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SYNTHESES, CHARACTERIZATION AND THERMAL PROPERTIES OF LANTHANIDE COMPLEXES WITH 2-MERCAPTONICOTINIC ACID

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Fourteen new complexes with the general formula of $Ln(Hmna)_3 \cdot nH_2O$ (n=2 for *Ln*=La–Ho and n=1 for Er–Lu, H_2mna=2-mercaptonicotinic acid) were synthesized and characterized by elemental analyses, IR spectra and thermogravimetric analyses. In addition, molar specific heat capacities were determined by a microcalorimeter at 298.15 K. The IR spectra of the prepared complexes revealed that carboxyl groups of the ligands coordinated with Ln(III) ions in bidentate chelating mode. Hydrated complexes lost water molecules during heating in one step and then the anhydrous complexes decomposed directly to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. The values of molar specific heat capacities for fourteen solid complexes were plotted against the atomic numbers of lanthanide, which presented as ‘tripartite effect’. It suggested a certain amount of covalent character existed in the bond of Ln^{3+} and ligands, according with nephelauxetic effect of 4f electrons of rare earth ions.

Keywords: *IR spectrum, 2-mercaptonicotinic acid, molar specific heat capacity, thermal analysis*

Introduction

There is currently considerable interest in the coordination chemistry of lanthanide elements, with biological and/or medicinal activities [1, 2]. Nicotinic acid (Vitamin B3) and its derivatives possess very interesting pharmaceutical properties [3, 4]. 2-Mercaptonicotinic acid, 2-HS(C_5H_3N)COOH, a derivative of nicotinic acid, exhibited three potential binding sites-pyridine N, thiol S and carboxylic O. In recent years, several metal complexes containing 2-mercaptonicotinic acid ligand have already been reported [5–17]. Some of them represented well antimicrobial activities [11, 12]. To the best of our knowledge, the complexes of rare earth elements have been less reported to date.

Herein, we synthesized fourteen rare earth elements complexes with 2-mercaptonicotinic acid in ethanol solution. The complexes were characterized by elemental analyses, IR spectra, thermogravimetric analyses and molar specific heat capacities. The aim of our work was to prepare the complexes of lanthanide(III) with 2-mercaptonicotinic acid, to determine their properties and to investigated their thermal decomposition in a static air atmosphere.

Experimental

Materials

Lanthanide chloride hydrates, $LnCl_3 \cdot xH_2O$ (*Ln*=La–Lu, x=3–4) were prepared in our experiment, which were attested by chemical analyses. Other chemicals used in the experiments were of analytical grade and commercial available without further purification.

Syntheses of the complexes

H_2mna (1.5 mmol) and NaOH (1.5 mmol) were added to absolute ethanol (20 mL) and dissolved under 323 K, then rare earth chloride (3.0 mmol) was added to the solution with continuous stirring. The mixture was further stirred for 1 h. The precipitates were isolated by filtration, washed with distilled water and absolute ethanol, respectively, and dried in vacuum and stored in a desiccator over P_4O_{10} ready to be used.

Methods

The contents of rare earth were assayed using EDTA titration method. C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. The IR spectra were recorded with a BEQ VZNDX-550 spectrometer using the KBr pellets technique over the range 4000–400 cm^{-1}. All TG tests were performed with a Perkin-Elmer thermogravimetric analyzer at a heating rate 10 K min^{-1}. Samples were heated in static air in ceramic crucibles to 1073 K using α-Al_2O_3 as a standard. The calorimetric experiments were performed with an RD496-III type microcalorimeter [18]. The calorimetric constant at 298.15 K was determined by the Joule effect before experiment, which is 63.901±0.030 $\mu V\ mW^{-1}$. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be

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17.238±0.048 kJ mol^{-1}, which was in good agreement with the value of 17.241±0.018 kJ mol^{-1} from [19].

Results and discussion

Elemental analyses

The composition analytical data were summarized in Table 1. From these values, we could find that the experimental data were consistent with the calculated values and the formula $Ln(Hmna)_3{\cdot}nH_2O$ (n=2 for Ln=La–Ho and n=1 for Er–Lu) were determined.

Table 1 Composition analytical data of the above complexes

Complex	Found (calcd.)/%			
	Ln	C	H	N
$LaL_3{\cdot}2H_2O$	21.87 (21.81)	33.79 (33.91)	2.40 (2.53)	6.46 (6.60)
$CeL_3{\cdot}2H_2O$	22.06 (21.93)	33.74 (33.86)	2.46 (2.53)	6.42 (6.59)
$PrL_3{\cdot}2H_2O$	22.01 (22.05)	33.75 (33.81)	2.43 (2.52)	6.43 (6.58)
$NdL_3{\cdot}2H_2O$	22.57 (22.18)	33.61 (33.75)	2.35 (2.52)	6.38 (6.56)
$SmL_3{\cdot}2H_2O$	23.29 (23.37)	33.15 (33.23)	2.33 (2.48)	6.34 (6.46)
$EuL_3{\cdot}2H_2O$	23.32 (23.49)	33.10 (33.18)	2.45 (2.48)	6.31 (6.45)
$GdL_3{\cdot}2H_2O$	23.89 (24.08)	32.79 (32.93)	2.32 (2.46)	6.35 (6.40)
$TbL_3{\cdot}2H_2O$	24.11 (24.19)	32.68 (32.88)	2.32 (2.45)	6.24 (6.39)
$DyL_3{\cdot}2H_2O$	24.70 (24.76)	32.63 (32.63)	2.34 (2.44)	6.23 (6.35)
$HoL_3{\cdot}2H_2O$	24.85 (24.88)	32.46 (32.58)	2.31 (2.43)	6.19 (6.34)
$ErL_3{\cdot}H_2O$	25.87 (25.69)	33.19 (33.44)	2.08 (2.18)	6.32 (6.50)
$TmL_3{\cdot}H_2O$	25.98 (26.03)	33.08 (33.29)	2.08 (2.17)	6.34 (6.47)
$YbL_3{\cdot}H_2O$	26.59 (26.60)	32.90 (33.03)	2.09 (2.16)	6.27 (6.42)
$LuL_3{\cdot}H_2O$	26.58 (26.69)	32.81 (32.98)	2.06 (2.15)	6.32 (6.41)

L=$Hmna^{-}$

IR spectra

The IR spectra of the fourteen complexes were similar, but different from that of the free ligand. The broad features at 3410–3423 cm^{-1} in the spectra of the complexes were attributed to water molecule. Because of the absence of the band at about 950 cm^{-1}, the water molecules occurred as crystallization water [20]. The vibration ν_{SH} around 2410 cm^{-1} in the complexes were shifted insignificantly (8–4 cm^{-1}) or did not change their position compared to the free ligand, suggesting that the sulfur atom of the complexes was not coordinated to the Ln(III) ions. The IR spectra of the complexes showed distinct vibrational bands at 1568–1562 and 1314–1308 cm^{-1}, which have been assigned as the ν_{CN} vibrations (thioamide I and II bands) and at 1074–1068 and 658–650 cm^{-1}, which were attributed to the ν_{CS} vibrations (thioamide III and IV bands). The corresponding thioamide bands of the free ligand were at 1562, 1310, 1071 and 650 cm^{-1}, respectively. No significant changes have been observed in the thioamide bands, supporting the sulfur atom did not coordinate to the metal ions.

The absorption band of C=O group at 1681 cm^{-1} disappeared in the complexes, and the complexes displayed both symmetric and asymmetric stretching vibrations of COO^{-} at 1422~1429 and 1548~1560 cm^{-1}, respectively. The $\Delta\nu=\nu_{as}-\nu_{s}$=125~134 cm^{-1} was smaller than that of sodium salt of H_2mna ($\Delta\nu$= 1603–1438=165 cm^{-1}), which indicated that the carboxyl groups of the complexes were coordinated with the Ln(III) ions in bidentate chelating coordination mode [21].

Thermogravimetric analyses

The thermal decomposition characteristics of the complexes was summarized in Table 2. The thermal behavior of all fourteen complexes was similar. Figure 1 presented the TG-DTG curves of thulium complex as an example. When heated the hydrated complexes of La–Lu, crystallization water molecules lost in one step over the range 323–348 to 343–353 K. This conclusion was consistent with the IR spectra.

Once dehydrated, all the anhydrous complexes decomposed directly to oxides Ln_2O_3 (Ln=La, Nd, Sm–Gd and Dy–Lu), CeO_2, Pr_6O_{11} and Tb_4O_7 over the range 543–573 to 953–988 K, as evidenced by X-ray powder diffraction analysis of samples obtained by heating small quantities of the complexes at 1073 K in an oven. These X-ray patterns were identical to the ones of the respective oxides calcinated at 1073 K.

The results suggested that the following schemes of the thermal decomposition of Ln(III) 2-mercaptonicotinates:

$$Ln(Hmna)_3{\cdot}2H_2O \rightarrow Ln(Hmna)_3 \rightarrow Ln_2O_3,\ Pr_6O_{11} \text{ and } Tb_4O_7$$

where Ln=La, Nd, Sm–Gd, Dy and Ho.

$$Ce(Hmna)_3{\cdot}2H_2O \rightarrow Ce(Hmna)_3 \rightarrow CeO_2$$

$$Ln(Hmna)_3{\cdot}H_2O \rightarrow Ln(Hmna)_3 \rightarrow Ln_2O_3,\ Ln\text{=Er–Lu}$$

Table 2 Thermoanalytical data of Ln(III) 2-mercaptonicotinates

Complex	ΔT_1/K	Mass loss/%		ΔT_2/K	Mass loss/%	
		calcd.	found		calcd.	found
$LaL_3 \cdot 2H_2O$	328–353	5.65	5.5	548–973	74.44	72.8
$CeL_3 \cdot 2H_2O$	328–348	5.64	5.7	543–963	73.05	71.2
$PrL_3 \cdot 2H_2O$	333–353	5.60	5.4	558–973	73.38	71.4
$NdL_3 \cdot 2H_2O$	338–353	5.63	5.3	563–968	73.83	72.7
$SmL_3 \cdot 2H_2O$	333–353	5.55	5.5	553–983	73.13	71.3
$EuL_3 \cdot 2H_2O$	323–348	5.53	5.7	553–983	72.95	71.0
$GdL_3 \cdot 2H_2O$	333–348	5.49	5.3	563–988	72.36	70.5
$TbL_3 \cdot 2H_2O$	333–353	5.48	5.6	553–983	71.57	69.8
$DyL_3 \cdot 2H_2O$	333–353	5.45	5.3	558–978	71.79	70.2
$HoL_3 \cdot 2H_2O$	333–353	5.43	5.1	553–978	71.52	69.6
$ErL_3 \cdot H_2O$	323–343	2.78	2.5	558–973	70.47	69.3
$TmL_3 \cdot H_2O$	328–343	2.77	2.6	573–948	70.29	69.5
$YbL_3 \cdot H_2O$	323–343	2.75	2.4	573–953	69.00	67.8
$LuL_3 \cdot H_2O$	323–343	2.75	2.4	573–968	69.65	68.3

L=Hmna$^-$, ΔT_1 – temperature range of dehydration process, ΔT_2 – temperature range of decomposition of anhydrous complexes to oxides: Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7.

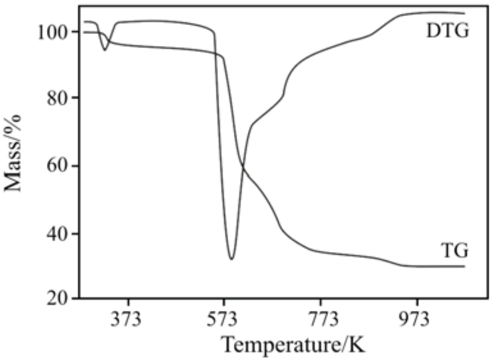

Fig. 1 TG-DTG curves of thulium complex

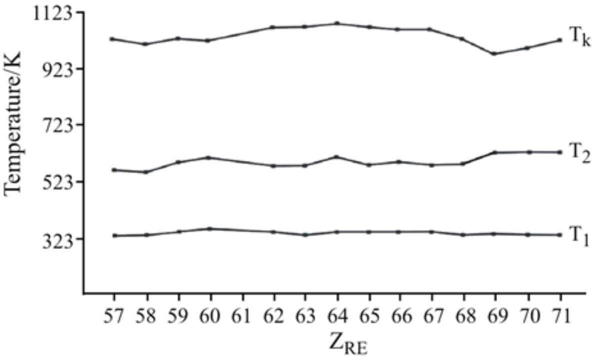

Fig. 2 Relationship between T_1, T_2, T_k and the atomic number Z_{RE}

The relationship between T_1, T_2, T_k and the atomic number of lanthanide Z_{RE} was shown in Fig. 2. The beginning temperature of dehydration (T_1) and of decomposition (T_2) changed indistinctively with the increasing atomic number Z_{RE}. However, the temperature of decomposition for the heavy rare earth having the smaller ionic radius showed the higher value (573 K) in the three complexes (Tm–Lu). The temperature that the corresponding lanthanide oxides (T_K) existed stably presented irregularly change. It was noted that Tm_2O_3 formed at the lowest temperature (948 K).

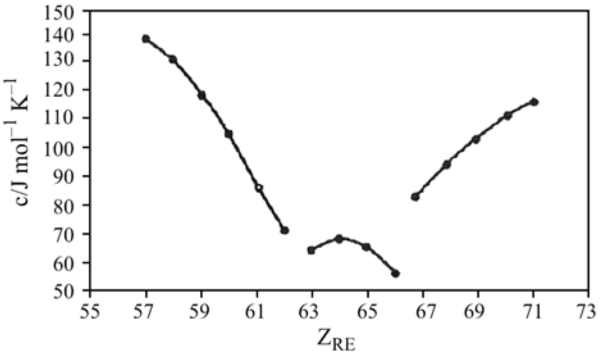

Fig. 3 The molar special heat capacities of complexes *vs.* Z_{RE}

Molar specific heat capacities of complexes

The molar specific heat capacities of the complexes were measured according to [22] (measuring 6 times for each sample), and their molar specific heat capacities are calculated from the data in Table 3 and presented in Table 4.

The molar specific heat capacities of the Ln(III) complexes c are plotted against the atomic numbers of

Table 3 Data of the heat and heat capability of the empty cell and the standard substances (298.15 K)[a]

Heats of disequilibrium and specific heat capacity	The empty cell	Standard α-Al_2O_3	Sublimed benzoic acid
$q(1)$/mJ	3689.151	3825.725	3909.248
$q(2)$/mJ	3686.060	3827.302	3912.490
$q(3)$/mJ	3687.238	3829.849	3911.858
$q(4)$/mJ	3690.008	3827.946	3908.362
$q(5)$/mJ	3691.445	3830.873	3912.998
$q(6)$/mJ	3691.994	3830.667	3914.650
q(mean±SD)/mJ	3689.316±0.495	3828.727±0.842	3911.601±0.968
Relative standard deviation	$2.578\cdot10^{-4}$	$2.200\cdot10^{-4}$	$2.476\cdot10^{-4}$
Specific heat capacity, c/J mol^{-1} K^{-1}		78.724±1.377 (79.03 [23])	145.891±1.003 (145.327 [24])

[a] $SD=\sqrt{\frac{\Sigma(x_1-\bar{x})^2}{n-1}}$

Table 4 Data of the molar specific heat capacities of the complexes (298.15 K)[b]

Complex	m/g	q(mean±SD)/mJ	c(mean±SD)/J mol^{-1} K^{-1}
$LaL_3\cdot2H_2O$	1.97856	3839.868±1.391	139.59±0.49
$CeL_3\cdot2H_2O$	2.23254	3847.851±2.498	130.27±0.64
$PrL_3\cdot2H_2O$	2.03125	3820.658±2.256	118.62±0.65
$NdL_3\cdot2H_2O$	2.00342	3803.004±2.933	104.11±0.81
$SmL_3\cdot2H_2O$	1.98467	3765.317±1.808	70.25±0.57
$EuL_3\cdot2H_2O$	2.27614	3769.195±1.761	64.38±0.49
$GdL_3\cdot2H_2O$	2.15118	3768.574±2.909	67.59±0.75
$TbL_3\cdot2H_2O$	2.00963	3761.298±2.544	65.71±0.72
$DyL_3\cdot2H_2O$	1.99975	3749.543±2.347	55.25±0.68
$HoL_3\cdot2H_2O$	2.35762	3796.317±2.083	83.26±0.53
$ErL_3\cdot H_2O$	2.23714	3804.104±2.250	94.13±0.59
$TmL_3\cdot H_2O$	2.02425	3803.684±1.911	103.65±0.58
$YbL_3\cdot H_2O$	1.99563	3809.435±2.295	110.42±0.67
$LuL_3\cdot H_2O$	2.15723	3826.770±2.729	116.89±0.71

[b] $SD=\sqrt{\frac{\Sigma(x_1-\bar{x})^2}{n-1}}$, $L=Hmna^-$

lanthanide Z_{RE} (Fig. 3), presenting an obvious 'tripartite effect', suggest that a certain amount of covalent character existed in the bond of Ln^{3+} and ligands, according with Nephelauxetic effect of 4f electrons of rare earth ions.

Conclusions

Complexes of lanthanide(III) with 2-mercaptonicotinic acid were prepared as solids with a molar ratio of metal to organic ligand of 1:3. During heating the hydrate complexes, they dehydrated in one step forming anhydrous and next decomposed to oxides Ln_2O_3 (Ln=La, Nd, Sm–Gd and Dy–Lu), CeO_2, Pr_6O_{11} and Tb_4O_7. The molar specific heat capacities of the complexes c against the atomic numbers of lanthanide Z_{RE} displayed an obvious 'tripartite effect', which thermodynamically witnessed a certain amount of covalent character existed in the bond of Ln^{3+} and ligands, according with Nephelauxetic effect of 4f electrons of lanthanide ions.

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