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Synthesis, characterization and thermal properties of some lanthanoid picrate complexes with 4-picoline-*N*-oxide (4-picNO)

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Abstract

Complexes with compositions $Ln(C_6H_2N_3O_7)_3 \cdot 3.5(4\text{-picNO}) \cdot H_2O$ (Ln = La, Pr), $Ln(C_6H_2N_3O_7)_3 \cdot 3(4\text{-picNO}) \cdot H_2O$ (Ln = Nd, Eu, Gd) and $Yb(C_6H_2N_3O_7)_3 \cdot 3(4\text{-picNO}) \cdot 3H_2O$ are described and characterized. The thermal behaviour of such complexes is also reported.

INTRODUCTION

Papers describing the preparation and properties of hydrated lanthanoid picrates have been published [1,2].

In this article we report the synthesis and characterization of hydrated complexes in which most of the water molecules were substituted by 4-picNO. The compounds with compositions $Ln(C_6H_2N_3O_7)_3 \cdot 3.5(4\text{-picNO}) \cdot H_2O$ (Ln = La, Pr), $Ln(C_6H_2N_3O_7)_3 \cdot 3(4\text{-picNO}) \cdot H_2O$ (Ln = Nd, Eu, Gd) and $Yb(C_6H_2N_3O_7)_3 \cdot 3(4\text{-picNO}) \cdot 3H_2O$ were characterized by elemental analysis, conductance measurements, IR spectra, visible neodymium absorption and europium emission spectra, TG and DSC analysis.

EXPERIMENTAL

Ethanolic solutions of the lanthanoid picrates and of the ligand were mixed (molar ratio 1:4, lanthanoid:ligand) and vigorously stirred with a glass rod. The mixture was left to stand for 24 h. The precipitate was filtered, washed with ethanol and dried in vacuo over anhydrous calcium chloride.

Lanthanoid ions were titrated with ethylenediaminetetraacetic acid (EDTA), using an acetate buffer (pH 5.8) and *ortho*-xylenol orange as indicator [3]. Carbon, hydrogen and nitrogen analyses were determined by microanalytical procedures. Conductance measurements were performed

TABLE 1

Summary of analytical results

Compound	Analysis (%)							
	Lanthanoid		Carbon		Nitrogen		Hydrogen	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$La(C_6H_2N_3O_7)_3\cdot 3.5(C_6H_7NO)\cdot H_2O$	11.35	11.38	38.29	38.49	14.30	14.09	2.68	2.64
$Pr(C_6H_2N_3O_7)_3\cdot 3.5(C_6H_7NO)\cdot H_2O$	11.50	11.66	38.24	37.78	14.29	14.24	2.67	2.61
$Nd(C_6H_2N_3O_7)_3\cdot 3(C_6H_7NO)\cdot H_2O$	12.29	12.48	36.83	37.54	14.32	14.55	2.49	2.62
$Eu(C_6H_2N_3O_7)_3\cdot 3(C_6H_7NO)\cdot H_2O$	12.86	12.47	36.59	36.70	14.22	13.48	2.47	2.54
$Gd(C_6H_2N_3O_7)_3\cdot 3(C_6H_7NO)\cdot H_2O$	13.25	13.50	36.43	36.70	14.16	13.68	2.46	2.49
$Yb(C_6H_2N_3O_7)_3\cdot 3(C_6H_7NO)\cdot 3H_2O$	13.97	13.93	34.91	34.69	13.57	13.26	2.69	2.65

using a resistance box, a pointer galvanometer and a cell ($K_c = 0.11597$ cm^{-1}) from Leeds and Northrup. IR spectra were recorded on a Perkin–Elmer FT-IR-1750 spectrophotometer using Nujol mulls between KBr plates. Visible absorption spectra were determined on a Varian–Cary 2300 apparatus using silicone mulls. Refractive indices were determined at 25 °C in an Abbé-type Bausch and Lomb refractometer. Electronic visible emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorimeter. Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were made in a dynamic nitrogen atmosphere (30 ml min^{-1}) at a heating rate of 5 K min^{-1}, using a Mettler TA 4000 system.

RESULTS AND DISCUSSION

Table 1 gives the formulae of the complexes and a summary of the analytical results.

Table 2 presents the conductance results in nitromethane and acetonitrile and the IR data. Both indicate coordination of 4-picNO and picrate anions through the oxygens [2,4].

Figure 1 shows the absorption spectra of the neodymium compound in the solid state, and in nitromethane and acetonitrile solutions. They are different, indicating an interaction with the solvents. The oscillator strengths calculated according to ref. 5 are: $P = 53.1 \times 10^{-6}$ for nitromethane (η (refraction index = 1.3865, conc. 0.0226 mol l^{-1}) and $P = 63.5 \times 10^{-6}$ for acetonitrile (η = 1.3465, conc. 0.0216 mol l^{-1}). From the solid absorption spectrum at room temperature it was possible to calculate, based on the

TABLE 2

Conductance data of millimolar solutions and IR data of the complexes

	Conductance		IR data (cm^{-1})			
	Nitromethane Λm (Ω^{-1} cm^2 mol^{-1})	Acetonitrile Λm (Ω^{-1} cm^2 mol^{-1})	$\nu_{as}(NO_2)$ [a]	$\nu(NO)$	$\delta(NO)$	$\gamma(CH)$
La	22.3	50.8	1540s–1572s	1237m	860w	770w
Pr	16.3	33.1	1541s–1574s	1236m	860w	770w
Nd	17.8	33.5	1541s–1574s	1234m	860w	769w
Eu	14.1	29.6	1542s–1576s	1228m	859w	771w
Gd	4.9	24.8	1542s–1575s	1236m	860w	773w
Yb	20.8	28.3	1542s–1574s	1237m	861w	775w
4-picNO	–	–	–	1252s	857m	758m

[a] Bands due to the picrate anion.

$^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transitions, the nephelauxetic parameter ($\beta = 0.986$), the covalent factor ($b^{1/2} = 0.083$) [6] and Sinha's parameter ($\delta = 1.42$) [7] indicating a small participation of the 4f electrons, with the bonds between the ligands and the central Nd^{3+} ion having an essentially electrostatic character.

Figure 2 shows the emission spectrum of the europium complex in the solid state at 77 K. The existence of a $^5D_0 \rightarrow {}^7F_0$ transition indicates that only C_{nv}, C_n or C_s symmetries are possible around the central Eu^{3+} ions [8]. The less intense bands due to $^5D_0 \rightarrow {}^7F_1$, in relation to the $^5D_0 \rightarrow {}^7F_2$ transition, indicate that there is no inversion centre and that the number of bands (6) attributed to the $^5D_0 \rightarrow {}^7F_2$ transition may be interpreted in terms of a C_{2v} symmetry [9]. It is interesting to mention that the compound shows an intense fluorescence at room temperature, which becomes about ten times more intense at 77 K, although both spectra are very similar. A better resolution was observed at 77 K.

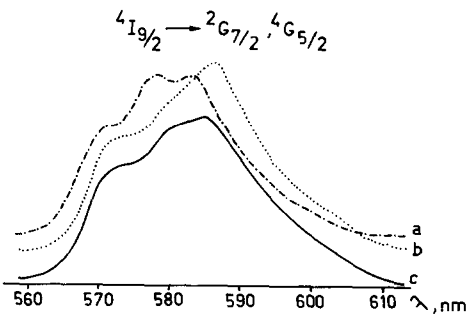

Fig. 1. Neodymium absorption spectra. Curve a, nitromethane solution; curve b, acetonitrile solution; curve c, solid state.

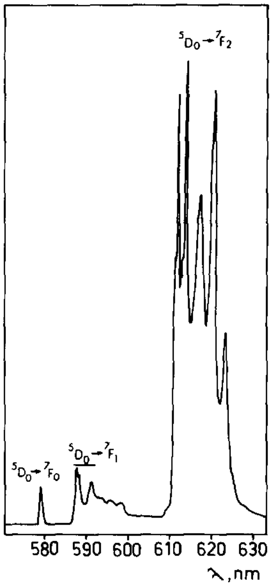

Fig. 2. Emission spectrum of the europium compound at 77 K.

Figure 3 shows the TG curves for the representative compounds of lanthanum, europium and terbium. Table 3 contains the thermo-analytical data for the same complexes. TG curves were also obtained for praseodymium, whose curve is fairly similar to that of lanthanum, and for neodymium and gadolinium which behave like the europium compound. The loss of water and of 4-picNO, the existence of an intermediate $Ln_2O(C_6H_2N_2O_7)_4$ and the residues of the oxides Ln_2O_3 (Ln = La, Nd, Eu, Gd, Yb) and Pr_6O_{11}, were detected in all cases.

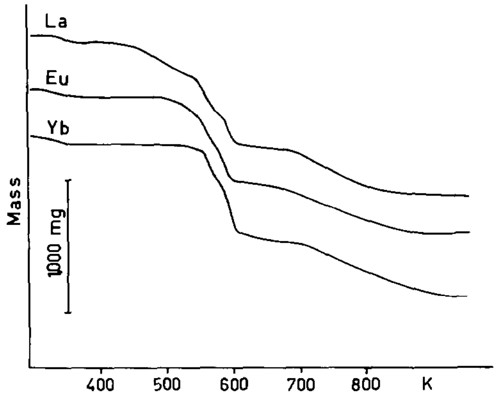

Fig. 3. Thermogravimetric curves for some representative complexes in dynamic nitrogen atmosphere.

TABLE 3

Summary of thermoanalytical data

Element	Temp. range (K)	Weight loss or residue (%)		DSC peak temp. (K)	ΔH (kJ mol^{-1})
		Theor.	Exp.		
La	335–400	1.47	2.0	378	+108
	440–550	22.31	21.0	–	–
	550–590	26.91	25.6	572	−472
	590–715	18.00	15.4	606	−865
	715–973	17.99	22.6	720	−4602
	973 (La_2O_3)	13.32	13.4		
Eu	323–363	1.52	1.6	349	+108
	553–585	27.70	28.3	575	−496
	585–628	22.24	23.1	610	−1163
	653–815	33.65	31.0	707	−5370
	973 (Eu_2O_3)	14.89	16.0		
Yb	343–373	2.90	3.0	358	+110
	373–385	1.45	1.4	380	+15
	553–593	26.42	26.6	580	−537
	593–625	20.67	21.0	610	−1270
	673–763	32.65	31.5	742	−6105
	973 (Yb_2O_3)	15.91	16.5		

EXHIBIT 1

Equations

$$\left.\begin{aligned}
&2Ln(C_6H_2N_3O_7)_3\cdot 3.5(4\text{-picNO})\cdot H_2O\,^{a} \rightarrow 2Ln(C_6H_2N_3O_7)_3\cdot 3.5(4\text{-picNO}) + 2H_2O\\
&2Ln(C_6H_2N_3O_7)_3\cdot 3.5(4\text{-picNO}) \rightarrow 2Ln(C_6H_2N_3O_7)_3\cdot(4\text{-picNO}) + 5(4\text{-picNo})\\
&2Ln(C_6H_2N_3O_7)_3\cdot(4\text{-picNO}) \rightarrow Ln_2O(C_6H_2N_3O_7)_4 + 2(4\text{-picNO}) + \text{gaseous products}\\
&2Ln_2O(C_6H_2N_3O_7)_4 \rightarrow 2LnO(C_6H_2N_3O_7) + \text{gaseous products}\\
&2LnO(C_6H_2N_3O_7) \rightarrow Ln_2O_3\,^{b} + \text{gaseous products}
\end{aligned}\right\}\quad (1)$$

$$\left.\begin{aligned}
&2Ln(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO})\cdot H_2O\,^{c} \rightarrow 2Ln(C_6H_2N_3O_7)\cdot 3(4\text{-picNO}) + 2H_2O\\
&2Ln(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO}) \rightarrow 2Ln(C_6H_2N_3O_7)_3\,^{d} + 6(4\text{-picNO})\\
&2Ln(C_6H_2N_3O_7)_3 \rightarrow Ln_2O(C_6H_2N_3O_7)_4 + \text{gaseous products}\\
&Ln_2O(C_6H_2N_3O_7)_4 \rightarrow Ln_2O_3 + \text{gaseous products}
\end{aligned}\right\}\quad (2)$$

$$\left.\begin{aligned}
&2Yb(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO})\cdot 3H_2O \rightarrow 2Yb(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO})\cdot H_2O + 4H_2O\\
&2Yb(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO})\cdot H_2O \rightarrow 2Yb(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO}) + 2H_2O\\
&2Yb(C_6H_2N_3O_7)_3\cdot 3(4\text{-picNO}) \rightarrow Yb_2O(C_6H_2N_3O_7)_4\,^{d} + \text{gaseous products}\\
&Yb_2O(C_6H_2N_3O_7)_4 \rightarrow Yb_2O_3 + \text{gaseous products}
\end{aligned}\right\}\quad (3)$$

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[a] Ln = La, Pr.

[b] $\frac{1}{3}(Pr_6O_{11})$ was obtained in the praseodymium complex.

[c] Ln = Nd, Eu, Gd.

[d] Very unstable.

It is important to mention that the enthalpies of decomposition are very high and, therefore, that the compounds are explosive (which occurred in some cases). A small amount of material (about 1 mg) and a slow heating rate was used in order to avoid explosion. The equations shown in Exhibit 1 are proposed for the different steps of the decompositions.

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REFERENCES

1 K. Nakagawa, K. Amita, H. Mizuno, Y. Inoue and T. Hakushi, Bull. Chem. Soc. Jpn., 60 (1987) 2037.
2 T. Yongchi, L. Yingqiu and N. Jiazan, J. Mol. Sci. (China), 5 (1987) 83.
3 S.J. Lyle and Md.M. Rahman, Talanta, 10 (1963) 1177.
4 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
5 W.T. Carnall, P.R. Fields and B.G. Wybourne, J. Chem. Phys., 42 (1965) 3797.
6 D.E. Henrie and G.R. Choppin, J. Chem. Phys., 49 (1968) 477.
7 S.P. Sinha, Spectrochim. Acta, 22 (1966) 57.
8 P. Caro and J. Derouet, Bull. Soc. Chim. Fr., 1 (1972) 46.
9 J.H. Forsberg, Coord. Chem. Rev., 10 (1973) 195.