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Journal of Solid State Chemistry 171 (2003) 212–216

JOURNAL OF
SOLID STATE
CHEMISTRY

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Synthesis, characterization, spectroscopic study and thermal analysis of rare-earth picrate complexes with L-arginine

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Received 28 March 2002; received in revised form 30 August 2002; accepted 12 September 2002

Abstract

Rare-earth picrate complexes with L-arginine were synthesized and characterized. Analysis of carbon, hydrogen, nitrogen and thermal analysis data suggest a general formula $\mathrm{Ln(pic)_3 \cdot 2L\text{-}Arg \cdot 2H_2O}$ (Ln = La–Lu, Y, pic = picrate, L-Arg = arginine). IR spectra indicate the presence of water molecules and suggest that L-arginine is coordinated to the central ion through the nitrogen of the amine group. Bands due to picrate ions also indicate that at least in part they are coordinated as bidentate through the phenoxo group and one oxygen of an *ortho*-nitro group. X-ray diffraction powder pattern results indicate that these complexes are very similar in structure. The parameters obtained from the absorption spectrum of the solid Nd compound indicated that the metal–ligand bonds present weak covalent character. The emission spectra of the Eu compound indicate the existence of different europium coordinaton environments. Thermal analyses results indicated that all the compounds present a similar behavior.

Keywords: Rare earths; Picrates; L-arginine; Synthesis and characterization; Spectroscopy; Thermal analysis

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1. Introduction

Interactions of rare earths with amino acids have been extensively investigated, due to their great importance in biological systems [1–4]. Rare-earth ions are often used as spectroscopic probes in studies of these systems. The interaction of rare earths with biological systems acquire particular importance in view of the similarities in the sizes of Ca(II) and Ln(III) ions and their preference for oxygen donors in complex formation [5]. The amino acids are important compounds of these systems because they participate in many biochemical processes essential to living systems.

Arginine is of particular interest in this regard as it has been demonstrated to have an array of desirable biological properties [6–7]. The guanidinium group of L-arginine in some enzymes is an important binding site for various hydrogen bond acceptors such as carboxylate, superoxide and phosphate groups, and is recently attracting much attention. Arginine stimulates anabolic hormone release, improves nitrogen balance, and has been demonstrated to be immunostimulatory and thymotrophic [8–10]. Arginine also is the major substrate for the production of nitric oxide. Another important function of arginine is to participate as an integral constituent of the urea cycle [11,12].

Rare-earth picrate addition compounds with several ligands have been synthesized involving synthesis, and characterized, in our laboratories [13–21]. Complexes of rare-earth picrates with arginine (α-amino-δ-guanidovaleric acid), one of the essential amino acids, have not yet been reported. In this article, we describe the synthesis, characterization, spectroscopic study and thermal analysis of rare-earth picrate complexes with L-arginine.

2. Experimental

The complexes were prepared by reaction between rare-earth picrates, $\mathrm{Ln(pic)_3 \cdot }x\mathrm{H_2O}$, dissolved in ethanol, and L-arginine (Sigma, purity above 98% and used as received), dissolved in water, separately, in a molar ratio 1:2 (salt:ligand). The alcoholic and aqueous solutions were mixed and stirred until a yellow precipitate formed. The adducts were filtered and dried in vacuum desiccators over anhydrous calcium chloride at room temperature.

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doi:10.1016/S0022-4596(02)00153-6

Table 1
Analytical data for $Ln(pic)_3 \cdot 2L\text{-}Arg \cdot 2H_2O$ compounds

Ln	C (%)		H (%)		N (%)		$2H_2O$ (%)		Ln_2O_3[a] (%)	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.[b]	Calc.	Exp.[b]
La	29.8	30.6	3.2	3.7	19.7	19.0	3.0	3.0	13.5	13.1
Ce	29.8	30.1	3.2	3.3	19.7	19.4	3.0	3.1	14.3	15.3
Pr	29.8	30.5	3.2	3.4	19.7	19.6	3.0	3.0	14.1	15.9
Nd	29.7	30.2	3.2	3.6	19.6	19.7	3.0	2.9	13.8	13.8
Sm	29.6	29.9	3.1	3.4	19.5	19.1	2.9	2.4	14.3	17.2
Eu	29.5	29.5	3.1	3.5	19.5	19.4	2.9	2.8	14.4	17.0
Gd	29.4	29.9	3.1	3.5	19.4	19.3	2.9	2.8	14.8	13.1
Tb	29.3	29.3	3.1	3.4	19.4	18.4	2.9	2.4	15.2	17.6
Dy	29.3	29.5	3.1	3.4	19.4	19.5	2.9	3.0	15.1	16.2
Ho	29.2	29.4	3.1	3.7	19.3	18.9	2.9	3.1	15.3	16.6
Er	29.2	29.6	3.1	3.6	19.2	19.0	2.9	3.0	15.5	19.7
Tm	29.1	30.0	3.1	3.5	19.2	19.3	2.9	3.0	15.6	16.1
Yb	29.1	30.0	3.1	3.5	19.2	19.4	2.9	3.1	15.8	14.2
Lu	29.0	29.3	3.1	3.5	19.1	19.5	2.9	2.9	16.0	19.9
Y	31.1	30.0	3.3	3.4	20.5	19.5	3.1	3.0	9.8	13.6

[a] CeO_2, Pr_6O_{11} and Tb_4O_7.
[b] TG data analysis for dehydration and residues.

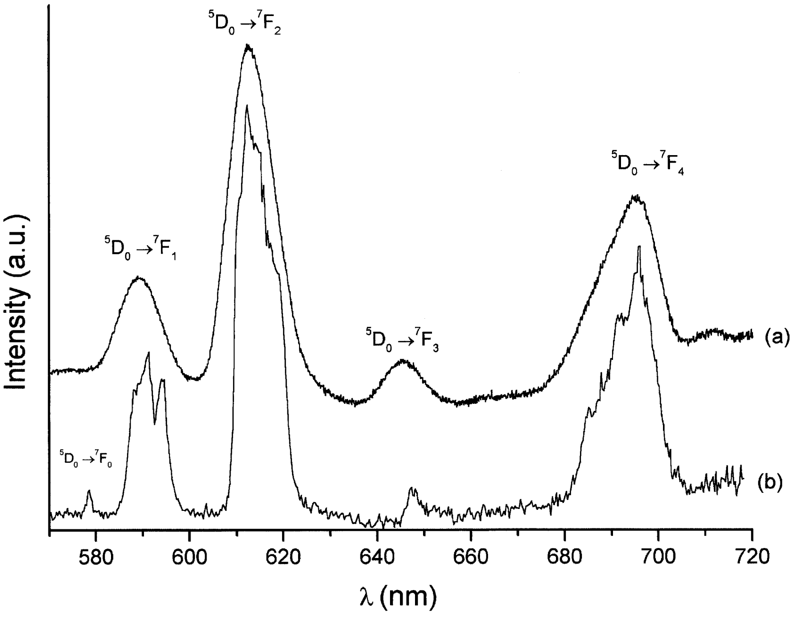

Fig. 1. Emission spectra of the $Eu(pic)_3 \cdot 2L\text{-}Arg \cdot 2H_2O$ complex, at room temperature (a) and 77 K (b).

Carbon, hydrogen and nitrogen contents of the complexes were obtained by microanalytical procedures using a Perkin–Elmer analyzer (Model 240). Infrared absorption spectra were recorded in the range 4000–400 cm^{-1} in Nujol, using a Nicolet FTIR-810 spectrometer. The absorption spectrum of the Nd compound was obtained in a Zeiss DMR-10 spectrophotometer in the solid state at room temperature using a silicone mull. The europium compound emission and excitation spectra were obtained at room temperature and 77 K on an SPEX-Fluorolog-1681 spectrofluorimeter.

Differential scanning calorimetry (DSC) curves were recorded on a DSC-50 instrument (Shimadzu) using aluminum crucibles with ca. 1.5 mg of samples, under dynamic nitrogen atmosphere (50 $mL\,min^{-1}$) and heating rate of 10°C min^{-1} in the temperature range 25–500°C. The DSC cell was calibrated with indium (m.p. 156.6°C; $\Delta H_{fus} = 28.54\,J\,g^{-1}$) and zinc (m.p. 419.6°C). Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained with a Shimadzu TGA-50 thermobalance in the temperature range 25–900°C, using platinum crucibles with ca. 1.5 mg of samples, under dynamic air atmosphere (50 mL min^{-1}) and heating rate of 10°C min^{-1}.

X-ray diffraction powder patterns were obtained on a Miniflex Rigaku diffractometer, with Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation, in the interval 10–40° (2θ).

3. Results and discussion

The stoichiometry of the complexes was determined from elemental (%C, %H and %N) and thermal analyses (%H_2O and %Ln_2O_3). The analytical results of the complexes are given in Table 1. The analysis data are consistent with the general formula $Ln(pic)_3 \cdot 2$L-Arg$\cdot 2H_2O$, where Ln = La–Lu, Y. All the compounds are hygroscopic solids, insoluble in acetone, ethanol, methanol, acetonitrile, nitromethane, nitrobenzene, chloroform and slightly soluble in water.

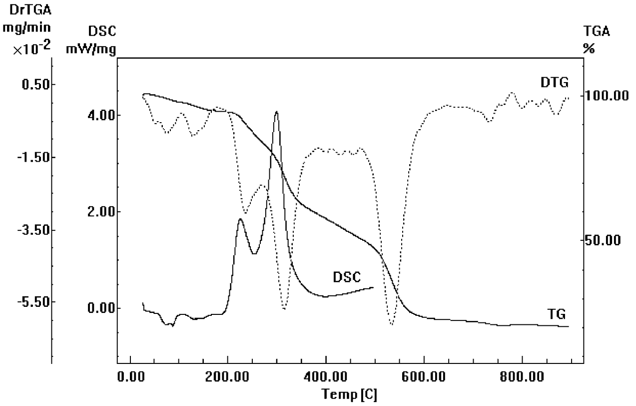

Fig. 2. TG/DTG and DSC curves of the $Lu(pic)_3 \cdot 2$L-Arg$\cdot 2H_2O$ complex obtained in dynamic air and nitrogen atmosphere (50 mL min^{-1}), respectively, heating rate 10°C min^{-1}.

All infrared spectra are similar and present as a general characteristic a shift of the νNH band of the L-arginine to lower and higher frequencies (3284, 3180, 3080 cm^{-1}) in relation to free ligand (3297, 3059 cm^{-1}) suggesting that the L-arginine is coordinated to the central ion through the nitrogen of the amine group. The bands at 1560 and 1374 cm^{-1} of the complexes attributed to ν_{as}COO and ν_sCOO, respectively, do not present significant changes in relation to the free ligand (ν_{as}COO, about 1561 cm^{-1} and ν_sCOO, about 1376 cm^{-1}). Bands due to picrate ions (νCO, about 1266 cm^{-1}, $\nu_{as}NO_2$, about 1611, 1500 cm^{-1} and ν_sNO_2, 1338, 1306 cm^{-1}) indicate that at least in part they are coordinated as bidentate through the phenoxo group and one oxygen of an *ortho*-nitro group. Bands near 3360–3440 cm^{-1} are attributed to νOH, indicating the presence of water molecules and this shows that these molecules in the complexes are hydrogen bonded [22–25].

The absorption spectrum of the solid neodymium compound registered at room temperature for the hypersensitive $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transitions. The calculated nephelauxetic parameter ($\beta = 0.989$), covalent factor ($b^{1/2} = 0.071$) and Sinha's parameter ($\delta = 1.03$) indicate a small covalent character of the bonds. The excitation spectra of the solid Eu compound at room temperature present broad absorption bands with maxima at ca. 394 nm. The emission spectra of the solid europium compound at room temperature and 77 K are similar, but at low temperature is better resolved. The number of peaks for a single complex is given by $2J+1$.

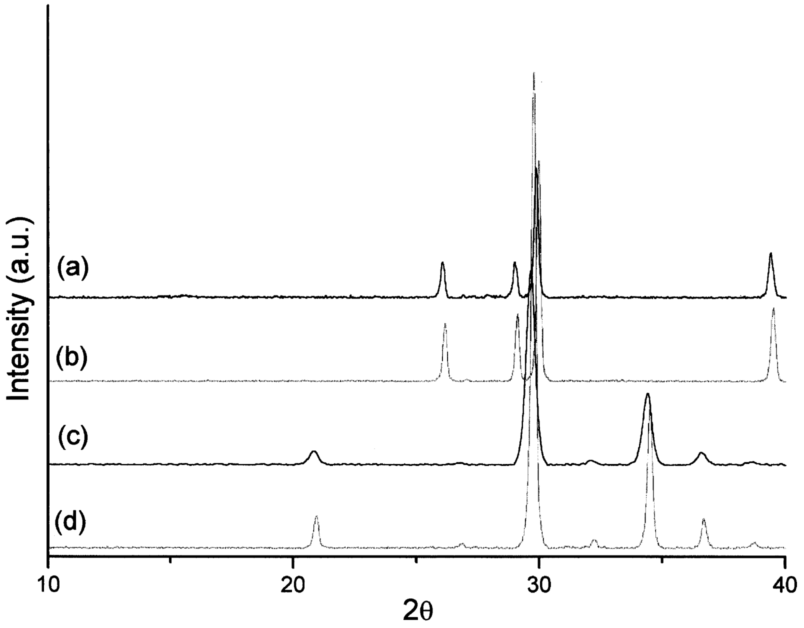

Fig. 3. XRD patterns of the residues of thermal decomposition of the complexes $La(pic)_3 \cdot 2$L-Arg$\cdot 2H_2O$ (a) and $Lu(pic)_3 \cdot 2$L-Arg$\cdot 2H_2O$ (c) and of the rare-earth oxides La_2O_3 (b) and Lu_2O_3 (d).

Table 2
Result from TG/DTG and DSC curves for Ln(pic)$_3 \cdot$ 2L-Arg $\cdot$ 2H$_2$O compounds

Ln	Step 1			Step 2			Step 1 + Step 2	Step 3			Step 4			Step 3 + Step 4	Step 5[a]	
	TG Mass loss (%)	DTG T (°C)	DSC T (°C)	TG Mass loss (%)	DTG T (°C)	DSC T (°C)	DSC ΔH (kJ mol^{-1})	TG Mass loss (%)	DTG T (°C)	DSC T (°C)	TG Mass loss (%)	DTG T (°C)	DSC T (°C)	DSC ΔH (kJ mol^{-1})	TG Mass loss (%)	DTG T (°C)
La	3.0	75	76	2.8	156	118	44	12.8	222	214	29.1	306	288	−1675	39.2	472
Ce	3.1	54	84	2.8	178	126	50	12.1	216	208	24.5	295	277	−1738	42.2	386
Pr	3.0	73	63	3.0	128	116	23	12.1	226	217	26.8	305	287	−2109	39.2	470
Nd	2.9	81	79	2.8	126	122	92	12.8	225	215	29.8	307	290	−1974	37.9	477
Sm	2.4	73	72	3.1	122	108	20	12.6	234	220	29.8	314	296	−2443	34.9	482
Eu	2.8	52	54	2.8	124	114	32	12.5	224	208	27.9	306	290	−2099	37.0	459
Gd	2.8	70	85	3.0	102	114	102	12.9	229	219	31.5	313	296	−1953	36.8	496
Tb	2.4	47	76	3.3	136	118	52	11.2	220	222	29.1	314	297	−2497	36.4	493
Dy	3.0	82	86	2.9	144	122	76	13.0	230	219	30.1	311	294	−2192	34.8	502
Ho	3.1	82	86	2.8	127	127	103	12.7	228	218	25.5	311	294	−2238	39.3	501
Er	3.0	75	74	2.9	128	135	119	12.6	235	224	24.4	311	295	−2447	37.4	511
Tm	3.0	73	73	2.8	130	121	72	13.9	235	224	27.9	314	298	−2350	36.3	519
Yb	3.1	83	73	2.8	131	133	142	14.9	235	225	31.6	317	301	−2165	33.4	518
Lu	2.9	75	74	2.8	128	132	87	12.1	236	225	30.8	316	300	−1959	31.5	535
Y	3.0	46	67	2.7	145	141	99	13.0	226	216	30.6	315	297	−2285	37.1	501

T = peak temperature.
[a] The last peak was not observed in the DSC.

For the transitions: (a) $^5D_0 \rightarrow {}^7F_0$ only one peak may be observed; for (b) $^5D_0 \rightarrow {}^7F_1$ three peaks; for (c) $^5D_0 \rightarrow {}^7F_2$ a maximum of five peaks, etc. In the spectrum obtained at 77 K a large number of bands are observed: (a) one peak and two shoulders; (b) two principal peaks and several shoulders; (c) more than fine peaks, etc., due to the probable existence of polymeric species. In this case, what we observe is an envelope of many transitions arising from different coordination environments (Fig. 1).

Results of thermal analysis indicate that all complexes exhibit a similar thermoanalytical profile. Fig. 2 shows TG/DTG and DSC curves in the temperature range 25–900°C and 25–500°C, respectively, for Lu(pic)$_3 \cdot$ 2L-Arg $\cdot$ 2H$_2$O as representative of the series. The TG/DTG curves of complex indicate five thermal decomposition stages. The first event of weight loss occurs in the temperature range 27–110°C ($\Delta m = 2.9\%$) corresponding to release of two water molecules. The second weight loss of 2.8%, in the temperature range 110–184°C, may be attributed to the loss of two ammonia molecules, attached to the carbon atom of the guanidine group [26]. The last three steps, in the temperature ranges 184–277°C ($\Delta m = 12.1\%$), 277–460°C ($\Delta m = 30.8\%$) and 460–900°C ($\Delta m = 31.5\%$) were attributed to the decomposition of the main carbon chain of arginine and the picrates. These data are corroborated by the microanalytical procedures and IR spectroscopy [27].

The thermal events observed in DSC curves are in concordance with those observed in TG/DTG curves. The DSC curve shows two endothermic events in the temperature ranges 27–106°C and 106–170°C, corresponding to removal of water and ammonia molecules, respectively. Besides, it also exhibits two exothermic peaks in the temperature interval 170–400°C with overall enthalpy of -1959 kJ mol^{-1}, assigned to thermal decomposition of the main carbon chain of the arginine and picrate species.

It is important to mention that small amounts of material were used in thermal analyses due to the explosive properties of the picrates.

The residues after thermal decomposition of the complexes at 900°C were characterized by X-ray powder patterns as rare-earth oxides. Fig. 3 shows the XRD patterns of the residues of thermal decomposition of the complexes La(pic)$_3 \cdot$ 2L-Arg $\cdot$ 2H$_2$O and Lu(pic)$_3 \cdot$ 2L-Arg $\cdot$ 2H$_2$O and of the rare-earth oxides La$_2$O$_3$ and Lu$_2$O$_3$. TG and DSC curves for the other Ln(pic)$_3 \cdot$ 2L-Arg $\cdot$ 2H$_2$O (omitting figures) presented similar profiles to those of the lutetium compound. TG and DSC results for all complexes are summarized in Table 2.

X-ray diffraction powder pattern results indicate that these complexes are very similar in their structures. Several attempts to obtain single crystals were unsuccessful.

Acknowledgments

The authors acknowledge the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support. One of us (TMS) is much indebted to FAPESP for a doctoral fellowship.

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