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Synthesis, characterization and thermal behaviour on solid pyruvates of some bivalent metal ions.

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Abstract: Solid state M-L compounds, were M stands for bivalent Mn, Fe, Co, Ni, Cu, Zn and L is pyruvate, have been synthesized. Thermogravimetry and derivative thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), X-Ray powder diffractometry, infrared spectroscopy, elemental analysis, and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to information about the composition, dehydration, ligand denticity, and thermal decomposition of the isolated compounds.

Keywords: bivalent metals, pyruvate, characterization, thermal behaviour.

Introduction

Investigations on pyruvic acid (HPy), as well as compounds derivatives of HPy, have been carried out in biological science researches. However little works on salts of pyruvic acid (H_3C-CO-COOH) have been described in the literature. In aqueous solutions the formation of some metal ions complexes with pyruvic acid in ratio of metal: ligand 1:1 and 1:2 have been established by the spectroscopic method [1-3]; the stability constants and thermodynamic functions of complexes formation of lanthanides with pyruvic acid: ΔG, ΔH, ΔS, have also been determined [4]. In the solid state, preparation of europium pyruvate [5], as well as the preparation and properties of lanthanides and yttrium pyruvates have also been described [6,7,8].

The aim of this work has been to obtain bivalent metal pyruvates in solid state and to investigate by means of complexometry, elemental analysis, X-Ray powder diffractometry, infrared spectroscopy, thermogravimetry (TG) and differential scanning calorimetry (DSC).

Experimental

The sodium pyruvate with 99% purity was obtained from Sigma. Aqueous solution of sodium pyruvate 0.8 mol L^{-1} was made by direct weighing of the solid salt. Aqueous solutions of bivalent metal ions 0.4 mol L^{-1} were prepared by dissolving the corresponding chlorides.

The solid state compounds were prepared by mixing 10 mL solutions of the corresponding metal chlorides with 10 mL solution of sodium pyruvate. The resulting solutions were evaporated in a water bath until dryness. The dry compounds were washed with a mixture of water:ethanol (6:4) until chloride ions were eliminated, filtered through and dried on whatman n° 42 filter paper and kept in a desiccator over anhydrous calcium chloride. For the Mn(II) and Fe(II) compounds, to avoid oxidation, all their solutions as well as the solution employed for washing their compounds were purged with nitrogen gas, even during the drying in a water bath.

In the solid state compounds, the metal ions contents were determined by complexometry with standard EDTA solution [9]. The metal ions contents were also estimated from their corresponding TG curves. The dehydration of the compounds was firstly pointed out by their DTG curves and subsequently confirmed by the broad endothermic peaks centered at 75-175 °C in the respective DSC curves. The water contents were then determined from the corresponding mass losses observed in the TG curves. Next, the ligand content was also assessed from the TG curves.

X-ray powder patterns were obtained by using a Siemens D-5000 X-Ray diffractometer with CuK_{α} radiation ($\lambda = 1,541$ Å) and under 40 kV and 20 mA settings. Infrared spectra for sodium pyruvate as well as for its metal-ion compounds were recorded on a Nicolet model Impact 400 FTIR Instrument in 4000-400cm^{-1} range. The solid samples were pressed into KBr pellets.

Carbon and hydrogen were determined by microanalytical procedures with an EA 1110 CHNSO, Elemental Analyser from CE Instruments.

The TG and DTG curves were obtained using a Mettler TA 4000 thermal analysis system with an air flow of 100 mL min^{-1}, a heating rate of 20 ºC min^{-1} and with sample weighing about 7 mg. An alumina crucible was used for the TG/DTG curves.

The DSC curves were obtained with thermal analysis system model Q10 from TA Instruments. The purge gas was an air flow of 50 mL min^{-1}. A heating rate of 20 ºC min^{-1} was adopted with samples weighing about 5 mg. Aluminium crucibles, with perforated cover, were used for recording the DSC curves.

Results and Discussion

Table 1 presents the analytical, thermoanalytical (TG) and elemental analysis (EA) data for the prepared compounds from which the general formula $M(L)_2.nH_2O$ can be established, where M represents bivalent metals, L is pyruvate and n = 2 (Cu), 3 (Fe, Zn), 3.5 (Mn, Co, Ni).

Table 1. Analytical and thermoanalytical (TG) data for $M(L)_2.nH_2O$, where M = bivalent metals and L = pyruvate.

Compound	Metal oxide (%)			L, lost (%)		Water (%)		Carbon (%)		Hidrogen (%)		Final Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd	E.A	Calcd	E.A	
$Mn(L)_2.3.5H_2O$	27.02	26.95	26.67	51.39	51.63	21.59	21.42	24.67	24.94	4.49	4.51	Mn_2O_3
$Fe(L)_2.3H_2O$	27.17	26.87	27.33	53.80	54.31	19.03	18.82	25.37	25.41	4.27	4.10	Fe_3O_4
$Co(L)_2.3.5H_2O$	27.10	26.32	27.35	51.60	51.85	21.30	21.33	24.33	24.40	4.43	4.65	Co_3O_4
$Ni(L)_2.3.5H_2O$	25.25	25.07	24.90	53.44	53.68	21.31	21.25	24.35	24.03	4.44	4.30	NiO
$Cu(L)_{2.}2H_2O$	29.06	29.31	29.34	57.77	57.69	13.17	13.00	26.33	26.67	3.69	3.50	CuO
$Zn(L)_2.3.5H_2O$	27.72	27.60	27.97	53.86	54.13	18.42	18.27	24.55	24.35	4.13	4.21	ZnO

The X-ray powder diffraction patterns, Fig. 1, show that all compounds, except iron compound, have a crystalline structure. The others compounds, except for the copper compound, evidence for formation of an isomorphous series is observed.

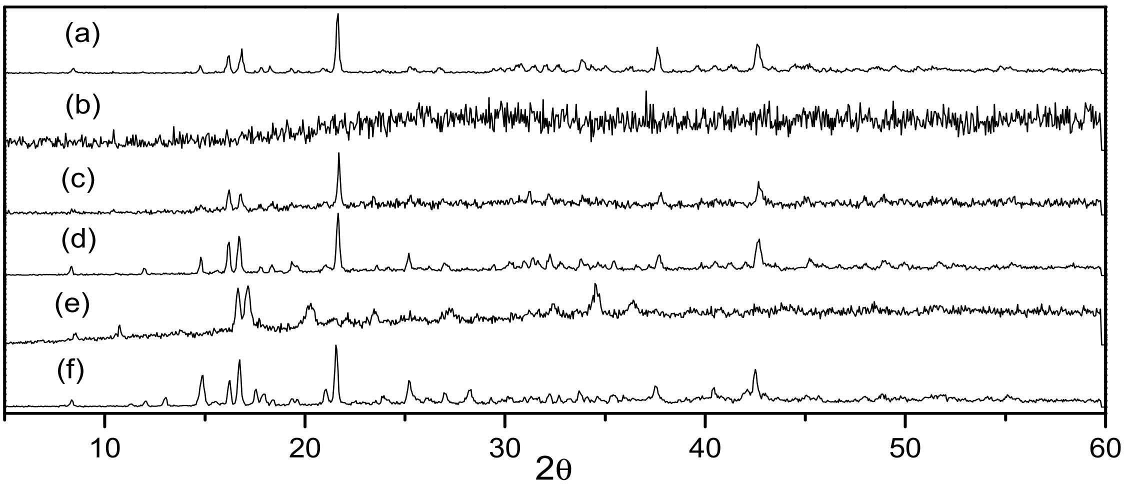

Fig. 1: X-ray powder diffraction patterns of (a) MnL2.3.5H2O; (b) FeL2.3H2O; (c) CoL3.3.5H2O; (d) NiL3.3.5H2O; (e) CuL3.2H2O; (f) ZnL3.3H2O. L= pyruvate.

The infrared spectroscopic data on sodium pyruvate and its compounds with the metal ions considered in this work are shown in Table 2. The investigation was focused mainly within 1750 – 1350 cm^{-1} range because this region is potentially most informative in attempting to assign coordination sites. In sodium pyruvate, strong band at 1709 cm^{-1} is attributed to the stretching frequency of the ketonic carbonyl group and strong bands at 1654/1631 cm^{-1} and 1405 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of carboxylate group, respectively [10,11]. Pyruvates are also twisted in the solid state, but the dihedral angle is not larger than 25°, and sodium interact with both the α-C=O and COO^- groups [12]. Mn, Co, Ni and Zn pyruvates are essentially identical, but Fe and Zn pyruvates show a different type of coordination, because of the increase $\nu_{(C=O)}$ of these compounds. It also suggest that the interaction Fe-O and Cu-O (α-C=O) is more weak than other compounds obtained. For the prepared compounds the infrared spectra show a broad band in the range of 3000-3500 cm^{-1} is attributed to hydration water.

Table 2. Spectroscopic data for sodium pyruvate and compounds with bivalent metal ions

Compound	$N_{(O-H)}H_2O^b$	$N_{(C=O)}^c$	$N_{asym\ (COO^-)}^d$	νsym (COO-)d
Na(Py)	-	1709_s	1654,1631s	1405s
$Mn(Py)_3.3.5H_2O$	3151_{br}	1704s	1674,1605s	1373s
$Fe(Py)_3.3H_2O$	3376_{br}	1734m	1635,1624s	1383s
Co(Py)3.3.5H2O	3244_{br}	1705s	1678,1605s	1396s
Ni(Py)3.3.5H2O	3320_{br}	1703s	1678,1602s	1398s
$Cu(Py)_3.2H_2O$	3408_{br}	1729s	1654br	1398s
$Zn(Py)_3.3H_2O$	3110^{br}	1712s	1676br	1394s

s: strong, m: medium,

br – broad; $N_{asym\ (COO^-)}$ and $N_{sym\ (COO^-)}$: symmetrical and anti-symmetrical vibrations of the COO^- group, respectively

$_\Delta N_{asym\ (COO^-)} = N_{asym\ (COO^-)\ NaL} - N_{asym\ (COO^-)\ metal\ complex)}$

$N_{(C=O),}$: ketonic carbonyl stretching frequency.

$N_{(O-H)}$: hydroxyl group stretching frequency;

The TG and DTG curves of the compounds are shown in Fig. 2. These curves show mass losses in three consecutive and/or overlapping steps and without evidence concerning the formation of stable anhydrous compounds. As previously stressed, the temperatures corresponding to the mass losses due to dehydration were depicted from the DTG curves.

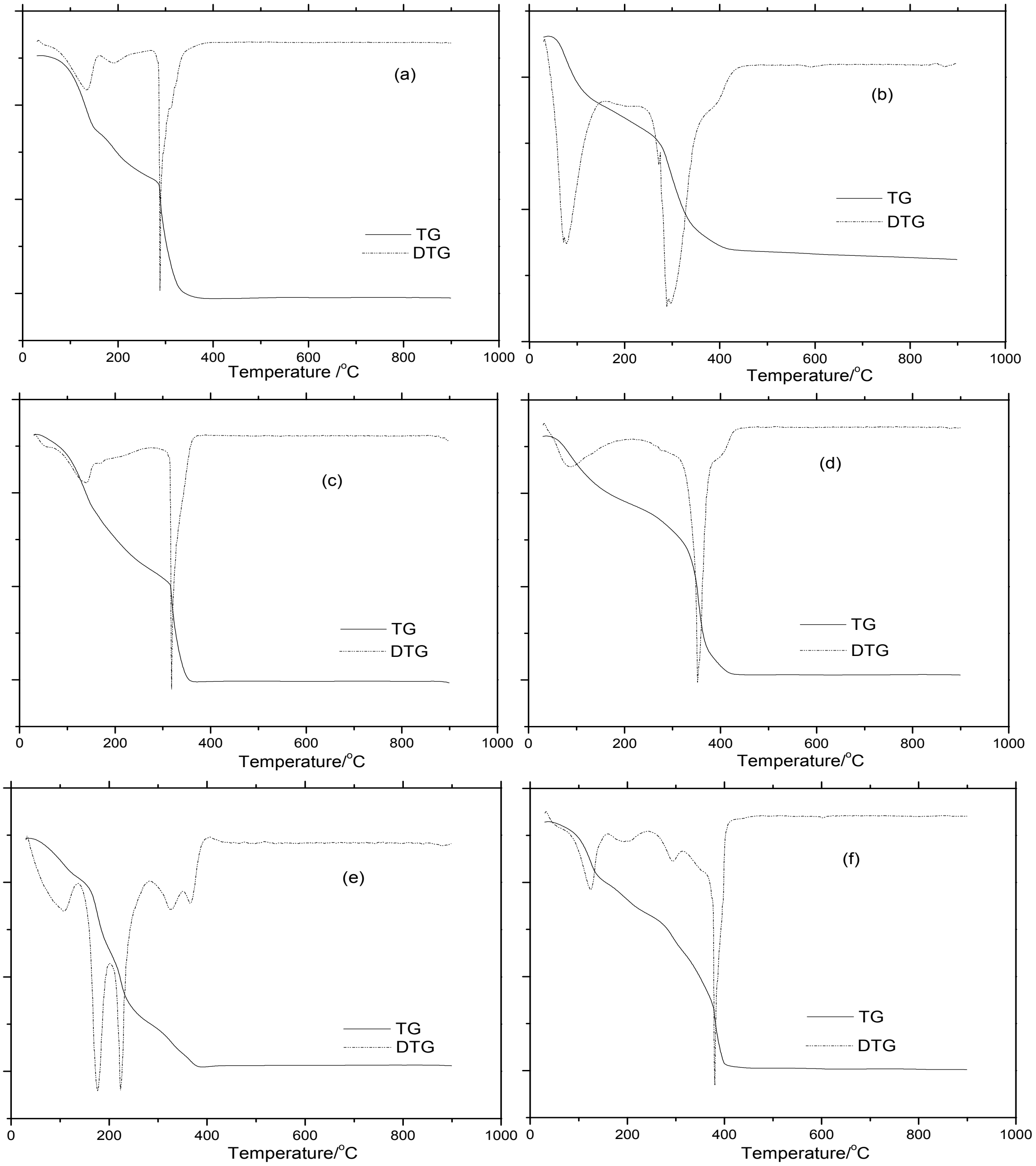

Fig. 2: The TG/DTG curves of (a) $MnL_2.3.5H_2O$ (m=7.053 mg); (b) $FeL_2.3H_2O$ (4.600 mg); (c) $CoL_3.3.5H_2O$ (7.254 mg); (d) $NiL_3.3.5H_2O$ (7.295 mg); (e) $CuL_3.2H_2O$ (6.933 mg); (f)$ZnL_3.3H_2O$ (7.289 mg). L= pyruvate.

For all compounds, the first mass loss up to 140 °C (Fe, Cu) and 150 °C (Mn, Co, Ni, Zn) is attributed to dehydration, which occurs in a single step.

Immediately after the dehydration the thermal decomposition of these compounds occurs in two (Co, Ni, Cu, Zn) and three (Mn, Fe) steps, with mass losses in each step characteristic of each compound.

For the manganese compound, Fig. 2(a), the first mass loss observed between 50 and 150 °C is due to dehydration, with loss of 3.5 H_2O (calcd. = 21.59%; TG = 21.42%). The thermal decomposition of the anhydrous compound occurs in two steps, between 150-290 °C and 290-390 °C, with losses of 16.87 and 34.76%, respectively. The total mass loss up to 390 °C is in agreement with the formation of Mn_2O_3 (Calcd = 72.98%; TG = 73.05%). The mass loss observed between 920-980 °C, is assigned to the reduction of Mn_2O_3 to Mn_3O_4 (Calcd = 0.91%; TG = 0.90 %) and confirmed by X-ray powder diffractometry, and in agreement with the thermal decomposition of manganese 4-methylbenzylidenepyruvate [13].

Literature reports on the thermal stability and reduction temperature of Mn_2O_3 are in disagreement among themselves [14-16] and with the data obtained in this work. This behaviour concerning manganese oxides has already been pointed out [14]; it is reported that the properties significantly depend on the preparation conditions, structural properties of the oxides and upon operational parameters during the reduction step [14].

For the iron compound, Fig. 2(b), the first mass loss between 50-140 °C is due to dehydration with loss of $3H_2O$ (Calcd = 19.03%, TG = 18.82%). After the dehydration the thermal decomposition occurs in three steps, being the first two between 140-270 °C and 270-425 °C fast processes, followed by a slow process for the third step (425-900 °C) with losses of 13.38, 37.78 and 3.15% respectively. The total mass loss up to 900 °C is in agreement with the formation of Fe_3O_4 (Calcd. = 72.83%, TG = 73.13%).

The formation of Fe_3O_4 was also confirmed by the black colour and magnetic property of the residue and by X-ray diffractometry.

For the cobalt compound, Fig. 2(c) the first mass loss between 40-150 °C is due to dehydration with loss of 3.5 H_2O (calcd.= 21.30%, TG = 21.33%). The thermal decomposition of the anhydrous compound occurs in two steps, between 150-320 °C and 320-370 °C, with losses of 23.33 and 28.52%, respectively. The total mass loss up to 370 °C is in agreement with the formation of Co_3O_4 (Calcd.= 72.90%, TG = 73.18%). The mass loss observed between 900 and 930 °C, is ascribed to the reduction of Co_3O_4 to CoO (Calcd. = 1.81%; TG = 1.74%) in agreement with the literature [17, 18].

For the nickel compound, Fig. 2(d) the first mass loss between 50-150 °C is due to dehydration with loss of 3.5 H_2O (Cald. = 21.31%, TG = 21.33%). The thermal decomposition of the anhydrous compound occurs in two steps, between 150-300 °C and 300-440 °C with losses of 11.78 and 41.90%, respectively. The total mass loss up to 440 °C is in agreement with the formation of NiO (Calcd = 74.75%, TG = 74.93%) and confirmed by X-ray diffractometry.

For copper compound, Fig. 2(e) the first mass loss between 40 and 140 ºC is due to dehydration with loss of $2H_2O$ (Calcd. = 13.17%, TG = 13.00 %). After the dehydration although the DTG curve to show mass loss in four overlapping steps, the TG curve suggests two steps between 140 – 245 ºC and 245 – 400 ºC with losses of 38.69 and 19.70%, respectively and formation of a mixture of Cu(I) and Cu (II) oxides. The mass gain between 400 – 430 ºC is attributed to the oxidation of Cu(I) to Cu(II). The total mass loss up to 430 ºC is in agreement with the formation of CuO (Calc. = 70.94%, TG = 70.69%) and confirmed by X-ray diffractometry.

For the zinc compound, Fig. 2(f) the first mass loss between 50 and 150 °C is due to dehydration with loss of $3H_2O$ (Calcd. = 18.42%, TG = 18.27%). The thermal decomposition of the anhydrous compound occurs in two steps between 150-275 °C and 275-450 °C with losses of 12.89 and 41.24%, respectively. The total mass loss up to 450 °C is in agreement with the formation of ZnO (Calcd. = 72.28%, TG = 72.40%) and confirmed by X-ray diffractometry.

The DSC curves of the compounds are shown in Fig. 3. These curves show endothermic and exothermic peaks that all accord with the mass losses observed in the TG curves. The broad endothermic peak at 162 °C (Mn), 129 °C (Fe), 170 °C (Co), 180 °C (Ni), 134 °C (Cu) and 161 °C (Zn) is attributed to the dehydration. The dehydration enthalpies found for these compounds were: 130.3, 80.7, 133.6, 135.1, 63.2 and 108.6 kJ mol^{-1}, respectively.

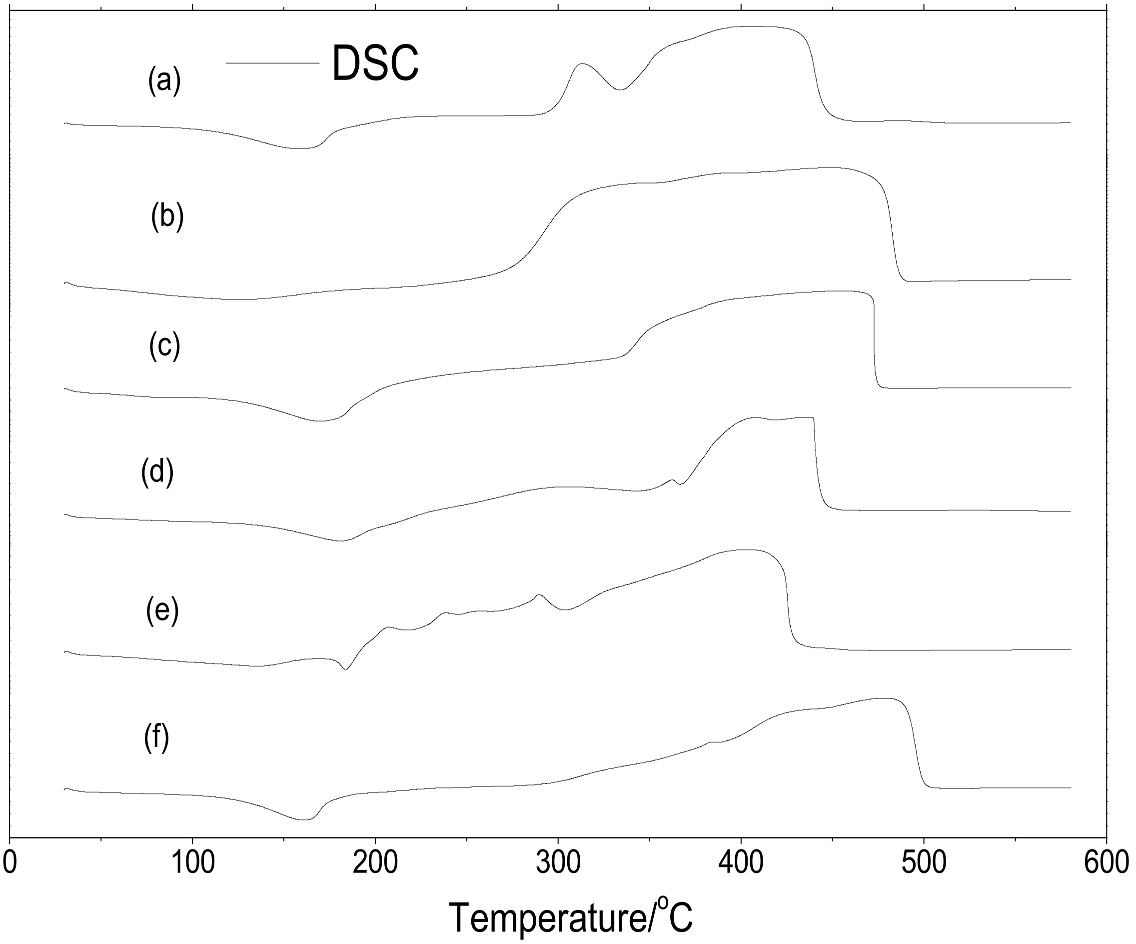

Fig. 3: The DSC curves of of (a) $MnL_2.3.5H_2O$ (m=5.060 mg); (b) $FeL_2.3H_2O$ (5.030 mg); (c) $CoL_3.3.5H_2O$ (5.026 mg); (d) $NiL_3.3.5H_2O$ (5.033 mg); (e) $CuL_3.2H_2O$ (5.012 mg); (f) $ZnL_3.3H_2O$ (4.992 mg). L= pyruvate

The endothermic peak at 184 °C that precede the exothermic events, observed only for copper compound, is attributed to the initial thermal decomposition. The exotherms observed for all the compounds with evidence of several overlapping events between 280-530 °C (Mn), 225-500 °C (Fe), 210-480 °C (Co), 210-460 °C (Ni), 190-470 °C (Cu) and 280-515 °C (Zn), are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in overlapping steps.

Conclusions

From TG curves, elemental analysis and complexometria results a general formula could be established for these compounds in the solid state.

The X-ray powder patterns of the synthesized compounds have a crystalline structure, except the iron compound.

The infrared spectroscopic data suggest that the pyruvate acts as a tridentate ligand towards the metal ions considered in this work.

The TG/DTG and DSC curves, provided information about the thermal stability and thermal decomposition of these compounds.

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Síntese, caracterização e comportamento térmico dos piruvatos de alguns metais bivalentes no estado sólido.

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Resumo: Compostos M-L foram sintetizados no estado sólido, onde M representa os íons bivalentes Mn, Fe, Co, Ni, Cu e Zn e L é o ânion piruvato. Esses compostos foram caracterizados e estudados utilizando-se as técnicas: termogravimetria e termogravimetria derivada (TG/DTG), calorimetria exploratória diferencial (DSC), difratometria de raios X pelo método do pó, espectroscopia de absorção na região do infravermelho, análise elementar e complexometria. Os resultados forneceram informações com respeito à composição, desidratação, sítio de coordenação e decomposição térmica dos compostos isolados.

Palavras chave: metais bivalentes, piruvato, caracterização e comportamento térmico.

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