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Compounds of lanthanide picrates and 2-azacyclononanone (aza): synthesis, characterization and thermal study

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Abstract

Addition compounds between lanthanide(III) picrates and azacyclononanone(aza) were characterized by spectroscopic, microanalytical and X-ray data, with special emphasis on thermogravimetric techniques.

Keywords: Lanthanide addition compounds; Thermogravimetry; Cyclic lactones

1. Introduction

Complexes between lanthanide picrates and ligands containing oxygen as donor atom have already been described in the literature [1]. This is part of a general fluorescence intensity/structure relationship study involving lactams [2] with different hydrocarbon chains (hydrophobic part) as ligands and lanthanide salts as picrate [3] perchlorates [2], etc.

In this paper, the synthesis, characterization and thermal study of complexes with composition $Ln(pic)_3 \cdot 3(aza)$ (Ln=Nd, Eu, Tb, Dy, Ho, Er, Tm and Y) are reported. The compounds were characterized by EDTA complexometric titration of Ln; C, H, N microanalysis; IR absorption spectrometry; and fluorescence and thermal techniques.

2. Experimental

The synthesis of hydrated picrates involves: (a) preparation of the lanthanide basic carbonates by reaction of the respective oxides with hot hydrochloric acid under stirring and maintaining pH at 2–3, followed by dilution, heating to boiling and addition of urea (pH 7.0). The precipitates were filtered and washed with water to eliminate chloride ions (test with Ag^+ ions). (b) The rare earth picrates were prepared by reaction of a water suspension of the basic carbonates with picric acid under stirring in a water bath at about 90°C and maintaining a small excess of the carbonates. The hot solution was filtered and left to stand at room temperature to crystallize. The yellow crystals were filtered and left to dry at room temperature. The complexes were obtained by reaction of ethanolic solutions of the hydrated picrates with an ethanolic solution of the ligand (molar ratio 1:3). The precipitates were filtered, washed with ethanol and dried in vacuo under anhydrous calcium chloride. Lanthanide ions were determined by EDTA complexometric titration [4]. C, H, N analyses were carried out on a Perkin-Elmer 240 equipment. IR spectra were recorded on a MIDAC Prospect FTIR spectrometer using nujol mulls between KBr plates. Fluorescence spectra were recorded at room temperature and at 77 K on a Hitachi MPF-4 spectrometer with excitation at 394 nm. TG and DTG, in N_2 dynamic atmosphere at several heating rates were obtained in a TGA-7 Delta series Perkin-Elmer thermobalance with platinum crucibles. DSC curves were obtained in the 25–600°C range on a 2010 DSC TA Instruments calorimeter. Low masses were used (ca. 1 mg) and a 3°C min^{-1} heating rate under N_2 (60 ml min^{-1}) atmosphere. The DSC was calibrated using metallic indium 99.99% pure, melting point 156°C and $\Delta H_f = 28.59$ J g^{-1}. X-ray diffraction patterns, powder method, were determined on a Rigaku RU-200B diffractometer employing Cu Kα 1.54060 Å radiation.

3. Results and discussion

Table 1 presents the analytical results compatible with a general composition $Ln(pic)_3 \cdot 3(aza)$, where Ln=Nd, Eu, Tb, Dy, Ho, Er, Tm and Y. From the X-ray diffraction

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Table 1
Summary of analytical results (%) for compounds with general formula $Ln(pic)_3 \cdot 3(aza)$

Ln	M		C		H		N	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Nd	11.52	11.80	40.26	40.11	4.07	4.03	13.42	13.07
Eu	12.06	12.04	40.01	40.01	4.05	3.97	13.34	13.25
Tb	12.55	12.40	39.79	39.81	4.03	3.93	13.26	13.26
Dy	12.79	12.80	39.68	39.44	4.02	3.98	13.23	13.52
Ho	12.96	13.10	39.60	39.54	4.01	3.89	13.20	12.95
Er	13.12	13.07	39.53	39.75	4.00	4.02	13.18	12.99
Tm	13.23	13.13	39.48	39.20	3.98	3.98	13.16	13.08
Y	7.43	7.26	42.12	42.05	4.26	4.07	14.04	13.97

patterns (powder method) it was possible to observe only one isomorphous series.

Infrared absorption spectral data are summarized in Table 2. The νCO shifts towards lower frequencies are an evidence of bonding through the aza carbonyl oxygen. Bands related to picrate ions are suggestive of different coordination modes involving the phenolic and *ortho* nitrogroup oxygen atoms, as observed in hydrated salts [5–8].

From the luminescence spectrum of the Eu compound at 77 K, a D_{3h} symmetry was inferred based on the $^5D_o \rightarrow {}^7F_1$ transition three energy levels (A_2 and E split) and five $^5D_o \rightarrow {}^7F_2$ peaks (two E and one A_2 species) [9]. A very weak $^5D_o \rightarrow {}^7F_o$ peak suggests a slight distortion towards C_{3v}. This is in agreement with the crystal structure determination [10], where the coordination polyhedron could be described as a slightly distorted tricapped trigonal prism, with aza coordinated through carbonyl oxygens and three bidentate picrates coordinated through the phenoxy and *o*-nitrogroup oxygens. This can be extended to the whole isomorphous series.

TG/DTG results show that the compounds are thermally stable until approximately 290°C and suffer thermal decomposition at ca. 300°C with ligand loss in practically one step. At higher temperatures, picrate decomposition occurs giving a Ln_2O_3 residue (Table 3), except for the terbium compound. Fig. 1 presents typical TG/DTG curves. Its seems that the heating rates (5 or 10°C min^{-1}) do not affect the thermal behaviour (Fig. 1), but at 15°C min^{-1} explosions may occur. (N_2 dynamic atmosphere). DSC techniques show that the complexes present a melting behaviour at ca. 180°C with a ΔH varying from 28.6 to 48.0 kJ g^{-1}. Decomposition with aza loss occurs endothermically at ca. 300°C with ΔH in the range 840–1478 kJ g^{-1} (Table 4). The ligand alone melts, as expected, at 78°C. Fig. 2 presents a typical DSC curve.

Table 2
Infrared absorption frequencies (cm^{-1}) for compounds with the general formula $Ln(pic)_3 \cdot 3(aza)$

Ln	$\nu_{as}NO_2$	ν_sNO_2	νCO	νCN	δNO_2
Nd	1534m1566sh	1368m1324w	1267w	921s720w	838m
Eu	1536m1568sh	1367m1326w	1269w	921s781w	839m
Tb	1536m1568sh	1365m1326w	1269m	920vs780w	838w
Dy	1534m1567sh	1367m1328w	1269w	920vs779w	839m
Ho	1538s1570sh	1370m1331m	1272w	922s782w	841m
Er	1535m1568sh	1368m1322w	1269w	921s778w	842m
Tm	1537m1569sh	1367w1330w	1272w	921s782w	839w
Y	1537s1569sh	1366m1329w	1271w	922vs780w	840m
aza			1288w	944s796w	

v=very strong; s=strong; m=medium; w=weak; sh=shoulder.

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Table 3
Summary of TG data for compounds with formula $Ln(pic)_3 \cdot 3(aza)$

Ln	Temp. range (°C)	Mass loss/residue		Attribution
		Theor. (%)	Exp. (%)	
Nd	209–368	33.83	33.8	–3aza
	760	13.46	13.3	Nd_2O_3 (residue)
Eu	208–382	33.62	34.0	–3aza
	850	13.97	14.0	Eu_2O_3 (residue)
Tb	215–385	33.44	34.3	–3aza
	860	14.75	12.9	Tb_4O_7 (residue)
Dy	220–389	33.34	33.0	–3aza
	800	14.68	14.8	Dy_2O_3 (residue)
Ho	217–372	33.28	34.0	–3aza
	760	14.84	14.6	Ho_2O_3 (residue)
Er	220–376	33.22	34.0	–3aza
	760	15.00	14.8	Er_2O_3 (residue)
Tm	220–386	33.18	33.6	–3aza
	850	15.11	15.1	Tm_2O_3 (residue)
Y	207–382	35.39	35.7	–3aza
	850	9.43	9.2	Y_2O_3 (residue)

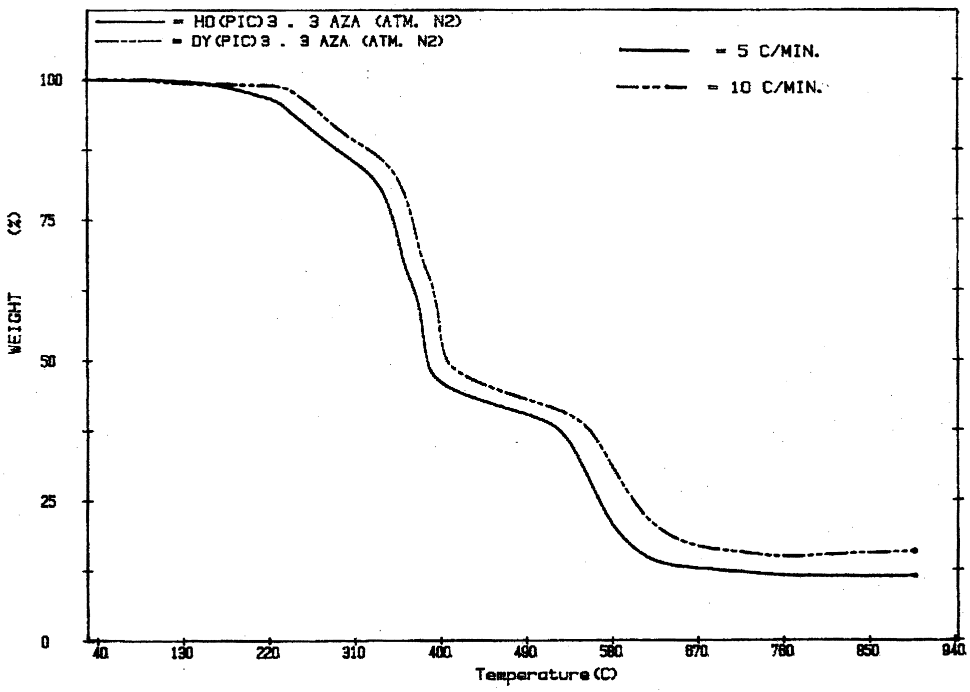

Fig. 1. TG curves under dynamic N_2 atmosphere and heating rates of 10 and 5°C min^{-1} of Dy and Ho compounds, respectively.

Table 4
ΔH values (kJ g^{-1}) and T (°C) for various steps of the melting and/or aza elimination of the compounds with formula $Ln(pic)_3 \cdot 3(aza)$

	Nd	Eu	Tb	Dy	Ho	Er	Tm	Y
T_1	171.4	173.5	179.0	180.0	180.4	181.9	182.0	176.0
ΔH_1	28.6	29.6	30.6	41.4	42.8	42.7	48.0	41.0
T_2	296.0	300.8	301.9	304.8	307.5	308.0	308.9	304.0
ΔH_2	846	856	1204	1291	1346	1455	1478	965

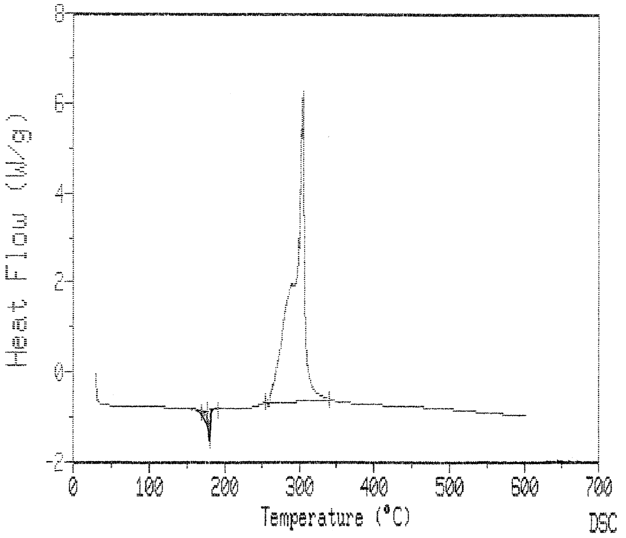

Fig. 2. DSC curve obtained for the compound $Eu(pic)_3 \cdot 3(aza)$ under N_2 atmosphere and heating rate of 3°C min^{-1}.

References

[1] M.A. Andrade da Silva, M.H. Zaim, P.C. Isolani, B. Wladislaw, L.B. Zinner, K. Zinner, J. Coord. Chem. 36 (1995) 311.
[2] L.R.F. Carvalho, L.B. Zinner, G. Vicentini, G. Bombieri, Inorg. Chim. Acta 191 (1992) 49.
[3] G. Vicentini, L.B. Zinner, K. Zinner, Koord. Khim. 17 (1991) 1422.
[4] S.J. Lyle, M.Md. Rahman, Talanta 10 (1973) 1177.
[5] T. Yongchi, Y. Guangdi, N. Jiazan, J. Mol. Sci. (China) 4 (1986) 55.
[6] T. Yongchi, L. Yingqiu, N. Jiazan, J. Mol. Sci. (Int. Ed.) 5 (1987) 83.
[7] K. Nakagawa, K. Amita, H. Mizuno, Y. Ynoue, T. Hakashi, Bull. Chem. Soc. Jpn. 60 (1987) 2037.
[8] L.F. Delboni, G. Oliva, E.E. Castellano, L.B. Zinner, S. Braun, Inorg. Chim. Acta 221 (1994) 169.
[9] J.H. Forsberg, Coord. Chem. Rev. 10 (1973) 195.
[10] E. Pinto Marinho, D.M. Araujo Melo, L.B. Zinner, K. Zinner, E.E. Castellano, J. Zukerman-Schpector, P.C. Isolani, G. Vicentini, Polyhedron. 16 (1997) 3519.