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Note

THERMOGRAVIMETRIC INVESTIGATION OF 4-PICOLINE-*N*-OXIDE (4-picNO) LANTHANOID TRIFLUOROMETHANESULFONATE COMPLEXES

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Complexes with composition $Ln(CF_3SO_3)_3 \cdot n(4\text{-picNO})$ ($n = 8$ for Ln = La–Gd, except Ce, and $n = 7$ for Ln = Tb–Lu, Y) have been recently reported [1]. In this note the thermogravimetric behaviour of such complexes are described.

EXPERIMENTAL

The adducts were prepared by reaction of an ethanolic solution of the hydrated lanthanoid trifluoromethanesulfonate with 4-picNO, followed by addition of triethylorthoformate. The precipitates were filtered, washed with teof and dried in vacuo over anhydrous chloride. Thermogravimetric studies were made in a nitrogen atmosphere with a Perkin–Elmer TGS-1 system, using samples of about 1 mg and a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

The compounds prepared present the formula $[Ln(4\text{-picNO})_n](CF_3SO_3)_3$ ($n = 8$ for Ln = La–Gd, except Ce and $n = 7$ for Ln = Tb–Lu, Y). The IR spectra show bands attributed to ionic trifluoromethanesulfonates. Shifts of ν NO to lower and δ NO to higher frequencies, in relation to the free ligand, due to coordination through the oxygen were observed.

Conductance data in acetonitrile and nitromethane show lower, but still close, values to 1 : 3 electrolytes.

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TABLE 1

Summary of TG data and apparent melting ranges

Ln	Residue	Temperature range (K)	Weight loss or residue (%)		Decomposition process	Apparent melting range (K)
			Theor.	Exp.		
La		455–595	52.36	51.2	1	386–389
		595–710	25.30	26.5		
		710–810	8.91	8.3		
	LaF_3	810–1070	13.43	14.1		
Pr		440–600	44.82	44.8	2	398–401
		600–710	32.73	32.3		
		710–795	8.91	6.6		
	PrF_3	795–1070	13.54	13.2		
Nd		435–615	52.15	49.6	1	403–406
		615–710	25.21	28.8		
		710–800	8.90	8.3		
	NdF_3	800–1070	13.74	13.3		
Sm		435–565	44.52	42.7	2	402–406
		565–720	32.52	41.3		
		720–780	8.86	3.7		
	SmF_3	780–1070	14.10	14.3		
Eu		435–695	51.87	53.6	1	402–405
		695–790	25.10	24.8		
		790–880	8.84	8.5		
	EuF_3	880–1070	14.19	13.1		
Gd		400–585	44.35	43.8	2	395–399
		585–720	32.44	34.2		
		720–795	8.71	7.9		
	GdF_3	795–1070	14.50	14.1		
Tb		465–550	31.88	31.3	3	434–438
		550–630	23.91	24.9		
		630–720	18.97	16.7		
		720–795	9.49	8.5		
	TbF_3	795–1070	15.61	15.5		
Dy		445–545	31.76	31.9	3	438–442
		545–650	23.82	23.8		
		650–715	18.93	19.4		
		715–795	9.47	5.9		
	DyF_3	795–1070	15.98	17.1		
Ho		460–545	31.72	28.3	3	439–443
		545–645	23.78	25.6		
		645–715	18.90	21.2		
		715–795	9.46	7.4		
	HoF_3	795–1070	16.13	16.2		

TABLE 1 (continued)

Ln	Residue	Temperature range (K)	Weight loss or residue (%)		Decomposition process	Apparent melting range (K)
			Theor.	Exp.		
Er		455–535	31.68	29.4	4	443–447
		535–655	33.19	35.0		
		655–715	18.86	20.2		
	ErF_3	715–1070	16.27	15.5		
Tm		470–545	31.61	29.1	3	443–447
		545–645	23.73	23.7		
		645–715	18.84	20.4		
		715–820	9.48	9.3		
	TmF_3	820–1070	16.37	16.7		
Yb		450–530	31.54	26.9	5	446–450
		530–625	7.88	11.6		
		625–745	34.56	31.2		
		745–840	9.40	11.6		
	YbF_3	840–1010	16.62	16.9		
Lu		435–525	31.48	29.4	5	447–451
		525–605	7.87	8.2		
		605–725	34.51	38.8		
		725–850	9.38	7.1		
	LuF_3	850–1070	16.74	16.5		
Y		465–545	33.56	30.6	4	439–443
		545–675	35.19	33.0		
		675–710	20.00	21.6		
	YF_3	710–1070	11.22	11.1		

X-ray powder patterns indicate the existence of two isomorphous series, corresponding to the compounds with eight and seven ligands.

When the complexes are heated, under a nitrogen atmosphere, melting occurs before decomposition. The melting range (Table 1) is 386–389 K for the lanthanum compound and some 60 K higher for the lutetium complex (447–451 K).

An analysis of the TG data (Table 1 and Fig. 1) reveals that, under the experimental conditions used, five different decomposition schemes exist, depending on the rare-earth ion. The data indicate that the compounds decompose with evolution of 4-picNO, followed by SO_2 and COF_2 [2], according to the equations:

$$\mathrm{Ln(CF_3SO_3)_3 \cdot 8(4\text{-picNO)} \rightarrow Ln(CF_3SO_3)_3 \cdot (4\text{-picNO)} + 7(4\text{-picNO)}}$$
$$\mathrm{Ln(CF_3SO_3)_3 \cdot (4\text{-picNO)} \rightarrow LnF_2(CF_3SO_3) + 4\text{-picNO} + 2COF_2 + 2SO_2}$$
$$\mathrm{LnF_2(CF_3SO_3) \rightarrow LnF_3 + COF_2 + SO_2} \quad (1)$$

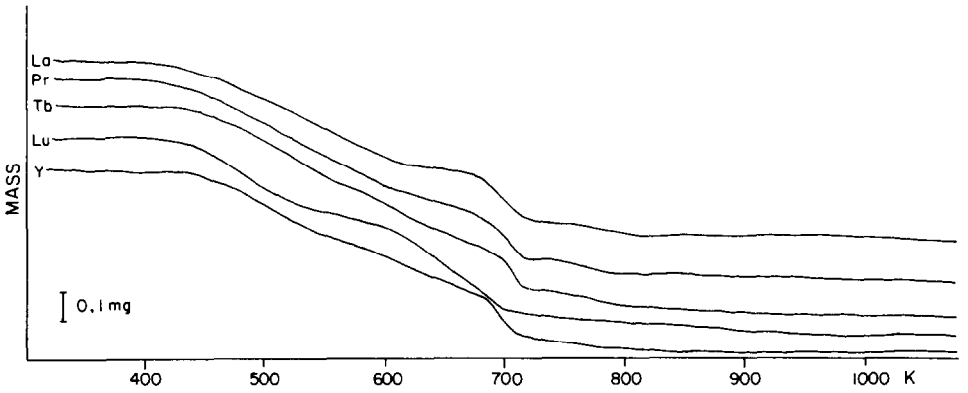

Fig. 1. Thermogravimetric curves for some representative complexes in a nitrogen atmosphere.

$$Ln(CF_3SO_3)_3 \cdot 8(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 \cdot 2(4\text{-picNO}) + 6(4\text{-picNO})$$
$$Ln(CF_3SO_3)_3 \cdot 2(4\text{-picNO}) \rightarrow LnF_2(CF_3SO_3) + 2(4\text{-picNO}) + 2COF_2 + 2SO_2$$
$$LnF_2(CF_3SO_3) \rightarrow LnF_3 + COF_2 + SO_2 \qquad (2)$$

$$Ln(CF_3SO_3)_3 \cdot 7(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) + 4(4\text{-picNO})$$
$$Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 + 3(4\text{-picNO})$$
$$Ln(CF_3SO_3)_3 \rightarrow LnF_2(CF_3SO_3) + 2COF_2 + 2SO_2$$
$$LnF_2(CF_3SO_3) \rightarrow LnF_3 + COF_2 + SO_2 \qquad (3)$$

$$Ln(CF_3SO_3)_3 \cdot 7(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) + 4(4\text{-picNO})$$
$$Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) \rightarrow LnF(CF_3SO_3)_2 + 3(4\text{-picNO}) + COF_2 + SO_2$$
$$LnF(CF_3SO_3)_2 \rightarrow LnF_3 + 2COF_2 + 2SO_2 \qquad (4)$$

$$Ln(CF_3SO_3)_3 \cdot 7(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) + 4(4\text{-picNO})$$
$$Ln(CF_3SO_3)_3 \cdot 3(4\text{-picNO}) \rightarrow Ln(CF_3SO_3)_3 \cdot 2(4\text{-picNO}) + 4\text{-picNO}$$
$$Ln(CF_3SO_3)_3 \cdot 2(4\text{-picNO}) \rightarrow LnF_2(CF_3SO_3) + 2COF_2 + 2SO_2$$
$$LnF_2(CF_3SO_3) \rightarrow LnF_3 + COF_2 + SO_2 \qquad (5)$$

All decompositions yield the respective lanthanoid fluoride as final solid residues, indicating that a complete rearrangement of bonds takes place. LnF_3 residues were also obtained in the decomposition of hydrated lanthanide trifluoromethanesulfonate [2] and in the complexes with thioxane-oxide [3], dimethylsulfoxide [4] and *trans*-1,4-dithiane-1,4-dioxide [5].

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