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THERMAL DECOMPOSITION OF METAL COMPLEXES
V. LANTHANIDE(III) COMPLEXES OF BENZO-15-CROWN-5

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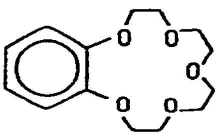
ABSTRACT

Thermal dissociation reactions of lanthanide(III) nitrates and thiocyanates solid complexes of the cyclic polyether benzo-15-crown-5 were studied in dynamic atmosphere of dry nitrogen and under reduced pressure ($5 \cdot 10^{-2}$ mm Hg). The complexes of lanthanide nitrates undergo dissociation with ligand decomposition while from those of lanthanide thiocyanates the ligand is released undecomposed. Values of enthalpy change and "activation energy" for the dissociation reactions of the complexes with lanthanide thiocyanate were obtained and briefly discussed.

INTRODUCTION

The macrocyclic polyethers dibenzo-18-crown-6 (systematic name: 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) and benzo-15-crown-5 (systematic name: 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene) can interact with lanthanide salts in appropriate organic solvents to form 1:1 isolable complexes[1,2]. As complexing agents the two polyethers are essentially characterized by the number of oxygen atoms and by the ring size (dibenzo-18-crown-6 has six oxygen atoms and a cavity size of 2.6–3.2 Å; benzo-15-crown-5 has five oxygen atoms and a cavity size of 1.7–2.2 Å) (ref. 3) and thus some difference between their complexing behaviours should be expected.

In a previous paper[4], we reported the results of an investigation of the solid-state thermal dissociation reactions of the complexes of lanthanide(III) nitrates and thiocyanates with the macrocyclic polyether dibenzo-18-crown-6. We now present an investigation of the solid-state thermal dissociation of the lanthanide(III) nitrate and thiocyanate complexes with the cyclic polyether benzo-15-crown-5 (L).



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EXPERIMENTAL

Preparation of the complexes

Complexes of all the lanthanide(III), Ln, nitrates and thiocyanates (except Pm) with the polyether benzo-15-crown-5, L, were prepared as previously reported[1]. The stoichiometries of the two series of complexes were $LnL(NO_3)_3$ and $LnL(NCS)_3 \cdot H_2O$.

Thermal analysis

Measurements were performed with all the complexes under two different experimental conditions: in dynamic atmosphere of dry nitrogen ($10\ l\ h^{-1}$) and under reduced pressure ($5 \cdot 10^{-2}$ mm Hg). Thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermal analysis (DTA) data were simultaneously obtained by the use of a Mettler thermoanalyzer with Pt/Pt–Rh thermocouples and Pt crucibles. Al_2O_3 as reference system for DTA was used. The heating rate was $4\,°C\ min^{-1}$. The samples masses ranged from 10 to 20 mg.

The "activation energy", E_a^*, and the enthalpy change, ΔH_d, of the dissociation reactions were calculated following approximate methods described in the literature[5–7] to the first part of TG curves.

RESULTS AND DISCUSSION

Thermal decomposition in nitrogen atmosphere

All the TG curves of the complexes $LnL(NCS)_3 \cdot H_2O$ show a first mass-loss in the temperature range of 110–150°C corresponding to the loss of a water molecule. A second dissociation process is shown above 200°C with a mass-loss corresponding to the loss of the benzo-15-crown-5. The DTA curves clearly indicate that both the processes are endothermic. However, there is some evidence for an exothermic process following the endothermic one before the dissociation is completed. This may be due to a partial ligand decomposition. Two examples of thermoanalytical curves obtained for these complexes are reported in Fig. 1.

The complexes $LnL(NO_3)_3$, under these experimental conditions, undergo violent thermal decomposition with rapid gas evolution. While the complexes of lighter lanthanides (La–Gd) are surely without solvating molecules, the TG curves for the heavier lanthanides show a mass-loss corresponding to one or two water molecules in the temperature range of 80–110°C, but after this mass-loss the desolvated complexes are quite stable up to 200°C.

The decomposition temperatures of all the complexes $LnL(NO_3)_3$ are above 200°C and their values, starting with 275°C for the lanthanum complex, decrease along the lanthanide series, though not in a regular manner. These observations agree with those reported by King and Heckley[2] for the same solvent-free complexes of the lighter lanthanides (Ln = La, Ce, Pr, Nd, and Sm).

The decomposition rate of the complexes with lanthanide nitrates was decreased by carrying out measurements with samples diluted in alumina. The DTG curves

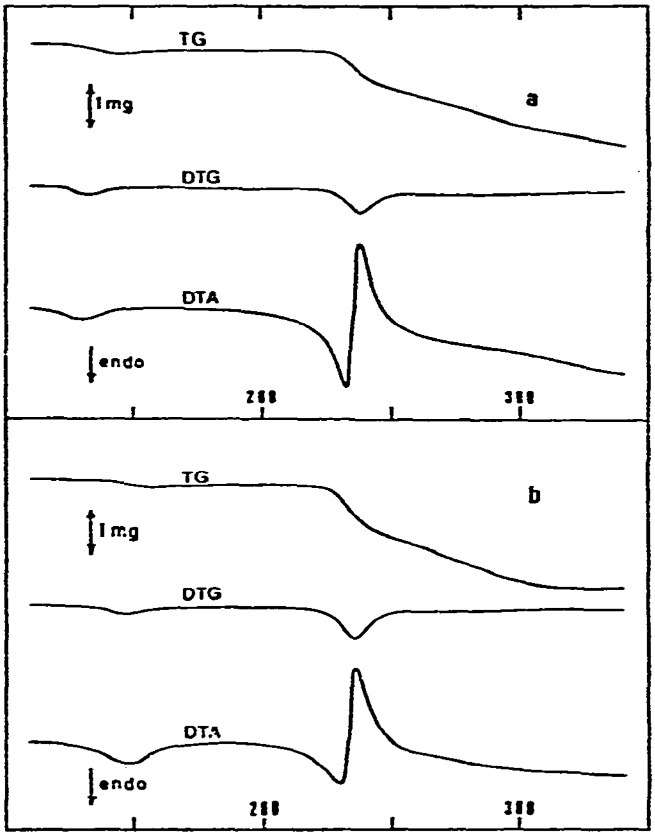

Fig. 1. Thermoanalytical curves at $\varnothing = 4\,^{\circ}\mathrm{C\ min^{-1}}$ and in dynamic nitrogen atmosphere. (a) $GdL(NCS)_3 \cdot H_2O$; and (b) $HoL(NCS)_3 \cdot H_2O$.

obtained in this way show that the decomposition reactions occur in more than one step, according to a possible ligand decomposition during the thermal dissociation.

Thermal decomposition under reduced pressure

The TG, DTG and DTA curves for all the complexes $LnL(NCS)_3 \cdot H_2O$ show an endothermic process with the loss of the water molecule followed, at higher temperature, by an endothermic dissociation reaction in one step with a mass-loss corresponding to the release of the benzo-15-crown-5. Examples of thermoanalytical curves for two complexes are reported in Fig. 2.

The ligand released was identified by carrying out thermal dissociation reactions under analogous experimental conditions in a vacuum line and measuring melting point (79 °C) and IR spectrum of the gaseous product collected by sublimation.

A simple dissociation reaction of the type:

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

may account for this thermal behaviour.

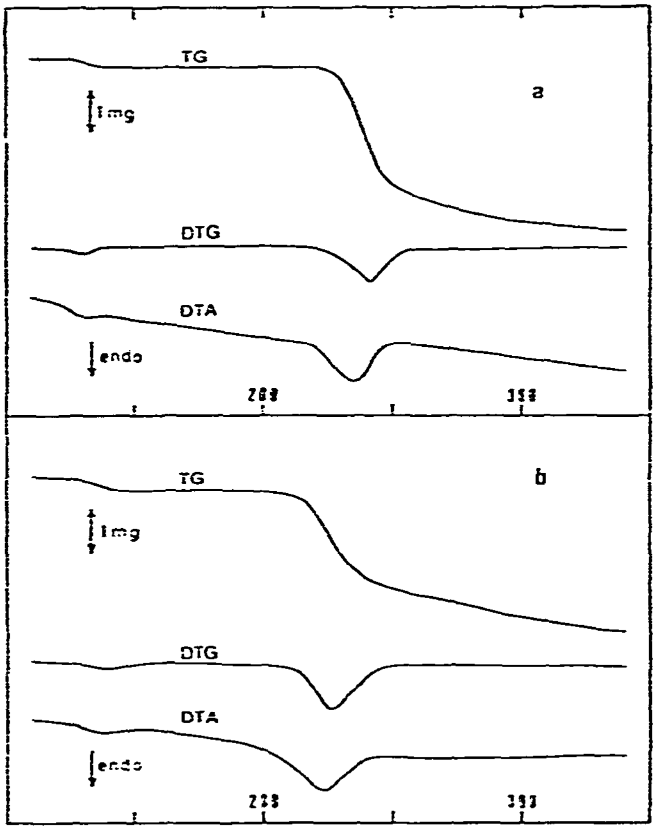

Fig. 2. Thermoanalytical curves at $\varnothing = 4\,^{\circ}\mathrm{C\,min^{-1}}$ under reduced pressure ($5 \cdot 10^{-2}$ mm Hg) (a) $\mathrm{GdL(NCS)_3 \cdot H_2O}$; and (b) $\mathrm{HoL(NCS)_3 \cdot H_2O}$.

As for the complexes $\mathrm{LnL(NO_3)_3}$, they all decompose with very fast reactions under these experimental conditions.

By applying appropriate treatment methods[5-7], the thermoanalytical curves of the complexes $\mathrm{LnL(NCS)_3 \cdot H_2O}$ allowed the calculation of the "activation energy", E_a^*, and the enthalpy change, ΔH_d, relative to the dissociation reactions. The obtained values are reported in Table 1.

As can be seen the values of E_a^* and ΔH_d for a given complex referring to nitrogen atmosphere and to reduced pressure are significantly different. This seems to indicate some difference in the reaction mechanism due to the different experimental conditions. Absorption of gaseous product on the surface of the solid compound may be considered as a cause influencing the dissociation reaction in dry nitrogen at atmospheric pressure[4].

The E_a^* and ΔH_d values obtained from measurements carried out under reduced pressure reflect a periodicity along the lanthanide series, such that the trend of the values for the lighter elements is roughly reproduced for the heavier elements with a discontinuity at Gd.

TABLE 1

TEMPERATURE AT WHICH REACTION BEGINS (T_i), "ACTIVATION ENERGY" (E_a^*), AND ENTHALPY CHANGE (ΔH_d) FOR THERMAL DISSOCIATION OF THE COMPLEXES $LnL(NCS)_3 \cdot H_2O$

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	230	65	22	220	98	26
Ce	220	40	33	212	54	17
Pr	226	55	15	210	49	23
Nd	222	97	19	210	48	22
Sm	218	67	40	224	40	30
Eu	218	46	36	200	52	41
Gd	220	40	34	216	56	44
Tb	218	44	38	204	22	26
Dy	218	48	52	215	19	24
Ho	220	59	64	219	13	24
Er	218	38	44	204	20	18
Tm	218	34	37	170	29	22
Yb	230	36	35	202	32	23
Lu	232	37	40	200	38	25

In general, a comparison of the experimental results of this investigation with the previously reported[4] points out very similar thermal behaviours of the corresponding lanthanide complexes of the two macrocyclic polyethers considered.

The values of enthalpy change of the dissociation reactions for the complexes with the polyether benzo-15-crown-5 are lower than those for the corresponding complexes with the polyether dibenzo-18-crown-6. This could be mainly due to the different number of oxygen donor atoms of the two crown ligands.

We cannot find an explanation for the observed periodic trend of the values E_a^* and ΔH_d as a function of the atomic number of the lanthanide elements. If an isomorphous crystalline form is assumed for all the lanthanide thiocyanate complexes of a given polyether, then the ΔH_d values should be correlated with the stability of the complexes. In this case an extra stability appears to distinguish the complexes formed by the lanthanide cations having $4f^0$, $4f^7$, and $4f^{14}$ electronic configurations. But this is just the opposite of what should be expected on the ground of some considerations about a possible crystal field effect[8].

The fact that during the thermal dissociation of the complexes of lanthanide thiocyanates the polyether ligands are released undecomposed, suggests a coordination structure in which the three thiocyanate anions are coordinated to the metal ion on the same side with respect to the plane of the crown of oxygen atoms.

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