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Thermal decomposition of some dimethylsulphoxide (DMSO) lanthanide complexes

J.R. Matos, Z.F. De Faria, I. Giolito, L.B. Zinner and G. Vicentini

Universidade de São Paulo, Instituto de Química, C.P. 20.780, CEP 01498, São Paulo, SP (Brazil)

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Abstract

Compounds of composition $LnCl_3 \cdot 3MDSO$ (Ln = Dy–Lu) were prepared and characterized. The thermal decomposition was investigated by TG and DSC techniques.

INTRODUCTION

Compounds of composition $LnCl_3 \cdot n$DMSO ($n = 4$, Ln = La–Sm, Gd; $n = 3$, Ln = Y) have been prepared and characterized by Ramalingam and Soundararajan [1]. Hydrated complexes of composition $LnCl_3 \cdot 5DMSO \cdot 4H_2O$ (Ln = Nd–Dy) have been obtained by Xie et al. [2].

In this article, the synthesis of compounds of composition $LnCl_3 \cdot 3DMSO$ (Ln = Dy–Lu), their characterization by microanalytical procedures, their electrolytic conductance measurements, IR spectra, and TG and DSC analyses, are presented.

EXPERIMENTAL

The complexes were prepared by reaction of the hydrated lanthanide chlorides with DMSO in acetone. The oily product was crystallized after stirring the mixture with a glass rod.

The crystals were filtered, washed with acetone and dried in vacuo over anhydrous calcium chloride.

Analysis and measurements

The lanthanide content was determined by complexometric titration with EDTA, using xylenol orange as indicator [3]. Carbon and hydrogen were

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Correspondence to: G. Vicentini, Universidade de São Paulo, Instituto de Química, C.P. 20.780, CEP 01498, São Paulo, SP, Brazil.

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TABLE 1

Summary of the analytical results (%) and conductance data for the compounds of formula $LnCl_3 \cdot 3DMSO$

Ln	Lanthanide			Carbon		Hydrogen		LnOCl		ΛM
	Theor.	Exp. [a]	Exp [b]	Theor.	Exp.	Theor.	Exp.	Theor.	Exp. [c]	(Ω^{-1} cm^2 mol^{-1})
Dy	32.29	32.0	32.6	14.32	13.9	3.60	3.7	42.52	42.9	103
Ho	32.61	31.6	32.7	14.25	13.9	3.59	3.6	42.80	42.9	96
Er	32.93	33.4	33.3	14.19	13.6	3.57	3.5	43.05	43.6	87
Tm	33.14	33.6	33.4	14.14	13.7	3.56	3.7	43.24	43.6	85
Yb	33.67	33.8	33.9	14.07	13.7	3.53	3.6	43.70	44.0	85
Lu	33.93	34.4	34.4	13.97	13.5	3.52	3.5	43.90	44.7	87

[a] Complexometric titration with EDTA.

[b] Calculated from the LnOCl percentage (TG).

[c] Obtained from the TG curves.

TABLE 2

IR data (cm^{-1})[a]

Ln	$\nu(SO)$	$\nu(C–S)$
Dy	1011s	715m
Ho	1009s	717m
Er	997sh 1011sh 1022s	717m
Tm	1008s	715s
Yb	1007s	717m
Lu	1002s	719m
DMSO	1058s[b] 1031vs[c] 1047vs[c]	698s[b] 702m[c]

[a] vs = very strong; s = strong; m = medium; sh = shoulder.

[b] Ref. 6.

[c] This work.

determined by microanalytical procedures. Electrolytic conductance measurements were performed at 25.00 ± 0.02°C with equipment composed of a resistance box, a pointer galvanometer and a Leeds and Northrup Co. cell ($k_c = 0.10708$ cm^{-1}). IR spectra were recorded on a Nicolet FTIR 510 spectrophotometer. TG curves were obtained with a Perkin-Elmer TGA-7 system, using platinum crucibles, a heating rate of 2, 5 or 10 K min^{-1}, and air or nitrogen dynamic atmosphere. DSC curves were recorded on a Mettler System TA 4000 with the same conditions and a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

Table 1 contains a summary of the analytical and conductance data. The compounds are hygroscopic, insoluble in acetonitrile and nitromethane, and behave as 1 : 1 electrolytes in methanol [4].

IR spectra (Table 2) show $\nu(SO)$ shifts to lower frequencies and $\nu(C–S)$ shifts to higher frequencies, compared to the free ligand, indicating a coordination through the oxygen [5].

Figure 1 gives the TG, DTG and DSC curves of the thulium compound, which is representative of the complexes. According to the data (Table 3), the compounds melt between 404 and 428 K (first endothermic peak on the DSC curve) and decompose between 472 and 488 K. The TG curves are practically identical. In all cases the residues at ≈ 820 K were identified as the lanthanide oxychlorides (Table 1). At ≈ 1170 K, the residues correspond to Ln_2O_3. It is interesting to note that the residues are the same in a dynamic nitrogen atmosphere, i.e. the oxygens originate from the ligand.

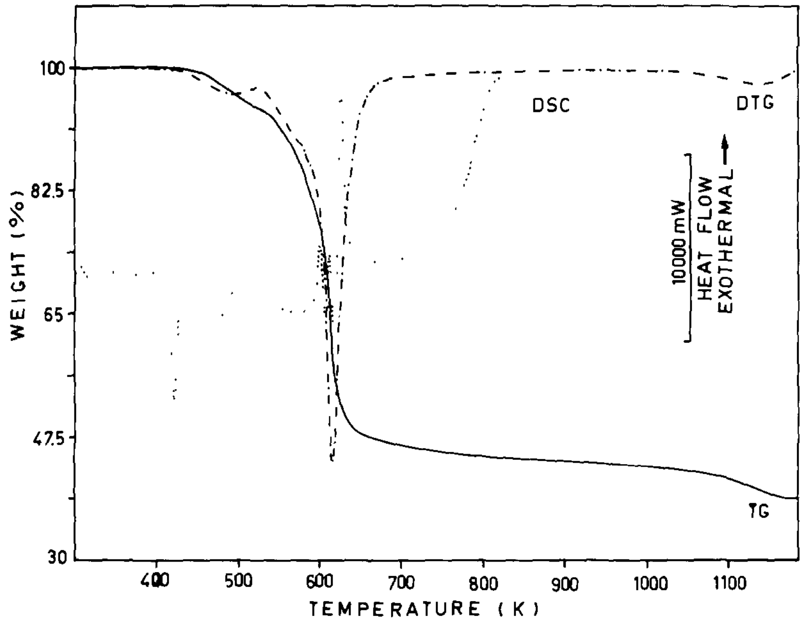

Fig. 1. TG, DTG and DSC curves of the thulium compound at a heating rate of 10 K $\min^{-1}$ and in dynamic air atmosphere.

There is no evidence of formation of anhydrous lanthanide chlorides. The TG curves were recorded at two different heating rates; it was observed that, at the slower rate, the events occur at lower temperatures, but without separation of the simultaneous reactions.

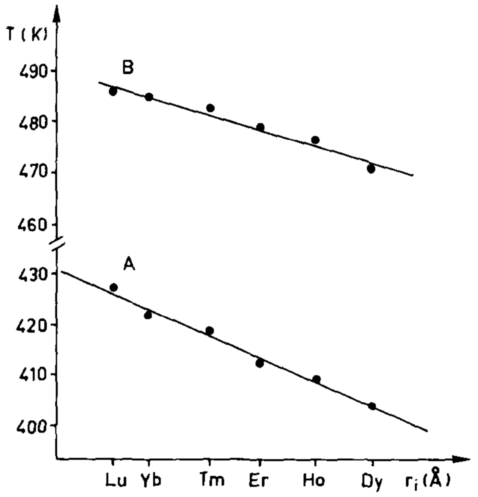

Fig. 2. Relations between melting and decomposition temperatures (K) (DSC endothermic peaks) and ionic radii (Å).

TABLE 3

Average ionic radius for Ln^{3+} and DSC data for the compounds of formula $LnCl_3 \cdot 3DMSO$

Ln	Ionic radius (Å)	Peak temp. (K)	ΔH (kJ mol^{-1})	Peak temp. (K)	ΔH (kJ mol^{-1})	Peak temp. (K)	ΔH (kJ mol^{-1})	Peak temp. (K)	ΔH (kJ mol^{-1})	Peak temp. (K)	ΔH (kJ mol^{-1})
Dy	0.912	404	43.6	472	18.8	604	−23.1	616	−40.8	634	−59.6
Ho	0.901	409	45.5	478	29.9	606	−30.1	616	−11.3	628	−92.3
Er	0.890	413	45.8	480	32.4	604	−23.1	615	−10.6	627	−71.4
Tm	0.880	419	42.2	484	16.3	604	−21.8	616	−15.9	628	−81.6
Yb	0.868	422	41.5	486	7.5	604	−36.1	616	−10.5	628	−79.0
Lu	0.861	428	38.6	488	5.8	606	−9.5	617	−9.6	631	−84.9

The DTG curves indicate a two-step decomposition but the DSC curves show one endothermic peak ($\approx$ 480 K) that corresponds to breaking of the bond between Ln^{3+} and DMSO, followed by a broad endothermic peak, most probably owing to evolution of gaseous material. Three exothermic peaks are then observed, owing to organic material burning in the dynamic air atmosphere. The last large, intense exothermic peak at about 825 K, is attributed to the formation of lanthanide oxychloride. The enthalpy of this peak was not calculated because it is incomplete owing to instrument limitations.

The temperatures of the two endothermic processes were plotted as a function of the Ln^{3+} average ionic radii (Fig. 2). The data indicate that the thermal stability of the complexes increases from Dy^{3+} to Lu^{3+}, owing to the increase of the acidity of the central ion and, consequently, to an increase in the Ln^{3+}–ligand interaction. The acidity seems to be of greater importance than the steric hindrance of the ligands.

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