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THERMAL DECOMPOSITION OF METAL COMPLEXES

IV. LANTHANIDE(III) COMPLEXES WITH DIBENZO-18-CROWN-6

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ABSTRACT

The solid-state thermal dissociation reactions of the complexes of all the lanthanide(III) nitrates and thiocyanates (except Pm) with the cyclic polyether dibenzo-18-crown-6 were investigated. Thermal analysis was carried out in a dynamic atmosphere of dry nitrogen and under reduced pressure ($5 \cdot 10^{-2}$ mm Hg). In both the conditions examined, the two series of complexes exhibit different thermal behaviours. The values of enthalpy change and "activation energy" for the dissociation reactions of the complexes with lanthanide thiocyanates show a periodic trend along the lanthanide series.

INTRODUCTION

A number of investigations on the solid-state thermal dissociation reactions of metal complexes involving mono- and polydentate neutral ligands have been reported in the literature[1–5]. In general, the purpose of these studies is to clarify the thermoanalytic behaviour of the complexes by determining the role played by various factors such as the nature of the central metal ion and the nature of the ligand, with special regard to its molecular structure and its steric characteristics[1–10]. It has also been pointed out that a thermal dissociation reaction may be strongly influenced by the experimental conditions. In this respect, the nature and pressure of the atmosphere, sample dilution, and heating rate have proved to be important factors in some cases[11,12].

A series of neutral molecules, which have drawn considerable interest because of their complexing properties, is constituted by numerous macrocyclic polyethers containing four to twenty oxygen atoms in the ring[13]. Complexes of these ligands with many salts, especially those of alkali and alkaline earth cations, have been reported. The bonds in these systems were attributed to ion–dipole interactions between the positively charged cation and the oxygen atoms of the polyether ring. One of the factors influencing the stability of the complexes was found to be the ratio between the size of the cation and that of the hole in the polyether ring[13,14].

Very recently we found that two of these complexing agents can interact with lanthanide salts in appropriate organic solvents. Some series of these complexes. all having the same 1:1 stoichiometry, were prepared and characterized[15]. Probably, the association in these lanthanide complexes is mainly electrostatic in nature and so the relative rigidity of this type of ligands combined with the decreasing size of the tripositive cations along the lanthanide series may determine some significant trend in the stabilities of the complexes.

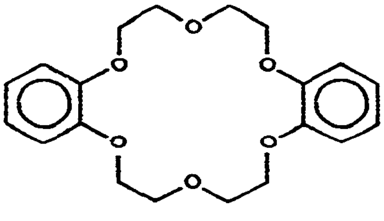
On account of this, we performed an investigation on the solid-state thermal dissociation reactions of these lanthanide complexes. This paper deals with TG, DTG, and DTA data for complexes of all the lanthanide(III) nitrates and thiocyanates (except Pm) with the cyclic polyether dibenzo-18-crown-6 (trivial name[13]).

The thermal dissociation reactions were studied under different experimental conditions in order to select suitable data for trying the determination of kinetic and thermodynamic parameters.

EXPERIMENTAL

Preparation of the complexes

The lanthanide(III), Ln, thiocyanate and nitrate complexes with the ligand, L, were prepared as previously reported[15] and their ascertained compositions were $LnL(NCS)_3$ and $LnL(NO_3)_3$, respectively.



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Thermal analysis

The thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermal (DTA) analyses were carried out simultaneously in dynamic atmosphere of dry nitrogen ($10\ l\ h^{-1}$) and under reduced pressure ($5 \cdot 10^{-2}$ mm Hg) on 5–15 mg samples. Heating rates ranging from 0.5 to 4°C min^{-1} were employed. In order to reduce the reaction rate in nitrogen atmosphere, samples diluted with alumina were also used (sample:alumina = 1:4). The apparatus was a Mettler thermoanalyzer with Pt/Pt–Rh 10% thermocouples, Pt crucibles. Al_2O_3 was used as reference system for DTA.

The "activation energy", E_a^*, and the enthalpy change, ΔH_d, of the dissociation reactions were calculated following approximate methods described in the literature[16–18].

RESULTS AND DISCUSSION

Thermal decomposition in nitrogen atmosphere

In all the TG curves of the complexes $LnL(NCS)_3$ a first decomposition process is shown with a mass-loss corresponding to the loss of the dibenzo-18-crown-6. As examples, the thermoanalytical curves for two lanthanides are reported in Fig. 1. The DTA curves for all these complexes clearly indicate that the decomposition reactions are endothermic, but a progressive change in the curves feature along the lanthanide series reveals that, at least for the complexes of the heavier lanthanide, the endothermic process is followed by an exothermic one before the dissociation is completed (Fig. 1b). This suggests the posibility of a partial ligand decomposition during the thermal dissociation reactions.

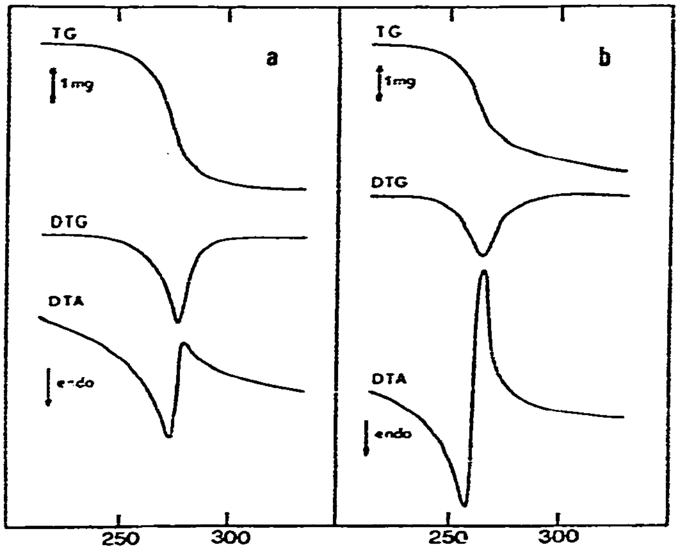

Fig. 1. Thermoanalytical curves at ϕ = 4°C min^{-1} and in dynamic nitrogen atmosphere. (a) $GdL(NCS)_3$ (7.7 mg); (b) $HoL(NCS)_3$ (6.8 mg).

As for the complexes $LnL(NO_3)_3$, once the reaction begins, they undergo a very fast decomposition. This causes sample escape from the crucible, due to a rapid gas formation.

In order to reduce the decomposition rate of the complexes $LnL(NO_3)_3$, measurements were also carried out with a sample diluted in alumina[12]. Indeed, under these experimental conditions the reaction rate appeared to be slower. However, the DTG curves show that the decomposition occurs in more than one step. This behaviour seems to indicate a ligand decomposition during the thermal dissociation.

Thermal decomposition under reduced pressure

For all the complexes $LnL(NCS)_3$, the TG, DTG and DTA curves indicate an endothermic dissociation reaction in one step with a mass-loss corresponding to the loss of the neutral ligand, L, according to the dissociation reaction:

$$\mathrm{LnL(NCS)_3(s) \rightarrow Ln(NCS)_3(s) + L(g)}$$

As examples, the thermoanalytical curves for two lanthanides are reported in Fig. 2. The ligand released, dibenzo-18-crown-6, was identified by carrying out some thermal dissociation reactions under analogous experimental conditions in a vacuum line. The gaseous product was collected by sublimation and recognized by its m.p. (164°C) and IR spectrum.

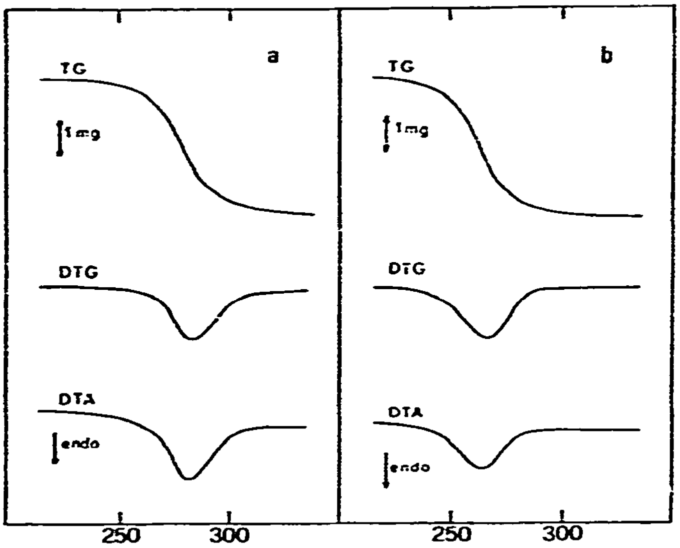

Fig. 2. Thermoanalytical curves at $\varnothing = 4\,^{\circ}\mathrm{C\ min^{-1}}$ under reduced pressure ($5 \cdot 10^{-2}$ mm Hg). (a) $\mathrm{GdL(NCS)_3}$ (6.7 mg); (b) $\mathrm{HoL(NCS)_3}$ (6.8 mg).

The complexes $\mathrm{LnL(NO_3)_3}$, under these experimental conditions, underwent a fast decomposition, very similar to the one shown in a dynamic atmosphere of dry nitrogen.

A comparative consideration of the data obtained under different experimental conditions for the two series of complexes suggests some remarks: (a) the thermal dissociation of the complexes $\mathrm{LnL(NCS)_3}$ seems to occur through the same mechanism in both nitrogen atmosphere and reduced pressure, the neutral ligand being released undecomposed, at least for the lighter elements; (b) the thermal dissociation of the complexes $\mathrm{LnL(NO_3)_3}$ takes place in any case with ligand decomposition. The temperatures at which reactions begin, for both the series of complexes, are scattered along the lanthanide series and also with respect to the different experimental conditions (see Table 1 for the $\mathrm{LnL(NCS)_3}$ complexes) so that they do not seem to indicate any logical or useful trend.

Since the thermal decomposition of the complexes with thiocyanates appear to be simple dissociation reactions, the relative enthalpy change, ΔH_d, and "activation energy", E_a^*, were calculated. The obtained values are reported in Table 1.

TABLE 1

TEMPERATURES AND DATA OBTAINED FOR THERMAL DISSOCIATION OF THE COMPLEXES $LnL(NCS)_3$

Ln	*N_2 atmosphere*			*Reduced pressure*		
	T_i (°C)	*E_a^* (kcal mol^{-1})*	*ΔH_d (kcal mol^{-1})*	*T_i (°C)*	*E_a^* (kcal mol^{-1})*	*ΔH_d (kcal mol^{-1})*
La	270	41	75	216	53	82
Ce	270	134	134	250	41	68
Pr	248	80	85	250	33	37
Nd	222	34	41	174	29	23
Sm	238	154	154	236	47	35
Eu	238	68	73	224	50	58
Gd	232	64	51	242	77	63
Tb	256	92	89	242	40	39
Dy	240	80	75	230	38	43
Ho	236	87	80	210	44	50
Er	230	73	98	220	46	54
Tm	260	171	183	234	52	58
Yb	224	42	57	212	55	63
Lu	235	53	67	228	59	66

Although, as above mentioned, the thermal behaviour of the complexes of lanthanide thiocyanates appears to be substantially the same in nitrogen atmosphere and under reduced pressure, the E_a^* and ΔH_d values reveal significant differences in the reaction mechanism due to the different experimental conditions. A reasonable possibility is that, at an external pressure equal to the atmospheric pressure, the thermal dissociation reaction of these complexes is characterized by a rate-limiting step, consisting of the absorption of the gaseous product, according to the reaction scheme:

$$A(s) \rightarrow B(s) + C(abs.\ gas) + C(g)$$

Evidently, the concentration of absorbed gas is not a constant during the dissociation reaction and therefore the influences on the TG curves are determined casually. The use of a very reduced pressure favours the gas desorption, removing in this way the rate-limiting step.

This hypotesis is further supported by the fact that the E_a^* and ΔH_d values referring to atmospheric pressure conditions do not show any regular trend as a function of ionic radius or atomic number of the lanthanide elements, while some regularity can be observed in the values obtained by the measurements performed under reduced pressure. This can be seen in Figs. 3 and 4, where E_a^* and ΔH_d values are plotted against the values of $1/r$ (r = ionic radius) for the lanthanide elements.

It is worth noting that the observed regularity reflects a sort of periodicity between the lighter cations (La^{3+}–Eu^{3+}) and the heavier cations (Gd^{3+}–Lu^{3+}) with a sharp discontinuity at Gd^{3+}. In this case an extra "thermal stability" appears to characterize the complexes of lanthanides having 4f^0, 4f^7 and 4f^{14} configurations. Such a trend was sometimes observed for chemical properties referring to lanthanide compounds^{19}.

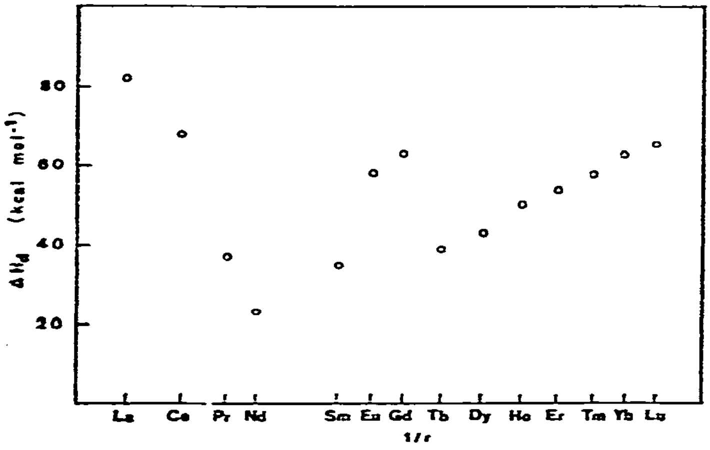

Fig. 3. Plot of E_a^* values against 1/r for the lanthanide elements.

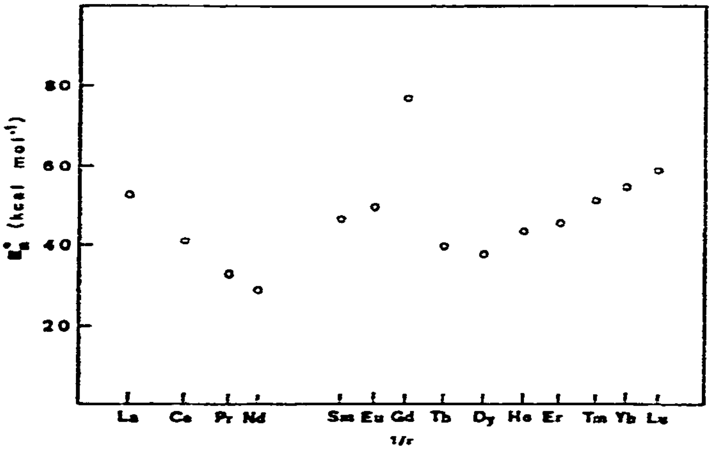

Fig. 4. Plot of ΔH_d values against 1/r for the lanthanide elements.

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