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2-METHOXYBENZYLIDENEPYRUVATE WITH HEAVIER TRIVALENT LANTHANIDES AND YTTRIUM(III)
Synthesis and characterization

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Solid-state Ln(2-MeO-BP) compounds, where *Ln* stands for trivalent Eu to Lu and Y(III) and 2-MeO-BP (which is 2-methoxybenzylidenepyruvate) have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), X-ray powder diffraction, infrared spectroscopy and other methods of analysis were used to characterize and to study these compounds. On the base of the obtained results an $Ln(2MeO\text{-}BP)_3{\cdot}nH_2O$ general formula can be established.

Keywords: *characterization, heavier lanthanides, yttrium, 2-methoxybenzylidenepyruvate, thermal behaviour*

Introduction

Synthesis of benzylidenepyruvic acid (HBP), as well as of phenyl-substituted derivatives of HBP have been reported in [1, 2]. These acids are of continuous interest as intermediates in pharmacological, industrial and chemical syntheses, in development of enzyme inhibitors and drugs, as model substrates of enzymes, etc. [2–7].

Synthesis and investigation of several metal ion complexes of phenyl-substituted derivatives of BP, have been carried out in aqueous solutions [8] and in solid-state [9–18]. In aqueous solutions these works reported mainly the thermodynamic stability (β_1) and spectroscopic parameters (ε_{1max}, λ_{max}), associated with 1:1 complex species, analytical applications of the ligands, e.g. in gravimetric analysis and as metallochromic indicator. In solid-state the establishment of the stoichiometry and detailed knowledge of the thermal behaviour of ligands and their metal ion compounds have been the main purposes of these studies.

In the present paper, solid-state compounds of heavier trivalent lanthanides (Eu to Lu) and yttrium(III) with 2-methoxybenzylidenepyruvate ($2\text{-}CH_3\text{–}O\text{–}C_6H_4\text{–}CH{=}CH\text{–}COCOO^-$) were prepared. The compounds were investigated by complexometry, elemental analysis, X-ray powder diffractometry, infrared spectroscopy, simultaneous thermogravimetry and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The results allowed us to acquire information concerning these compounds in the solid-state including their thermal stability, thermal decomposition, ligand's denticity and crystallinity.

Experimental

Materials

Sodium salt of 2-methoxybenzylidenepyruvic acid (Na-2-MeO-BP) was prepared following the same procedure as described in [19]. Aqueous solution with 0.1 mol L^{-1} concentration of Na-2-MeO-BP was prepared by direct weighing of the salt.

Lanthanides and yttrium chlorides were prepared from the corresponding metal oxides by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues were dissolved in distilled water and the solutions were again evaporated to near dryness to eliminate the excess of hydrochloric acid. The residues were redissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.1 mol L^{-1} solutions, whose pH were adjusted to 5 by adding diluted sodium hydroxide or hydrochloric acid solutions.

The solid-state compounds were prepared by adding slowly with continuous stirring, the solution of the ligand to the respective metal chloride solutions, until total precipitation of metal ions. The precipitates were washed with distilled water until elimination of chloride ion, filtered through and dried on Whatman n° 42 filter paper and kept in a desiccator over anhydrous calcium chloride under reduced pressure.

Methods

After igniting the compounds to the respective lanthanide or yttrium oxides and dissolving them in a hot solution of concentrated hydrochloric acid their metal ions contents were determined by complexo-

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metric titration with standard EDTA solution using xylenol orange as indicator [20]. The lanthanides and yttrium contents of the compounds were also estimated from their corresponding TG curves. The dehydration of the compounds was also estimated from their corresponding TG curves. The dehydration of the compounds was firstly pointed out by their DTA curves and subsequently confirmed by the broad endothermic peaks centered at 90–120°C in the respective DSC curves. The water contents were then determined from the corresponding mass losses observed in the TG curves. Next, the ligands' content was also assessed from TG curves.

Simultaneous TG-DTA and DSC curves were recorded in models SDT 2960 and Q 10, both from TA instruments. The purge gas was an air flow of 100 mL min^{-1} for TG-DTA and 50 mL min^{-1} for DSC. A heating rate of 20°C min^{-1} was adopted with samples weighing about 7 mg for TG-DTA and 5 mg for DSC. Alumina and aluminum crucibles, the latter with perforated covers, were used for TG-DTA and DSC, respectively.

Carbon and hydrogen microanalysis were performed by using EA 1110, CHNS-O Elemental Analyzer (CE Instruments).

X-ray powder patterns were obtained by using a Siemens D-5000 X-Ray Diffractometer, employing CuK_α radiation (λ=1.541 Å) and settings of 40 kV and 20 mA. Infrared spectra for Na–2-MeO-BP as well as for its trivalent lanthanides and yttrium compounds were recorded on a Nicolet mod. Impact 400 FT-IR instrument, within the 4000–400 cm^{-1} range. The solid-state samples were pressed into KBr pellets.

Results and discussion

The analytical and thermoanalytical (TG) data are shown in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the $\text{Ln(2-MeO-BP)}_3\cdot n\text{H}_2\text{O}$ general formula where *Ln* represents trivalent lanthanides or yttrium, 2-MeO-BP is 2-methoxybenzylidenepyruvate and n=1.5 (Gd, Dy, Lu); 2 (Eu, Tb, Ho, Er, Yb); 2.5 (Y) and 3 (Tm).

The X-ray diffraction powder patterns show that all the compounds were obtained in the amorphous state. The amorphous state is undoubtedly related to the low solubility of these compounds, as already observed in the lanthanides and yttrium compounds with other phenyl substituted derivatives of BP [8]. All attempts at growing good single crystals of the presently investigated compounds or at obtaining them, as polycrystalline powders were unsuccessful. Their amorphous state, the absence of definite melting points and insolubility in a wide variety of solvents suggest that these compounds might be polymeric in nature. It is known that high molecular mass metal coordination polymers bearing oxygen or sulfur as donor atoms are generally hard, fiber or film-like materials, stable at relatively elevated temperatures (i.e., up to 400°C) [21, 22]. The presently prepared compounds do not display these features. So if polymeric, they should be almost certainly of low nuclearity.

Infrared spectroscopic data on 2-methoxybenzylidenepyruvate and its compounds with the metal ions considered in this work are shown in Table 2. The investigation was focused mainly within the 1700–1400 cm^{-1} range because this region is potentially the most informative in attempting to assign coordination sites. In 2-MeO-BP (sodium salt) strong band at 1679 cm^{-1} and a medium intensity band located at 1479 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [23, 24]. The band centered at 1713 cm^{-1} is typical of a conjugated ketonic carbonyl group [23–25]. For all the compounds the bands assigned to the anti-symmetrical stretching carboxylate

Table 1 Analytical data for the $\text{Ln(L)}_3\cdot n\text{H}_2\text{O}$ compounds

Compound	*Ln*/%			Ligand lost/%		Water/%		C/%		H/%		Final residue
	calcd.	TG	EDTA	calcd.	TG	calcd.	TG	calcd.	EA	calcd.	EA	
$\text{Eu(L)}_3\cdot 2\text{H}_2\text{O}$	18.91	18.79	18.62	73.62	73.84	4.48	4.40	49.31	48.80	3.90	4.20	Eu_2O_3
$\text{Gd(L)}_3\cdot 1.5\text{H}_2\text{O}$	19.66	19.75	19.42	73.96	73.84	3.38	3.40	49.35	49.88	3.79	3.92	Gd_2O_3
$\text{Tb(L)}_3\cdot 2\text{H}_2\text{O}$	19.60	19.63	20.04	72.48	72.41	4.45	4.50	48.90	49.10	3.86	3.69	Tb_4O_7
$\text{Dy(L)}_3\cdot 1.5\text{H}_2\text{O}$	20.18	20.25	19.81	73.48	73.36	3.36	3.46	49.23	49.12	3.76	3.69	Dy_2O_3
$\text{Ho(L)}_3\cdot 2\text{H}_2\text{O}$	20.20	19.90	20.02	72.45	72.61	4.41	4.60	48.54	48.32	3.83	3.64	Ho_2O_3
$\text{Er(L)}_3\cdot 2\text{H}_2\text{O}$	20.42	20.40	21.02	72.24	72.13	4.40	4.54	48.40	48.66	3.82	3.41	Er_2O_3
$\text{Tm(L)}_3\cdot 3\text{H}_2\text{O}$	20.14	20.04	20.30	70.54	70.50	6.45	6.50	47.26	47.34	3.97	3.20	Tm_2O_3
$\text{Yb(L)}_3\cdot 2\text{H}_2\text{O}$	20.98	20.95	21.05	71.74	71.75	4.37	4.40	48.06	47.66	3.80	3.12	Yb_2O_3
$\text{Lu(L)}_3\cdot 1.5\text{H}_2\text{O}$	21.35	21.58	21.09	72.40	72.25	3.31	3.20	48.50	48.80	3.71	3.87	Lu_2O_3
$\text{Y(L)}_3\cdot 2.5\text{H}_2\text{O}$	12.01	12.13	12.14	79.88	79.29	4.87	5.00	52.88	53.04	4.31	4.22	Y_2O_3

Ln: heavier trivalent lanthanides and yttrium(III); *L*: 2-methoxybenzylidenepyruvate

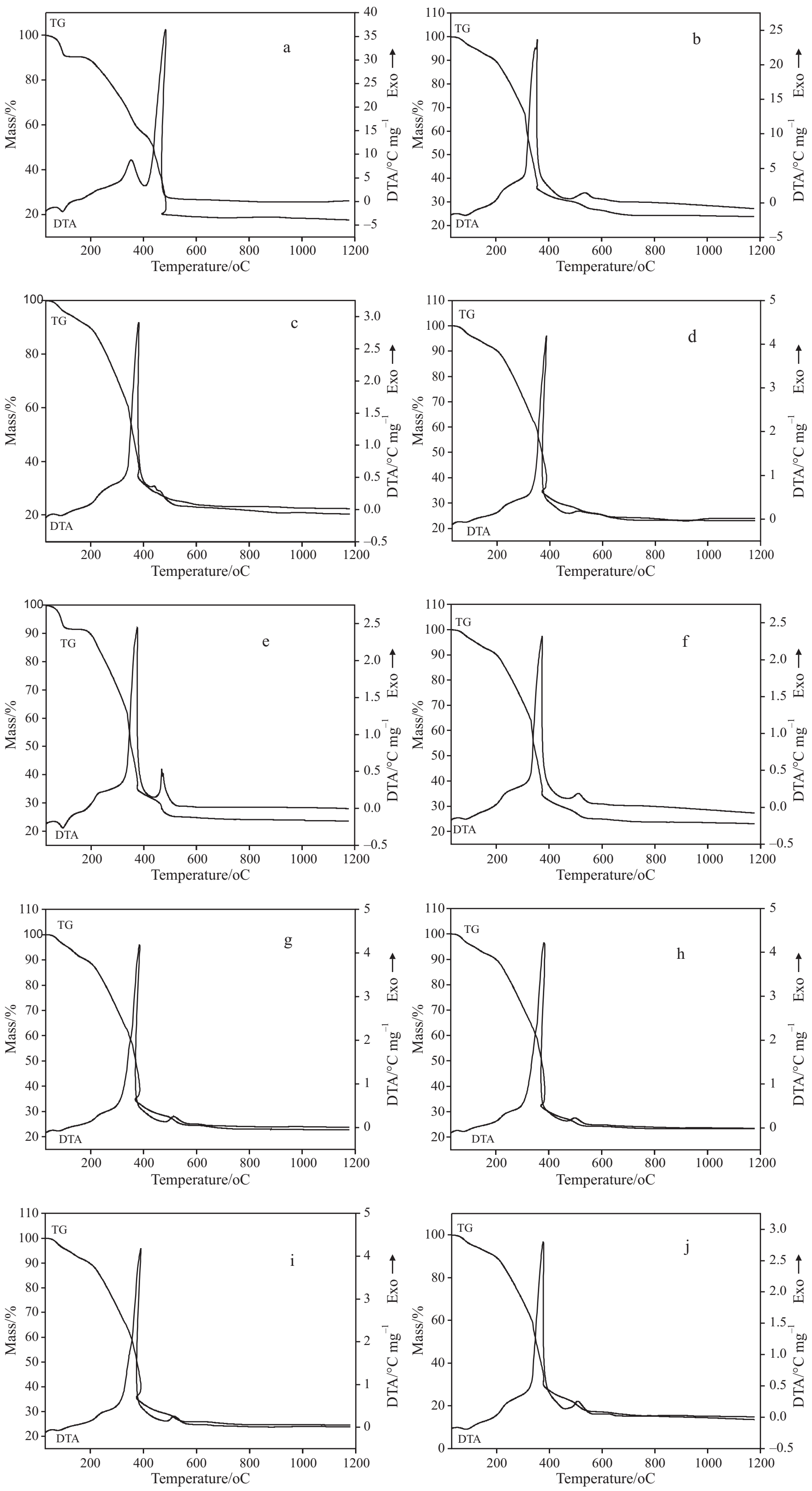

Fig. 1 Simultaneous TG-DTA curves: a – Eu(2-MeO-BP)$_3$·2H$_2$O, *m*=7.0514 mg; b – Gd(2-MeO-BP)$_3$·1.5H$_2$O, *m*=7.216 mg; c – Tb(2-MeO-BP)$_3$·2H$_2$O, *m*=7.1450 mg; d – Dy(2-MeO-BP)$_3$·1.5H$_2$O, *m*=6.9983 mg; e – Ho(2-MeO-BP)$_3$·2H$_2$O, *m*=6.92 mg; f – Er(2-MeO-BP)$_3$·2H$_2$O, *m*=7.0970 mg; g – Tm(2-MeO-BP)$_3$·3H$_2$O, *m*=6.932 mg; h – Yb(2-MeO-BP)$_3$·2H$_2$O, *m*=7.0593 mg; i – Lu(2-MeO-BP)$_3$·2H$_2$O, *m*=7.0279 mg; j – Y(2-MeO-BP)$_3$·1.5H$_2$O, *m*=7.0836 mg; heating rate: 20°C min^{-1}; air flow: 100 mL min^{-1}

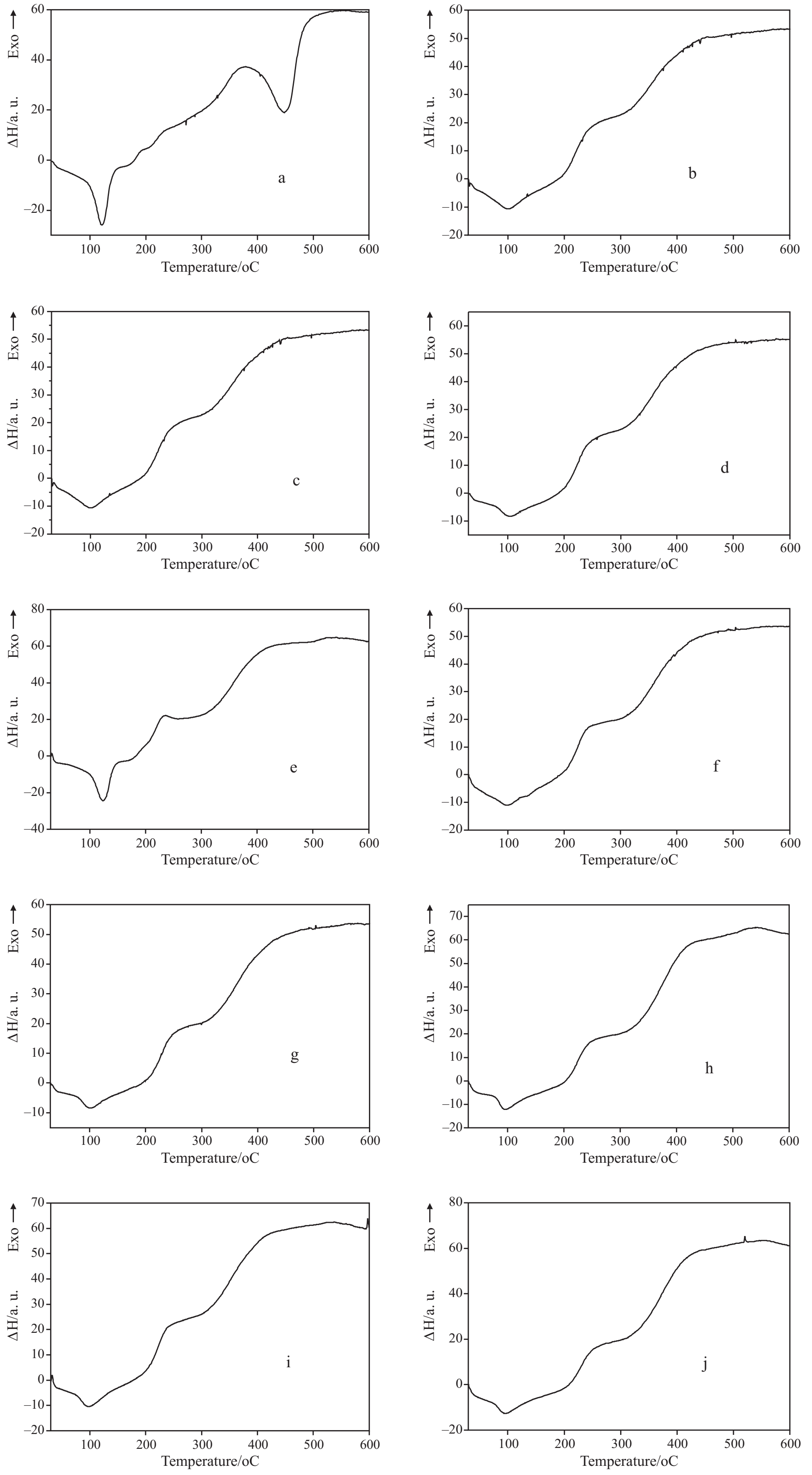

Fig. 2 DSC curves of the compounds a – Eu(2-MeOBP)$_3$·2H$_2$O; b – Gd(2-MeOBP)$_3$·2H$_2$O; c – Tb(2-MeOBP)$_3$·2H$_2$O; d – Dy(2-MeOBP)$_3$·2H$_2$O; e – Ho(2-MeOBP)$_3$·2H$_2$O; f – Er(2-MeOBP)$_3$·2H$_2$O; g – Tm(2-MeOBP)$_3$·2H$_2$O; h – Y(2-MeOBP)$_3$·2H$_2$O; i – Lu(2-MeOBP)$_3$·2H$_2$O; j – Y(2-MeOBP)$_3$·2H$_2$O

frequencies, 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 [25, 26]. The data displayed in Table 2 show that these shifts are dependent on the metal ions.

Simultaneous TG-DTA curves of the compounds are shown in Fig. 1. These curves exhibit mass losses in three consecutive and/or overlapping steps and thermal events corresponding to these losses. Two patterns of thermal behaviour are observed up to 300°C. Firstly, a close similarity is noted concerning the TG-DTA profiles of the europium and holmium compounds Figs 1a and e. On the other hand, Gd, Tb, Dy, Er to Lu and Y compounds display another set of very similar TG-DTA profiles, Figs 1b–d and f–j.

For all compounds the first mass loss (in the 60–110°C range) associated to endothermic peaks at 95–100°C is ascribed to the dehydration, which occurs in a single step. For the europium and holmium compounds the TG curves show that the anhydrous compounds are stable up to 160°C, while for the Gd, Tb, Dy, Er to Lu and Y compounds the mass losses occur without evidence concerning the formation of stable anhydrous compounds and as previously stressed, the temperature corresponding to the mass losses due to dehydration were depicted from the DTA curves.

Once dehydrated, the mass losses above 160°C (Eu, Ho) and 110°C (Gd, Tb, Dy, Er to Lu, Y) corresponding to exothermic events are attributed to the oxidation of the organic matter. Only for the europium compound the oxidation of the organic matter occurs with combustion with the mass losses in two consecutive steps through a fast processes with formation of europium oxide as can be seen in Fig. 1a.

For the other compounds (Gd to Lu, Y) the mass losses also occur in two steps and the change in the slope above 300–350°C that occurs in the first step of the TG curves is ascribed to the increase in the reaction rates. The similarity among these curves suggests that the decomposition mechanism should be the same for the aforementioned compounds. Test with hydrochloric acid solution on these samples heated above 350°C (Gd), 375°C (Er), 380°C (Tb, Tm, Yb, Y) and 390°C (Dy, Ho, Lu), evolution of CO_2 and presence of carbonaceous residue was observed. The evolution of CO_2 shows that in this step the formation of carbonate or a carbonate derivative occurs. In agreement with the mass losses in this step the DTA curves show small exothermic peaks for the Gd, Ho to Lu and Y compounds. For the Tb and Dy compounds this peak is not observed and this is probably due to balance between exothermic process (oxidation of carbonaceous residue) and an endothermic one (decomposition of the metal dioxycarbonate) resulting net heats produce only small exothermic peak or no thermal events.

For all compounds, the final thermal decomposition residues were the respective oxides, Tb_4O_7 and Ln_2O_3 (*Ln*=Gd, Dy–Lu, Y) as proven by X-ray powder diffractometry.

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

The DSC curves of the compounds are shown in Fig. 2. These curves show endothermic and exothermic peaks that all are in agreement with mass losses observed in the TG curves.

Table 2 IR spectroscopic data for sodium 2-methoxybenzylidenepyruvate (2-MeO-BP) and for compounds with heavier trivalent lanthanides or yttrium (cm^{-1})

Compound	ν_{O-H}	$\nu_{as(COO^-)}$	$\Delta\nu_{as(COO^-)}$	$\nu_{sym(COO^-)}$	$\nu_{C=O}$	$\Delta\nu_{C=O}$
2-MeOBP-Na	3488m	1679s	–	1479m	1713s	–
$Eu(L)_3{\cdot}2H_2O$	3507m	1575s	104	1479m	1641s	72
$Gd(L)_3{\cdot}1.5H_2O$	3416m	1588s	91	1485m	1642s	71
$Tb(L)_3{\cdot}2H_2O$	3416m	1589s	90	1487m	1642s	71
$Dy(L)_3{\cdot}1.5H_2O$	3428m	1589s	90	1488m	1642s	71
$Ho(L)_3{\cdot}2H_2O$	3380m	1588s	91	1485m	1642s	71
$Er(L)_3{\cdot}2H_2O$	3429m	1632s	47	1558m	1709s	4
$Tm(L)_3{\cdot}3H_2O$	3412m	1630s	49	1557m	1706s	7
$Yb(L)_3{\cdot}2H_2O$	3418m	1652s	27	1559m	1703s	10
$Lu(L)_3{\cdot}1.5H_2O$	3399m	1658s	21	1558m	1711s	2
$Y(L)_3{\cdot}2.5H_2O$	3387m	1624s	55	1549m	1704s	9

L=2-methoxybenzylidenepyruvate; s: strong; m: medium; ν_{O-H}=hydroxyl group stretching frequency; $\nu_{as(COO^-)}$ and $\nu_{sym(COO^-)}$=symetrical and anti-symetrical vibrations of the COO^- group, respectively; $\nu_{C=O}$=ketonic carbonyl stretching frequency.
$\Delta\nu_{as(COO^-)} = \nu_{as(COO^-)(\text{Na salt})} - \nu_{as(COO^-)(\text{metal complex})}$; $\Delta\nu_{(C=O)} = \nu_{(C=O)(\text{Na salt})} - \nu_{(C=O)(\text{metal complex})}$

Table 3 Temperature ranges θ, mass losses (%) and peak temperatures observed for each step of TG-DTA curves of the compounds

Compound		Steps		
		first	second	third
$Eu(L)_3{\cdot}2H_2O$	θ/°C	60–110	160–400	400–490
	loss/%	4.4	38.2	35.6
	peak/°C	100 (endo)	360 (exo)	490 (exo)
$Gd(L)_3{\cdot}1.5H_2O$	θ/°C	60–110	110–350	350–700
	loss/%	3.4	62.7	11.2
	peak/°C	95 (endo)	360 (exo)	540 (exo)
$Tb(L)_3{\cdot}2H_2O$	θ/°C	60–110	110–380	380–600
	loss/%	4.5	62.5	9.9
	peak/°C	100 (endo)	380 (exo)	440, 460 (exo)
$Dy(L)_3{\cdot}1.5H_2O$	θ/°C	60–110	110–390	390–700
	loss/%	3.5	62.9	10.5
	peak/°C	95 (endo)	390 (exo)	500 (exo)
$Ho(L)_3{\cdot}2H_2O$	θ/°C	60–110	160–390	390–700
	loss/%	4.6	62.1	10.6
	peak/°C	95 (endo)	390 (exo)	475 (exo)
$Er(L)_3{\cdot}2H_2O$	θ/°C	60–110	110–375	375–700
	loss/%	4.5	62.1	10.1
	peak/°C	95 (endo)	375 (exo)	505 (exo)
$Tm(L)_3{\cdot}3H_2O$	θ/°C	60–110	110–380	380–650
	loss/%	6.5	59.9	10.6
	peak/°C	95 (endo)	380 (exo)	520 (exo)
$Yb(L)_3{\cdot}2H_2O$	θ/°C	60–110	110–380	380–600
	loss/%	4.4	64.4	7.3
	peak/°C	95 (endo)	380 (exo)	500 (exo)
$Lu(L)_3{\cdot}1.5H_2O$	θ/°C	60–110	110–390	390–600
	loss/%	3.2	62.7	9.6
	peak/°C	95 (endo)	390 (exo)	510 (exo)
$Y(L)_3{\cdot}2.5H_2O$	θ/°C	60–110	110–380	380–700
	loss/%	5.0	66.1	13.2
	peak/°C	95 (endo)	380 (exo)	510 (exo)

The endothermic peak at 95–100°C is assigned to the dehydration, which occurs in a single step. The dehydration enthalpies found for these compounds (Eu to Lu and Y) were: 236.9, 133.4, 228.8, 119.2, 280.5, 127.5, 123.4, 99.8, 125.3 and 93.7 kJ mol^{-1}, respectively.

Conclusions

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

The infrared spectroscopic data suggest that 2-MeO-BP acts as a bidentate ligand, both by α-ketonic carbonyl and carboxylate groups of the ligand towards the metal ions considered in this work.

The TG-DTA, TG/DTG and DSC curves provided previously unreported information concerning the thermal behaviour and thermal decomposition of these compounds.

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