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Synthesis, thermal and spectroscopic study of light lanthanide nicotinate, in the solid state

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ABSTRACT

Characterization, thermal stability and thermal decomposition of light trivalent lanthanide nicotinates, $Ln(C_6H_4NO_2)_3 \cdot nH_2O$ (Ln = La to Gd, except Pm) were synthesized and investigated employing simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC), Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry, complexometry and TG–DSC coupled to FTIR. In all the compounds the dehydration occurs in two consecutive steps and the thermal decomposition of the anhydrous compounds occurs in single, two, three or four consecutive steps, with the formation of the respective oxides CeO_2, Pr_6O_{11} and Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd), as final residue. The results also provided information about the composition, thermal behavior, identification of gaseous products evolved during the thermal decomposition of these compounds. Furthermore, the theoretical and experimental spectroscopic data suggest the possible modes of coordination of the ligand with the metals.

1. Introduction

Nicotinic acid (3-picoline, vitamin B_3 or pyridine-3-carboxylic acid) is the biological precursor of the co-enzymes: nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) [1]. It can be used as a ligand in the synthesis of compounds rare earths. Belong to the lanthanide rare earth metals and always aroused interest because of their magnetic and spectroscopic properties. Because of this many studies are being conducted with these elements and their compounds for the development of contrast agents, luminescent probes, magnetic materials, etc. [1,2].

A survey of the literature shows that the papers involving bivalent transition metal and nicotinic acid reported the spectroscopic, thermogravimetic, magnetic studies, thermochemical behavior, thermal decomposition and polymeric structure [1–5]. Synthesis, characterization, thermal analysis, hydrothermal synthesis, crystal structure, anti-ulcer actives, as well as grow and characterization of a novel polymer, have also been reported [6–13]. However, some works were found about thermal and spectroscopic studies of nicotinic acid with lanthanide ions in the solid state, in general these studies are aiming at the determining structural, luminescence studies, synthesis, characterization, thermal studies and thermodynamic properties [14–21].

Thus, the present paper deals the preparation of solid-state compounds of light trivalent lanthanides (La–Gd, except Pm) with nicotinate and investigate by means of complexometry in the TG–DSC curves simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC), infrared spectroscopy (FTIR), X-ray powder diffractometry and TG–DSC coupled to FTIR which make possible a correct interpretation for the mechanism of a thermally induced reactions involving the formation of gaseous evolved during the thermal decomposition [22].

2. Experimental

2.1. Material

The nicotinic acid ($C_6H_5NO_2$) with 99.5% purity was obtained from Sigma and it was used as received. The lanthanides were used from the oxides (Ln_2O_3 Ln = La, Nd, Sm, Eu, Gd and Pr_6O_{11}) except cerium where was used cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ all from Sigma with purity of 99.9%.

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2.2. Synthesis

Lanthanide chloride solutions were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid, following the procedure described in the literature [23].

Lanthanide carbonates were prepared by adding slowly with continuous stirring saturated sodium hydrogen carbonate solution to the corresponding metal chloride or nitrate (for cerium), suspension heated to near boiling, until quantitative precipitation of the metal ions and cooled to room temperature. The precipitates were washed with distilled water until elimination of chloride or nitrate ions (qualitative test with $AgNO_3/HNO_3$ solution for chloride ions or diphenylamine/H_2SO_4 solution for nitrate ions) and maintained in aqueous suspension.

Solid-state lanthanide compounds were obtained by mixing the corresponding metal carbonates maintained in aqueous suspension with nicotinic acid, in slight excess. The aqueous suspension was heated up to ebullition until total neutralization of the carbonate. The solutions of the respective metal nicotinates were evaporated up to dryness in a water bath, washed with ethanol, heated to near boiling to remove excess nicotinic acid, dried at 323 K in a forced circulation air over during 12 h, and kept in a desiccator over anhydrous calcium chloride.

2.3. Experimental equipment and conditions

In the solid-state, metal ions, hydration water and nicotinate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution [24,25].

Carbon, nitrogen and hydrogen contents were determined by microanalytical procedures, with a CNH Elemental Analyzer from PerkinElmer, model 2400, as well as was determined by calculation based on the mass losses observed in TG curves, since the hydration water and ligand lost during the thermal decomposition occur with the formation of the respective oxides with stoichiometry known, as final residues.

The X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer, employing CuKα radiation ($\lambda = 1.541$ Å) and setting of 40 kV and 20 mA.

Infrared spectra were obtained by using a Nicolet iS10 FTIR spectrophotometer, using ATR accessory with Ge window. The FTIR spectra were recorded with 32 scans per spectrum at resolution of 4 cm^{-1}.

The DSC curves were obtained by using a thermal analysis system model DSC Q10 from TA Instruments. The purge gas was a nitrogen flow of 50 mL min^{-1}. A heating rate of 10 K min^{-1} was adopted, with sample weighing about 2 mg. Aluminum crucible with perforated cover was used for recording the DSC curve.

Simultaneous TG–DSC curves were obtained by using a TGA–DSC 1 star^e system, from Mettler Toledo. The purge gas was an air flow of 50 mL min^{-1} and a heating rate of 10 K min^{-1} was adopted, with samples weighing about 10 mg. Alumina crucibles were used for recording the TG–DSC curves.

The measurements of the gaseous products were carried but using a TG–DSC Mettler Toledo coupled to a FTIR spectrophotometer Nicolet, with gas cell and DTGS KBr detector. The furnace and the heated gas cell (523 K) were coupled through a heated (498 K) 120 cm stainless steel line transfer with diameter of 3 mm, both purged with dry air (50 mL min^{-1}). The FTIR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm^{-1}.

2.4. Computational details

In this study, the employed quantum chemical approach to determine the molecular structures was Becke three parameter hybrid theory [26] using the Lee–Yang–Par (LYP) correlation functional [27], and the basis sets used for calculations were: [4s] for H (2S) [28], [5s4p] for C (3P), N (4S) and O (3P) [28], [10s6p] and [17s11p7d] for La (2D) [29]. The diffuse functions for the lanthanum atom (2D) were calculated according to the procedure described in [28] and these values are: $\alpha s = 0.00669534$, $\alpha p = 0.079333735$, $\alpha d = 0.096432865$.

In order to better describe the properties of the compound in the implementation of the calculations, it was necessary to include polarization functions [28–30] for all atoms of the compound.

The polarization functions are: $\alpha p = 0.33353749$ for H (2S), $\alpha d = 0.72760279$, $\alpha d = 0.35416230$ and $\alpha d = 0.36059494$ for C (3P), N (4S) and O (3P) respectively, and $\alpha f = 0.36935391$ for La (2D) atoms. The role of a basis set is a crucial point in theoretical studies of metal complexes, since the description of the configuration of the metal in the complex differs from the neutral state. The performed molecular calculations in this study were done using the Gaussian 09 routine [31].

The theoretical infrared spectrum, it was calculated using a harmonic field [32] based on C1 symmetry (electronic state 1A). Frequency values (not scaled), relative intensities, assignments, and description of vibrational modes are presented. The crystal geometry of the $La(C_6H_4NO_2)_3{\cdot}2H_2O$ was proposed based on ref. [15] and it was optimized using Berny Algorithm [33] and the calculations of vibrational frequencies were also implemented to determine an optimized geometry constitutes minimum or saddle points. The principal infrared active fundamental modes assignments and descriptions were done by the GaussView 5.0.2 W graphics routine [34].

3. Results and discussion

The analytical and thermoanalytical (TG) results are shown in Table 1. From these data the stoichiometry of compounds were established, which are in agreement with the general formula Ln $(L)_3{\cdot}2H_2O$, where Ln represent light trivalent lanthanides, except promethium and L is nicotinate.

Table 1

Analytical, thermoanalytical (TG) and elemental analysis (EA) results for the $Ln(C_6H_4NO_2)_3{\cdot}nH_2O$ compounds.

Compounds	Ln(oxide)/%			L (lost)/%		H_2O/%		C/%			N/%			H/%			Metal oxide
	Calc.	EDTA	TG	Calc.	TG	Calc.	TG	Calc.	TG	EA	Calc.	TG	EA	Calc.	TG	EA	
$La(L)_3{\cdot}2H_2O$	30.10	29.83	29.75	63.24	63.34	6.66	6.91	39.94	40.14	40.24	15.53	15.61	15.89	2.99	3.00	3.35	La_2O_3
$Ce(L)_3{\cdot}2H_2O$	31.73	30.96	31.63	61.63	61.73	6.64	6.64	39.85	39.91	39.60	15.50	15.52	15.20	2.98	2.98	3.25	CeO_2
$Pr(L)_3{\cdot}2H_2O$	31.34	31.31	31.12	62.03	62.38	6.63	6.50	39.79	39.92	39.39	15.47	15.52	15.83	2.97	2.98	3.05	Pr_6O_{11}
$Nd(L)_3{\cdot}2H_2O$	30.78	30.53	31.08	62.63	62.15	6.59	6.77	39.55	38.38	39.93	15.34	15.27	15.60	2.96	2.94	2.56	Nd_2O_3
$Sm(L)_3{\cdot}2H_2O$	31.54	31.05	31.51	61.94	62.07	6.52	6.42	39.12	39.13	39.39	15.21	15.22	15.63	2.92	2.92	2.50	Sm_2O_3
$Eu(L)_3{\cdot}2H_2O$	31.75	32.07	31.83	61.75	61.45	6.50	6.72	39.00	38.95	38.65	15.16	15.14	14.81	2.92	2.91	3.21	Eu_2O_3
$Gd(L)_3{\cdot}2H_2O$	32.39	32.05	33.01	61.17	60.82	6.44	6.17	38.63	38.28	38.78	15.02	14.88	15.44	2.89	2.86	2.58	Gd_2O_3

L: nicotinate; Ln: lanthanides (La to Gd, except Pm).