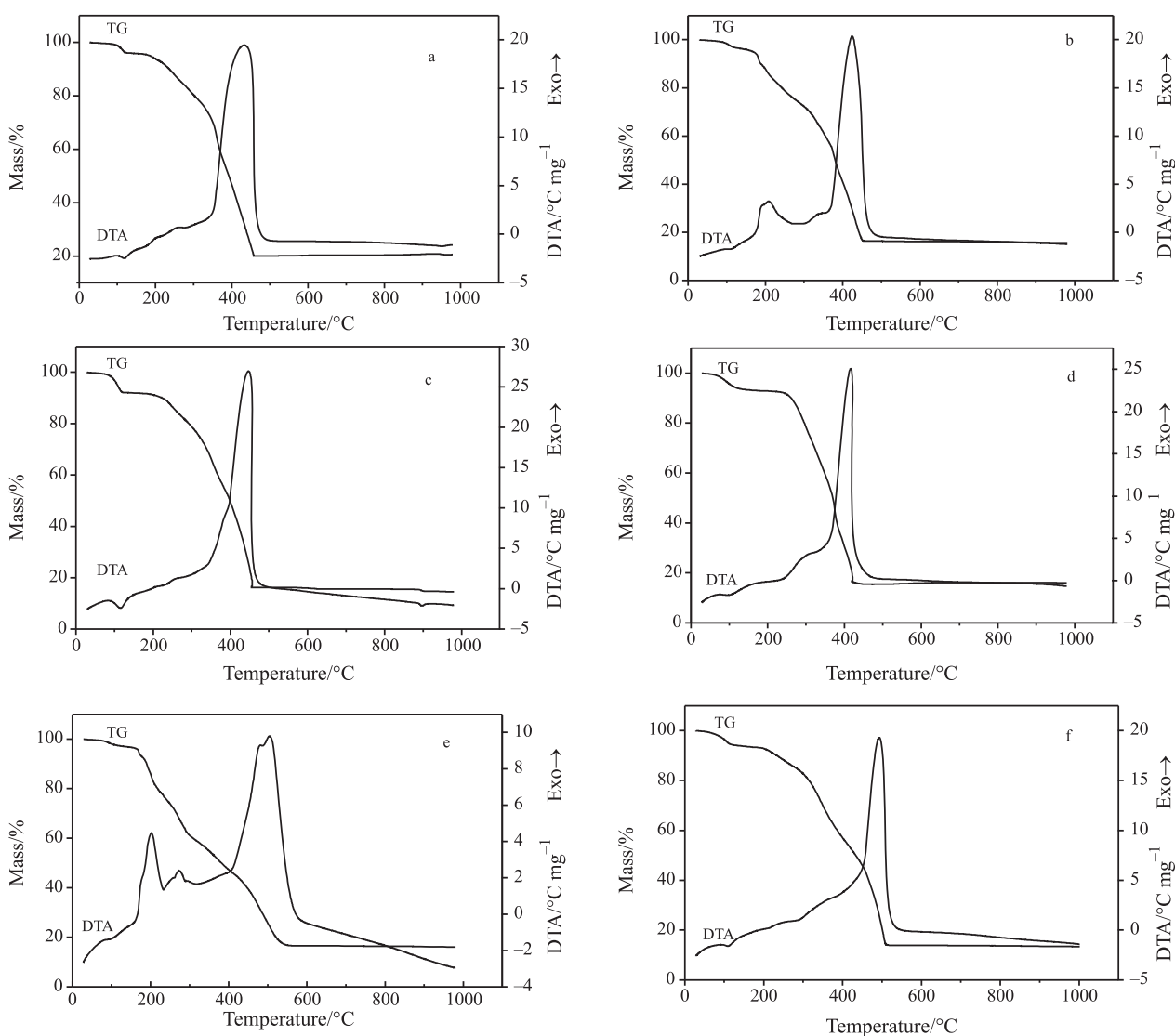
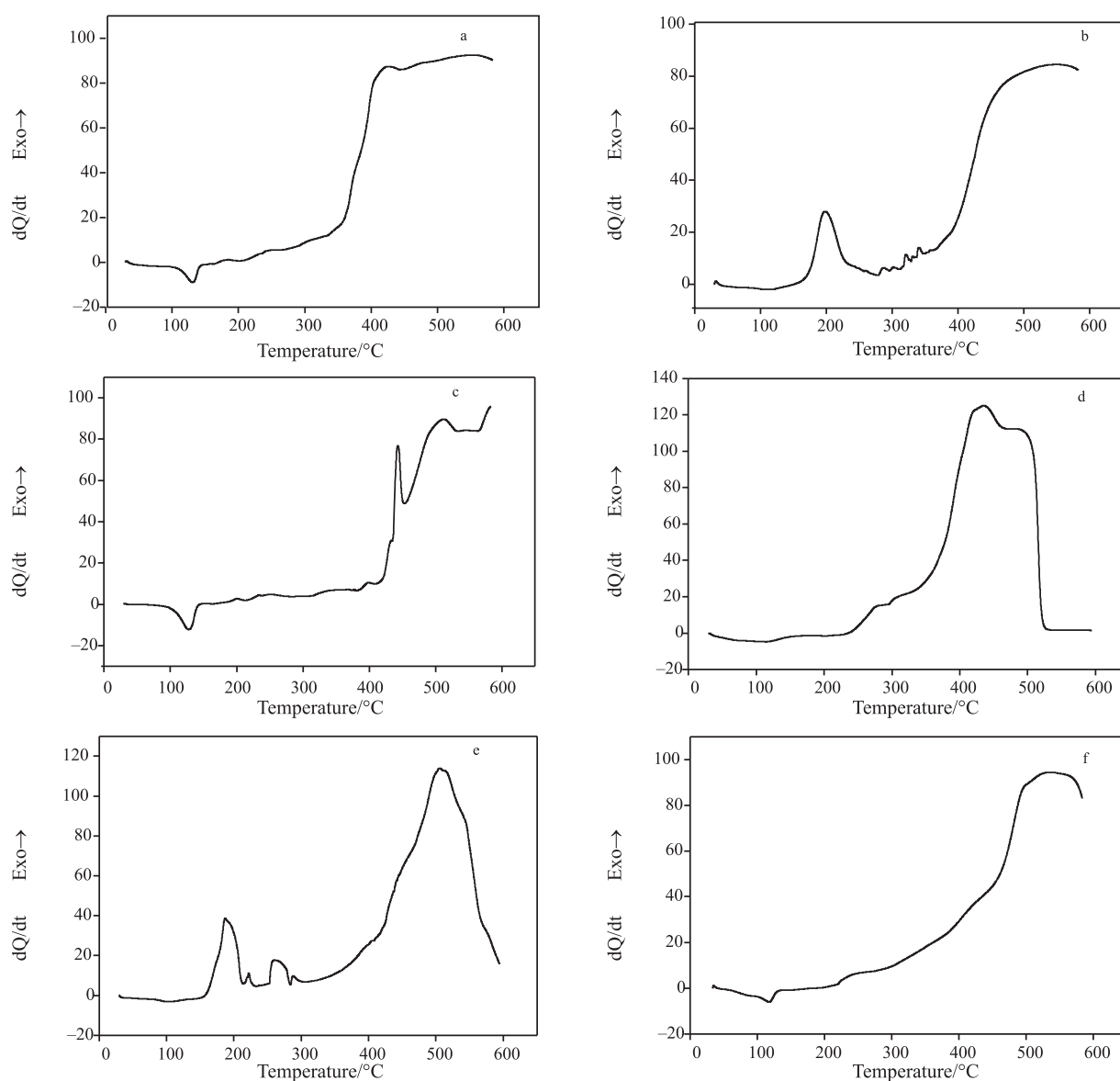


Fig. 1 TG-DTA curves of the compounds: a – $\text{Mn}(\text{2-MeO-BP})_2 \cdot 1.5\text{H}_2\text{O}$ ($m=7.410 \text{ mg}$); b – $\text{Fe}(\text{2-MeO-BP})_2 \cdot \text{H}_2\text{O}$ ($m=7.093 \text{ mg}$); c – $\text{Co}(\text{2-MeO-BP})_2 \cdot 2.5\text{H}_2\text{O}$ ($m=7.266 \text{ mg}$); d – $\text{Ni}(\text{2-MeO-BP})_2 \cdot 2\text{H}_2\text{O}$ ($m=7.017 \text{ mg}$); e – $\text{Cu}(\text{2-MeO-BP})_2 \cdot \text{H}_2\text{O}$ ($m=7.060 \text{ mg}$) and f – $\text{Zn}(\text{2-MeO-BP})_2 \cdot 2\text{H}_2\text{O}$ ($m=6.941 \text{ mg}$)

Table 1 Data of analysis and thermogravimetric experiments of the $ML_2 \cdot nH_2O^a$ compounds

Compound	Metal/%			L/% lost		H ₂ O/%		C/%		H/%	
	theor.	TG	EDTA	theor.	TG	theor.	TG	theor.	TG	theor.	TG
Mn(L) ₂ ·1.5H ₂ O	11.16	11.27	11.51	79.01	78.79	5.49	5.50	53.66	53.51	4.31	4.29
Fe(L) ₂ ·H ₂ O	11.53	11.45	11.44	79.79	79.86	3.72	3.68	54.56	54.61	4.17	4.17
Co(L) ₂ ·2.5H ₂ O	11.46	11.42	11.52	75.64	75.83	8.76	8.62	51.37	51.50	4.52	4.53
Ni(L) ₂ ·2H ₂ O	11.62	11.94	11.60	76.50	76.35	7.13	7.09	52.31	52.21	4.40	4.39
Cu(L) ₂ ·H ₂ O	12.92	12.99	13.00	80.18	79.92	3.65	3.81	53.71	53.54	4.11	4.10
Zn(L) ₂ ·2H ₂ O	12.78	13.02	13.05	77.06	76.76	7.04	7.09	51.62	51.42	4.34	4.32

^aL=2-methoxybenzylidenepyruvate and M=metal

Fig. 2 DSC curves of the compounds: a – Mn(2-MeO-BP)₂·1.5H₂O (*m*=3.581 mg); b – Fe(2-MeO-BP)₂ (*m*=3.364 mg); c – Co(2-MeO-BP)₂·2.5H₂O (*m*=3.560 mg); d – Ni(2-MeO-BP)₂ (*m*=3.700 mg); e – Cu(2-MeO-BP)₂·H₂O (*m*=3.720 mg) and f – Zn(2-MeO-BP)₂·2H₂O (*m*=3.488 mg)

in Table 2. The investigation was focused mainly in the 1700–1400 cm⁻¹ range because this region is the potentially most informative to assign coordination sites.

In 2-MeO-BP (sodium salt), strong doublet bands (at 1625 and 1589 cm⁻¹) and a medium intensity band located at 1398 cm⁻¹ are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [22, 23]. The band centered at 1690 cm⁻¹ is typical for a conjugated ketonic carbonyl group [22]. For all the compounds, the doublet bands assigned to the antisymmetrical stretching carboxylate frequencies are retained in the complexes. Both these bands as well as that assigned to the ketonic carbonyl are shifted to lower values relative to the corresponding frequencies in 2-MeO-BP itself (sodium salt). This behaviour indicates that both groups act as coordination centres in the metal compounds [24, 25].

Simultaneous TG/DTA curves of the compounds are shown in Fig. 1. These curves show mass losses in two (Mn, Co, Ni) and three (Fe, Cu, Zn) steps and thermal events corresponding to these mass losses are between 50 and 560°C.

The first mass loss between 70–140°C (Mn, Fe, Co), 50–140°C (Ni) or 50–130°C (Cu, Zn), corresponding to endothermic peak at 120°C (Mn, Fe, Co) and 100°C (Ni, Cu, Zn) is attributed to dehydration, which occurs in a single step. After dehydration the anhydrous compounds are stable up to 150°C (Fe, Cu), 170°C (Mn), 180°C (Co, Zn), 230°C (Ni) and above these temperatures the thermal decomposition occurs in a single (Mn, Co, Ni) or two overlapping steps (Fe, Cu, Zn). For all the compounds the mass losses up to 470°C (Mn), 460°C (Fe, Co), 440°C (Ni) and 550°C (Cu, Zn) corresponding to exo-

Table 2 Spectroscopic data for sodium 2-methoxybenzylidenepyruvate (2-MeO-BP) and compounds with some bivalent metal ions^a

Compounds	$\nu_{\text{asym}(\text{COO}^-)}$ ^b	$\Delta\nu_{(\text{COO}^-)}$ ^c	$\nu_{\text{sym}(\text{COO}^-)}$ ^b	$\nu_{\text{C=O}}$ ^d	$\Delta\nu_{\text{C=O}}$ ^e
2-MeO-BP Na ⁺	1625 _s ;1589 _s	–	1398 _m	1690 _m	–
Mn(2-MeO-BP) ₂ ·1.5H ₂ O	1641 _s ;1568 _s	24;21	1408 _m	1683 _{sh}	7
Fe(2-MeO-BP) ₂ ·H ₂ O	1595 _s ;1548 _s	30;41	1401 _m	1655 _{sh}	34
Co(2-MeO-BP) ₂ ·2.5H ₂ O	1591 _s ;1566 _s	34;23	1398 _m	1651 _m	39
Ni(2-MeO-BP) ₂ ·2H ₂ O	1637 _s ;1562 _s	26;27	1396 _m	1669 _{sh}	22
Cu(2-MeO-BP) ₂ ·H ₂ O	1595 _s ;1552 _s	29;33	1387 _m	1640 _{sh}	50
Zn(2-MeO-BP) ₂ ·2H ₂ O	1645 _s ;1566 _s	25;23	1396 _m	1671 _{sh}	45

^as=strong; m=medium; sh=shoulder; ^b $\nu_{\text{as}(\text{COO}^-)}$ and $\nu_{\text{sym}(\text{COO}^-)}$ =anti-symmetrical and symmetrical vibrations of the COO⁻ group, respectively; ^c $\nu_{\text{as}(\text{COO}^-)}$ (Na⁺ salt) – $\nu_{\text{as}(\text{COO}^-)}$ (metal complex); ^d $\nu_{\text{C=O}}$ =ketonic carbonyl stretching frequency; ^e $\nu_{\text{C=O}}$ (Na⁺ salt) – $\nu_{\text{C=O}}$ (metal complex).

Table 3 Temperature ranges, θ , mass losses and peak temperatures observed for each step of the TG-DTA curves of the compounds M(2-MeO-BP)₂·nH₂O^a

Compounds		Steps		
		first	second	third
Mn(2-MeO-BP) ₂ ·1.5H ₂ O	$\theta/^\circ\text{C}$	70–140	170–470	–
	mass loss/%	5.50	78.79	–
	peak temperature/ $^\circ\text{C}$	120(endo)	430(exo)	–
Fe(2-MeO-BP) ₂ ·H ₂ O	$\theta/^\circ\text{C}$	70–140	150–310	310–460
	mass loss/%	3.68	24.42	55.44
	peak temperature/ $^\circ\text{C}$	120(endo)	200(exo)	415(exo)
Co(2-MeO-BP) ₂ ·2.5H ₂ O	$\theta/^\circ\text{C}$	70–140	180–460	–
	mass loss/%	8.62	75.83	–
	peak temperature/ $^\circ\text{C}$	120(endo)	415(exo)	–
Ni(2-MeO-BP) ₂ ·2H ₂ O	$\theta/^\circ\text{C}$	50–140	230–440	–
	mass loss/%	7.09	76.35	–
	peak temperature/ $^\circ\text{C}$	100(endo)	410(exo)	–
Cu(2-MeO-BP) ₂ ·H ₂ O	$\theta/^\circ\text{C}$	50–130	150–300	300–550
	mass loss/%	3.81	36.41	43.51
	peak temperature/ $^\circ\text{C}$	100(endo)	200(exo), 270(exo)	500(exo)
Zn(2-MeO-BP) ₂ ·2H ₂ O	$\theta/^\circ\text{C}$	50–130	180–430	430–550
	mass loss/%	4.40	42.22	34.54
	peak temperature/ $^\circ\text{C}$	100(endo)	300(exo)	490(exo)

^a2-MeO-BP=2-methoxybenzylidenepyruvate

thermic peaks at 430°C (Mn); 200 and 415°C (Fe); 415°C (Co); 410°C (Ni); 200, 270 and 500°C (Cu); 300 and 490°C (Zn) are attributed to the oxidation of organic matter. Calculations based on the mass losses up to the final temperature of thermal decomposition are in agreement with the formation of the respective oxides: Mn₃O₄, Fe₂O₃, Co₃O₄, NiO, CuO and ZnO. These oxides were confirmed by X-ray powder diffraction patterns. For the cobalt compound the mass loss that occurs between 885 and 920°C, corresponding to the endothermic peak at 895°C is due to the reduction of Co₃O₄ to CoO and in agreement with the literature [14, 26].

The mass losses, temperature ranges and the peak temperatures observed in each step of the TG-DTA curves are shown Table 3.

The DSC curves of the compounds are shown in Fig. 2. These curves show endothermic and exothermic peaks in agreement with mass losses observed in the TG curves. For iron, nickel and copper compounds no endothermic peak is observed in the DSC curves due to the dehydration, in disagreement with the TG-DTA curves. This disagreement probably must be dehydration of these compounds in the desiccator over anhydrous calcium chloride, because the DSC curves were obtained six month after the TG-DTA curves.

The endothermic peak at 130°C (Mn, Co), 120°C (Zn) is assigned to the dehydration. The exothermic peak 200°C (Fe) and 180°C (Cu), probably is due to the elimination of methoxy group, and the exothermic peaks or exotherm are attributed to the oxidation of the organic matter.

Conclusions

From TG and complexometry data, a general formula can be established for the synthesized compounds. The X-ray powder diffraction patterns pointed out that the manganese and cobalt compounds have a crystalline structure while the other compounds were amorphous. Infrared spectroscopic data suggest that 2-MeO-BP acts as a bidentate ligand towards the metal ions considered in this work. The TG-DTA and DSC curves provided previously unreported information on the thermal stability and thermal decomposition of these compounds.

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