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Synthesis, characterization and thermal behavior of some addition compounds between rare earth picrates (pic) and 2,2′-dithiobis(pyridine-N-oxide)

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Abstract

Rare earth picrates addition compounds with 2,2′-dithiobis(pyridine-N-oxide) (dithio) were synthesized and characterized. CHN analysis suggest a general formula $Ln(pic)_3 \cdot 1.5dithio \cdot 4H_2O$ (Ln = La, Nd, Eu, Dy, Ho). IR spectra indicate: (a) the presence of water molecules; (b) the presence of picrate in bidentade form; and (c) a bond of dithio to the RE through NO groups. Parameters, calculated from Nd absorption spectra at room temperature are in agreement with a small covalent character of the Ln:L interaction.

Thermogravimetric data under N_2 and air atmospheres, show that: (a) the water molecules loss is the first decomposition step (up to 453 K); (b) the residue, at ca. 1173 K, is essentially Ln_2O_3. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth; Picrates; 2,2′-Dithiobis(pyridine-N-oxide); Synthesis and characterization; Thermogravimetry

1. Introduction

Rare earth picrate addition compounds are being systematically investigated in our group due to the possibility of several types of coordination modes [1]. 2,2′-Dithiobis(pyridine-N-oxide) (dithio) is an amine-N-oxide where the N-oxide group can be reduced only with strong agents [2]. It can be prepared by reaction of a suspension of 2-mercaptopyridine-1-oxide in water with an aqueous solution of 30% H_2O_2 to 318 K [3]. These compounds have commercial importance as fungicides and preservatives. Their biological activity is attributed to the presence of the N-oxide group adjacent to the carbon bearing a sulfur atom [1,4].

2. Experimental

Rare earths were titrated with EDTA [5]. CHN analyses were performed on a 240 Perkin-Elmer equipment. IR spectra were obtained on a FTIR Prospect MIDAC apparatus with Nujol mulls between KBr plates. Neodymium compound absorption spectrum were done on a Zeiss DMr-10 spectrophotometer. Europium compound emission spectra at room temperature and 77 K, were obtained on a Hitachi Perkin-Elmer MPF-4 fluorimeter. For the

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Table 1
Analytical data of compounds with general formula $Ln(pic)_3 \cdot 1.5dithio \cdot 4H_2O$

Metal	Ln		C		H		N	
	Theoretical (%)	Experimental (%)	Theoretical (%)	Experimental (%)	Theoretical (%)	Experimental (%)	Theoretical (%)	Experimental (%)
La	10.9	10.4	31.1	33.0	2.0	2.0	13.2	12.7
Nd	11.3	10.8	31.0	31.0	2.0	2.0	13.1	12.5
Eu	11.8	11.4	30.8	30.9	2.0	2.0	13.1	12.5
Dy	12.5	12.0	30.5	31.0	2.0	2.2	12.9	12.4
Ho	12.7	11.9	30.5	31.4	2.0	2.0	12.9	14.2

thermogravimetric measurements ca. 1.0 mg samples were used under air or nitrogen atmospheres with a 50 ml min^{-1} flow and 2, 5 and 10 K min^{-1} heating rates on a Perkin-Elmer TGA7 balance.

The system employed for detection and analysis of the gaseous products during the thermal decomposition studies was obtained by coupling simultaneous thermoanalytical techniques: (a) TG/DTA using a DTG-50H; (b) gas chromatography and mass spectrometry employing a CG/MS model GC/14B and QP-5000, both from Shimadzu.

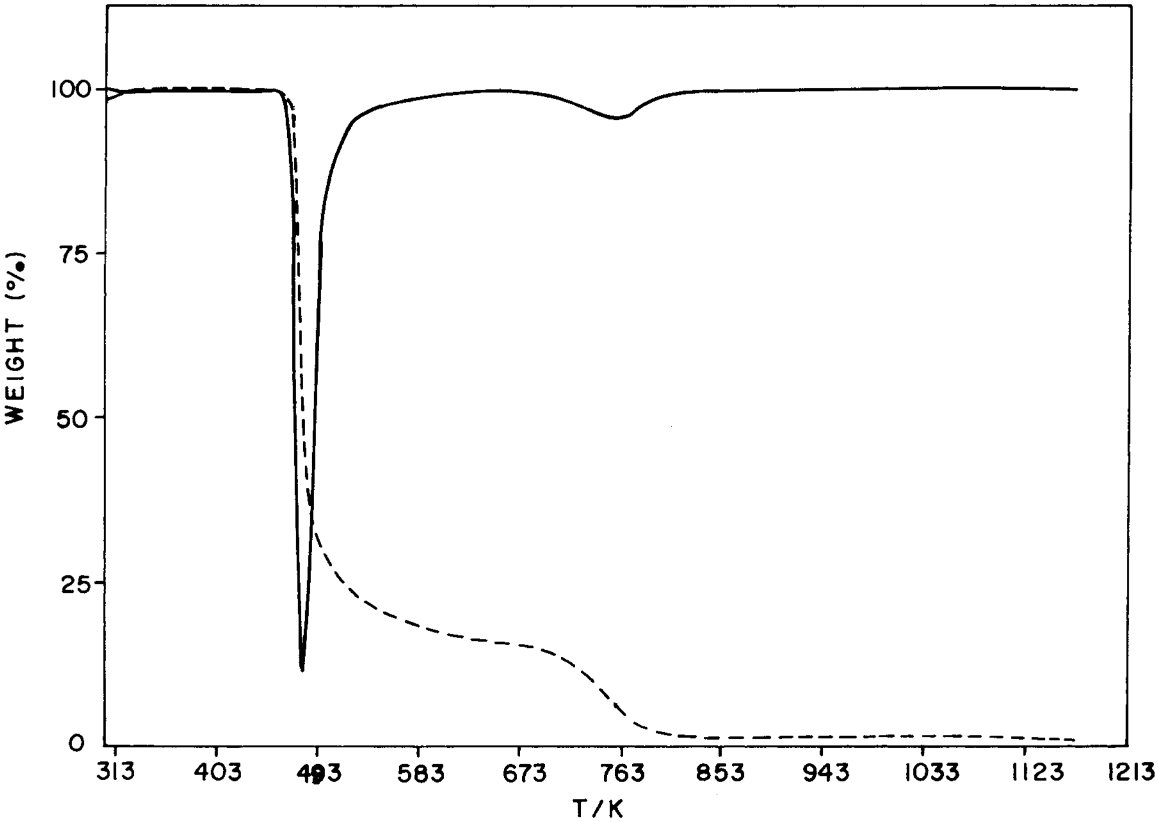

Fig. 1. Thermal decomposition of the ligand.

Table 2
IR absorption frequencies (cm^{-1}) of compounds with general formula $Ln(pic)_3 \cdot 1.5dithio \cdot 4H_2O$[a]

Ln	H_2O	νCC	$\nu_{as}NO_2$	ν_sNO_2	νCO	νNO	νCN	δNO_2
La	3067 sh	1610 s	1571 w	1370 m	1270 s	1217 w	920 w	838 w
	3096 sh		1537 m	1329 m				
Nd	3069 sh	1612 s	1566 w	1370 m	1271 s	1215 w	916 w	837 w
	3130 sh		1539 w	1336 m				
Eu	3068 sh	1612 s	1569 sh	1371 s	1271 s	1216 w	918 w	837 w
	3098 sh		1536 w	1333 w				
Dy	3064 sh	1610 s	1537 w	1370 sh	1275 s	1211 m	919 w	838 w
	3094 sh		1542 sh	1336 w				
Ho	3088 sh	1616 s	1568 w	1368 sh	1274 s	1216 m	919 w	837 w
			1538 w	1338 w				
2,2′dithio						1246 sh		

[a] s, strong; m, medium; w, weak; sh, shoulder.

The process of thermal decomposition liberates a complex mixture of gaseous products, a previous chromatographic separation being necessary. For these determinations a mass of ca. 0.5 mg was submitted to decomposition in the DTG-50H system, under an inert high degree purity Helium atmosphere

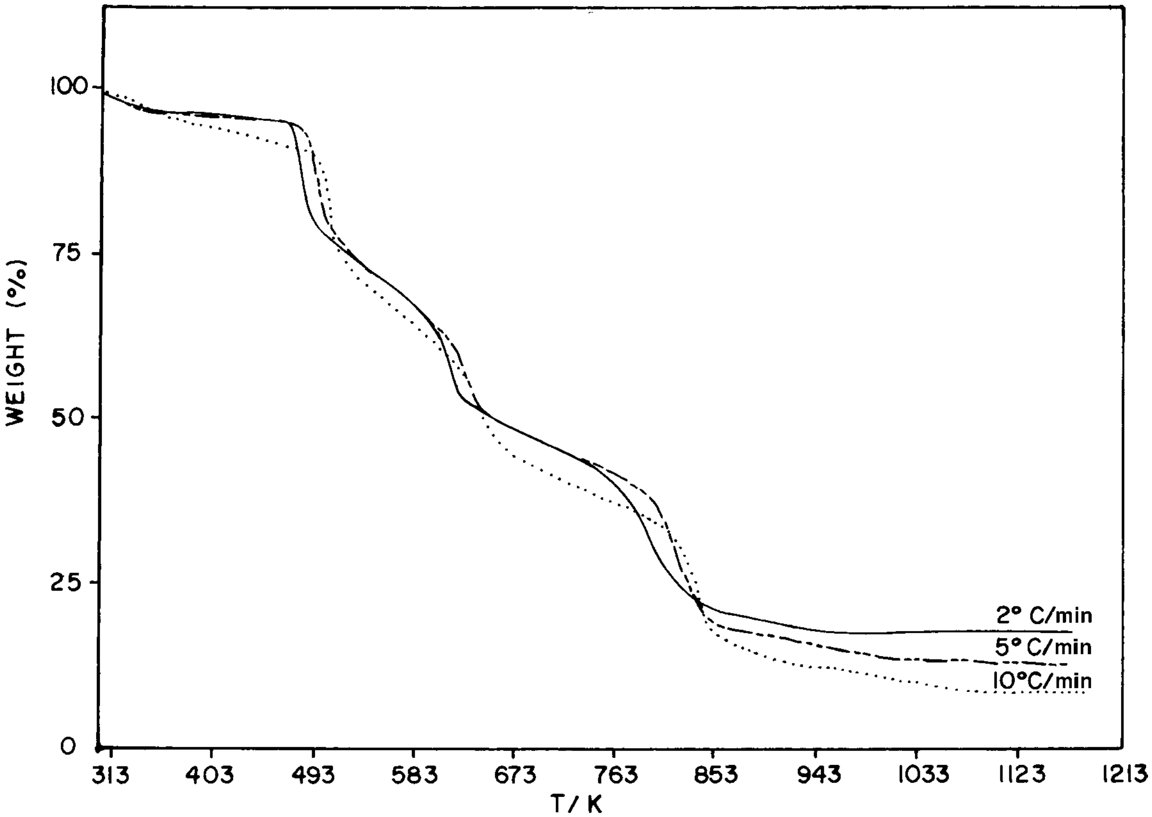

Fig. 2. TG curves for the holmium compound (2, 5 and 10 K min^{-1} heating rates).

(99.999%). The gases were trapped at 523 K in a system containing Tenax TA (60/80 mesh), recovered by a dry ice refrigeration system. This unit was then substituted by a heating system, maintained at 573 K in order to inject the materials in a chromatographic column, using pure Helium at a 50 ml min^{-1} flow rate. The column Tenax TA (60/80 mesh) where the products are separated in increasing order of polarity. After separation the gaseous products were submitted to a high energy electron source (70 eV).

3. Results and discussion

CHN analyses and EDTA titrations (Table 1) suggest a general formula Ln(pic)$_3$·1.5dithio·4H$_2$O where Ln is La, Nd, Eu, Dy and Ho. This means that the ligand coordinates to the metal ions either in a mono or a bidentate form. IR spectra (Table 2) show 3000 cm^{-1} bands attributed to water. Symmetric (ν_sNO$_2$) and asymmetric (ν_{as}NO$_2$), stretching (NO$_2$) bands and CO (νCO) stretching bands are indicative of the presence of picrates and their bidentate interaction [6]. Dithio NO group bands are shifted toward lower energies in the complexes when compared to the free ligand as consequence of an interaction through the oxygen atom.

The emission spectrum of the europium complex shows one $^5D_0 \rightarrow ^7F_0$ transition; $^5D_0 \rightarrow ^7F_1$ presents three broad peaks and $^5D_0 \rightarrow ^7F_2$ shows an intense broad peak and shoulders. The existence of a $^5D_0 \rightarrow ^7F_0$ transitions indicates that only C$_{nv}$, C$_n$ or C$_s$ symmetries are possible around the central Eu^{3+} ions. These are not compatible with a symmetry center [7].

The absorption spectra of the neodymium compound along the hypersensitive $^2G_{7/2}$, $^4G_{5/2} \rightarrow ^4I_{9/2}$ transitions indicate that the symmetry around the

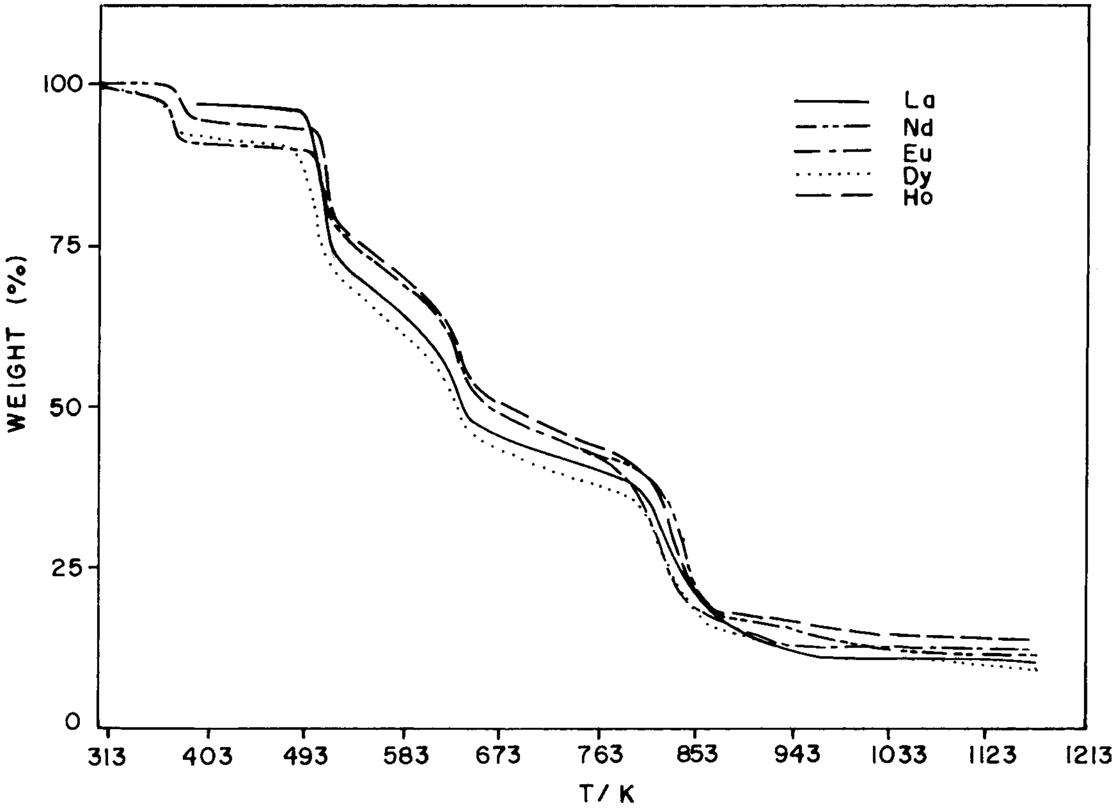

Fig. 3. TG curves for the La, Nd, Eu, Dy and Ho compounds (air atmosphere, heating rate 10 K^{-1}).

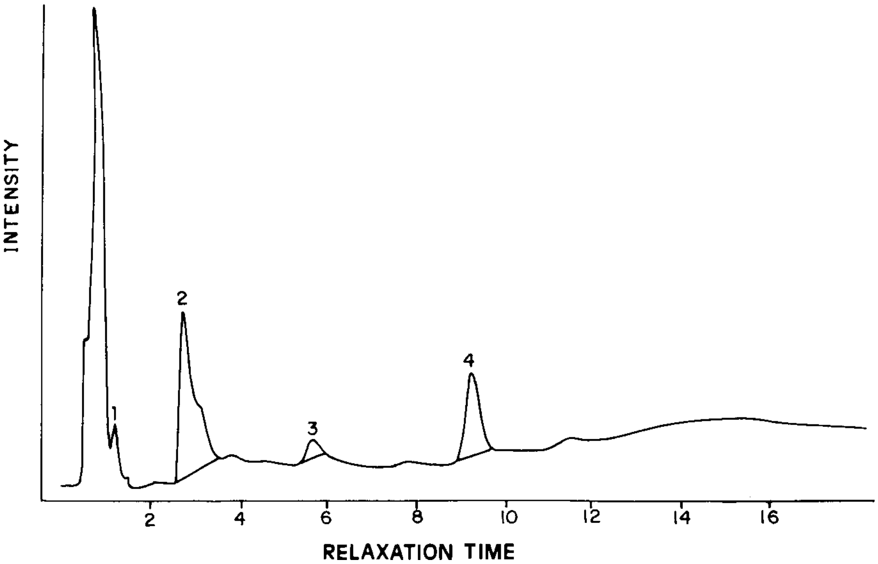

Fig. 4. Peaks of the relaxation time of the gaseous products of $La(pic)_3 \cdot 1.5dithio \cdot 4H_2O$.

central ion is not cubic. Calculations around the baricenter show for the different parameters: nephelauxetic ($\beta = 0.989$) [8]; covalency factor ($b^{1/2} = 0.072$) [9] and Sinha's ($\delta = 1.05$) [10] indicative of a slight metal-ligand covalent character.

Fig. 1 shows the thermal decomposition of the ligand. The sharp mass loss at ca. 473 K was interpreted as the formation of dipyridine-N,N-dioxide followed by sulfur vaporization. Fig. 2 contains a comparison between several curves performed at different heating rates. It has to be noted that there are no significant differences for the loss of four water molecules. The same behavior is observed with ligand loss. The decomposition pattern of the compounds appears to be atmosphere independent. The final residue (at ca. 1123 K), Ln_2O_3, is obtained, as expected, at low temperatures when air is used.

Fig. 3 contains curves obtained under air at $10\,K\,min^{-1}$. It can be seen that the decomposition mechanisms are essentially the same; first step corresponding to four water molecule loss, the second to one dithio molecule leaving and third (and fourth) to a half ligand loss and picrate decomposition. The residue at ca. 1073 K corresponds essentially to Ln_2O_3.

From the IR spectra it is seen that the residue at 623 K still shows dithio and picrate bands which disappears for the 1123 K residue. The residue color is the one expected for rare earth oxides.

Fig. 4 contains the peaks corresponding to the four gaseous products identified by the system CG/MS: (1) dinitrogen oxide (2) sulfur dioxide (3) acetronitride and (4) pyridine in the thermal decomposition of the compound $La(pic)_3 \cdot 1.5dithio \cdot 4H_2O$.

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