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Synthesis, characterization, thermal and spectroscopic studies of solid glycolate of light trivalent lanthanides, except promethium

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ABSTRACT

Solid-state Ln–L compounds, where Ln stands for light trivalent lanthanide (La to Gd, except Pm) and L is glycolate ($C_2H_3O_3$) have been synthesized. Characterization and investigation were made by means of complexometry, X-ray diffractometry, Fourier transform infrared spectroscopy (FTIR), simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC), and TG–DSC coupled to FTIR. All the compounds were obtained in the anhydrous state. The thermal decomposition of the anhydrous compounds occurs in a single, three, four or five steps and the final residue was CeO_2, Pr_6O_{11} and Ln_2O_3 (Ln = La, Nd to Gd). The results also provide information concerning thermal behavior and identifications of the 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

Several M-glycolate compounds (M = Am, Cm, Bk, Mn, Zn, Ni, Ti) have been investigated in the solid-state. These works reported the complexation, preparation, crystal structure, some application, thermal decomposition, as well as the use as precursor in other synthesis [1–6]. The works involving lanthanide glycolates reported the structural study on lanthanum and gadolinium glycolates [7], synthesis, characterization and crystal structure of La, Ce, Nd involving the two ligands, glycolate and carbonate [8], crystal structure of Dy and Lu glycolate complexes [9] and synthesis and structure of two cerium complexes with mixed-ligands oxalate and glycolate [10]. A survey of literature shows that no paper on synthesis, characterization and thermoanalytical studies with all trivalent lanthanide glycolates were found in the literature.

In this paper the object of the present research was to prepare solid-state compounds of light trivalent lanthanides (i.e. La, Ce, Pr, Nd, Sm, Eu and Gd) with glycolate ($C_2H_3O_3^-$) and to investigate by means of complexometry, elemental analysis, X-ray powder diffractometry, infrared spectroscopy (FTIR), simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) and TG–DSC coupled to FTIR. The results allowed us to acquire information concerning these compounds in the solid-state, including their thermal stability and thermal decomposition in dynamic dry air atmosphere.

2. Experiment

2.1. Synthesis

The glycolic acid, $C_2H_4O_3$ with 99% purity was obtained from Sigma–Aldrich and used without any additional purification.

Lanthanide chlorides (ca. 0.1 mol L^{-1}) were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid, following the procedure described in the literature [11]. Cerium (III) was used as its nitrate and ca. 0.1 mol L^{-1} aqueous solution of this ion was prepared by direct weighing of the salt.

Lanthanide carbonates were prepared by adding slowly with continuous stirring, saturated sodium hydrogen carbonate solution to the corresponding metal chlorides or nitrate for cerium, until quantitative precipitation of the metal ions. The precipitates were washed with distilled water until elimination of chloride or nitrate ions (qualitative test with $AgNO_3/HNO_3$ for chloride and 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 glycolic acid in slight excess. The aqueous suspension was heated up to ebullition until total neutralization of the carbonate.

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The solutions of the respective glycolates were evaporated up to about 20 mL and ethanol was added to occur the precipitation of the compounds. The precipitates were filtered and washed 5 times with 20 mL of ethanol, to eliminate the glycolic acid in excess, dried at 50 °C in a forced circulation air oven during 24 h and kept in a desiccator over anhydrous calcium chloride.

2.2. Experimental equipment and conditions

In the solid-state lanthanide ions, water and glycolate contents were determined from TG curves. The lanthanide ions were also determined by complexometry with standard EDTA solution, using xylenol orange as indicator, after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution [12,13].

Carbon and hydrogen contents were determined by calculation based on the mass losses observed in the TG curves, since the ligand lost in the thermal decomposition occur with the formation of the respective oxides with stoichiometry known, as final residues.

X-ray powder patterns were obtained by using a Siemens D-5000 X-Ray Diffractometer employing CuKα radiation (λ = 1.541 Å) and setting of 40 kV and 20 mA.

The attenuate total reflectance infrared spectra were run on a Nicolet iS10 Fourier transform infrared spectrophotometer (FTIR), using an ATR accessory with Ge window. The FTIR spectra were recorded with 32 scans per spectrum at resolution of 4 cm^{-1}.

Simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) curves were obtained by using a TG–DSC 1 Star^e system, from Mettler Toledo. The purge gas was a dry air flow of 50 mL min^{-1} and a heating rate of 10 °C 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 out using a TG–DSC1 Mettler-Toledo coupled to a FTIR spectrophotometer Nicolet with gas cell and DTGS KBr detector. The furnace and the heated gas cell (250 °C) were coupled through a heated (225 °C) 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}.

2.3. Computational strategy

In this study, the employed quantum chemical approach to determine the molecular structures was Becke three parameter hybrid theory [14] using the Lee–Yang–Par.

(LYP) correlation functional [15], and the basis sets used for calculations were: 4s for H (^{2}S) [16], [5s4p] for C (^{3}P) and O (^{3}P) [16], [17s11p7d] for La (^{2}D) [17] and [20s12p8d5f] for Eu (^{8}S). The diffuse functions for the lanthanum atom (^{2}D) were calculated according to the procedure described in Ref. [16] and these values are: αs = 0.00669534, αp = 0.079333735, αd = 0.096432865.

Basis set for Eu (^{8}S) atom. The 29s19p14d8f [discretization parameters: Ω(s) = −0.567, $\Delta\Omega$(s) = 0.120, N(s) = 6.0; Ω(p) = −0.282, $\Delta\Omega$(p) = 0.116, N(p) = 6.0, Ω(d) = −0.037, $\Delta\Omega$(d) = 0.110, N(d) = 6.0; Ω(f) = −0.150, $\Delta\Omega$(f) = 0.140, N(f) = 6.0]/20s12p8d5f (9,1,1,1,1,1,1,1,1,1,1,2,1,1,1,1,1,1,1/6,1,1,1,1,1,2,2,1,1,1,1/7,1,1,1,1,1,1,1/4,1,1,1,1) basis set were built with the add of the Generator Coordinate Hartree–Fock method. The polarization function is αg = 0.94743211. The diffuse functions for the europium atom (^{8}S) were calculated according to the procedure described in Ref. [16] and these values are: αs = 0.01329988, αp = 0.15567263, αd = 0.61140237, αf = 0.29582122. Full details about the wave function developed in this work are available upon request to the e-mail address: oswatreu@iq.unesp.br.

In order to better describe the properties of the compound in the implementation of the calculations, it was necessary to include polarization functions [16–18] for all atoms of the compound. The polarization functions are: αp = 0.33353749 for H (^{2}S), αd = 0.72760279, and αd = 0.36059494 for C (^{3}P), O (^{3}P), respectively, and αf = 0.36935391 for La (^{2}D) atoms. For the atom Eu (^{8}S) polarization function was presented in the previous paragraph. 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 [19].

The theoretical infrared spectrum, it was calculated using a harmonic field [20] based on C_1 symmetry (electronic state ^{1}A). Frequency values (not scaled), relative intensities, assignments, and description of vibrational modes are presented. The crystal geometry of the $La(C_2H_3O_3)_3$ and $Eu(C_2H_3O_3)_3$ is not available in the literature, so a geometry was optimized using Berny Algorithm [21] 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 [22].

3. Results and discussion

The analytical and thermoanalytical (TG) results of the synthesized compounds are shown in Table 1. Based on these results the stoichiometry of these compounds was stablished which is in agreement with the general formula $Ln(C_2H_3O_3)_3$, where Ln represents light trivalent lanthanides and $C_2H_3O_3^-$ is glycolate.

3.1. XRD

The X-ray powder patterns (Fig. 1) showed that all the compounds have crystalline structure, with evidence for formation of two isomorphous groups, being the lanthanum, praseodymium and neodymium compounds the first one and samarium and europium compounds the other group. The cerium and

Table 1
Analytical and thermoanalytical (TG) data for the $Ln(C_2H_3O_3)_3$ compounds.

Compounds	Metal oxide (%)			L (lost) (%)		C (%)		H (%)		Final residue
	Calc.	EDTA	TG	Calc.	TG	Calc.	TG	Calc.	TG	
$La(L)_3$	44.75	44.48	43.96	55.25	56.04	19.79	20.07	2.47	2.51	La_2O_3
$Ce(L)_3$	47.63	47.23	47.17	52.53	52.83	19.87	19.98	2.51	2.52	CeO_2
$Pr(L)_3$	46.51	46.83	45.97	53.49	54.03	19.69	19.89	2.48	2.51	Pr_6O_{11}
$Nd(L)_3$	45.55	45.16	45.55	54.45	54.45	19.51	19.51	2.46	2.46	Nd_2O_3
$Sm(L)_3$	46.43	46.65	46.22	53.57	53.78	19.19	19.27	2.42	2.43	Sm_2O_3
$Eu(L)_3$	46.67	46.33	46.59	53.33	53.41	19.11	19.14	2.41	2.41	Eu_2O_3
$Gd(L)_3$	47.40	46.57	46.82	52.60	53.18	18.84	19.04	2.38	2.41	Gd_2O_3

Ln, light lanthanide; L, glycolate.