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THERMAL DECOMPOSITION OF METAL COMPLEXES. IX. POLYNUCLEAR COMPLEXES OF LANTHANIDE(III) IONS WITH A METAL SCHIFF BASE COMPLEX AS LIGAND

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ABSTRACT

The kinetics of the thermal decomposition of some binuclear and trinuclear complexes of lanthanide(III) ions with the ligand *N*, *N'*-propilenbis (salicylideniminato) Cu(II) were studied under high vacuum (2×10^{-6} mm Hg) and in isothermal conditions. The trend of E_a^* values of the heavier lanthanoid complexes does not fit a reliable relation with the ionic radius, while the lighter lanthanoid complexes parallel those observed in other already studied lanthanoid derivatives.

INTRODUCTION

Neutral metal Schiff base complexes behave as complexing agents with various metal salts, giving polynuclear species. Their complexing ability has been widely studied against transition metals[1]. Recently, the polynuclear species formed with some "f" elements has been described[2].

Along with our studies on the thermal behaviour of the lanthanide(III) complexes[3-5], we investigated the kinetics of the thermal decomposition of some binuclear and trinuclear complexes of lanthanide(III) ions with the ligand *N*, *N'*-propylenbis (salicylideniminato) Cu(II), herewith indicated as Cu (1,3PS). The studied complexes have the general formula

$$[Cu(1,3PS)]_2Ln(NO_3)_3 \qquad (A)$$

for the lighter lanthanide(III) ions (La–Sm, except Pm), and

$$Cu(1,3PS)\ Ln(NO_3)_3 \cdot 2\ H_2O \qquad (B)$$

for the heavier ones. They will be hereafter labelled (A) and (B), respectively.

EXPERIMENTAL

All the complexes were prepared through the procedure described previously[6]. The simultaneous TG, DTG and DTA were performed under high vacuum (2×10^{-6}

TABLE 1

E_a* (KCAL MOLE^{-1}) AND "n" VALUES RELATIVE TO THE DECOMPOSITION OF THE ANHYDROUS OR DEHYDRATED POLYNUCLEAR COMPLEXES IN ISOTHERMAL CONDITIONS

Lanthanide(III) ion	*Isothermal T (°C)*			*n*	E_a*
La	275	280	285	0.63	132
Ce	272	275	278	0.70	121
Pr	270	275	280	0.59	110
Nd	272	275	278	0.64	109
Pm					
Sm	275	280	285	0.71	111
Eu	270	272	274	0.60	151
Gd	262	265	268	0.69	168
Tb	265	270	275	0.66	202
Dy	265	270	275	0.63	215
Ho	270	275	280	0.70	218
Er	270	272	275	0.65	220
Tm	268	270	272	0.72	190
Yb	265	270	275	0.69	160
Lu	280	282	285	0.61	152

mm Hg) with a Mettler thermoanalyzer. Preliminary screenings were carried out at a heating rate of 0.5 °C min^{-1}. Thermal analytical data were obtained from isothermal running at three temperature values near that at which the decomposition reaction begins. All the binuclear complexes (B) were first dehydrated in non-isothermal conditions and were then kept isothermally near the temperature at which they begin to decompose. The thermal decomposition was also simulated on a vacuum line and the products of the reaction analyzed by conventional methods.

RESULTS AND DSICUSSION

Thermal decomposition in non-isothermal conditions

Near 100 °C (Fig. 1), the hydrated binuclear complexes (B) lose endothermically, in a single step, the two coordinated molecules of water

$$\mathrm{Cu(1{,}3PS)\ Ln(NO_3)_3 \cdot 2\ H_2O\ (s) \rightarrow Cu(1{,}3PS)\ Ln(NO_3)_3\ (s) + 2\ H_2O\ (v)} \tag{1}$$

The solid species Cu(1,3PS) $Ln(NO_3)_3$ obtained through the above reaction will be hereafter labelled (C). The presence of an exothermal effect following the release of the two water molecules indicates structural rearrangement in the solid state, probably due to the lowering of the coordination number around the lanthanoid ions, involving some rearrangements to polymeric structures.

At higher temperatures, both anhydrous trinuclear (A) or dehydrated binuclear (C) complexes behave similarly. Around 270 °C (Fig. 1) they undergo a fast exothermal decomposition. Due to the gas formation, sample-escape from the crucible is

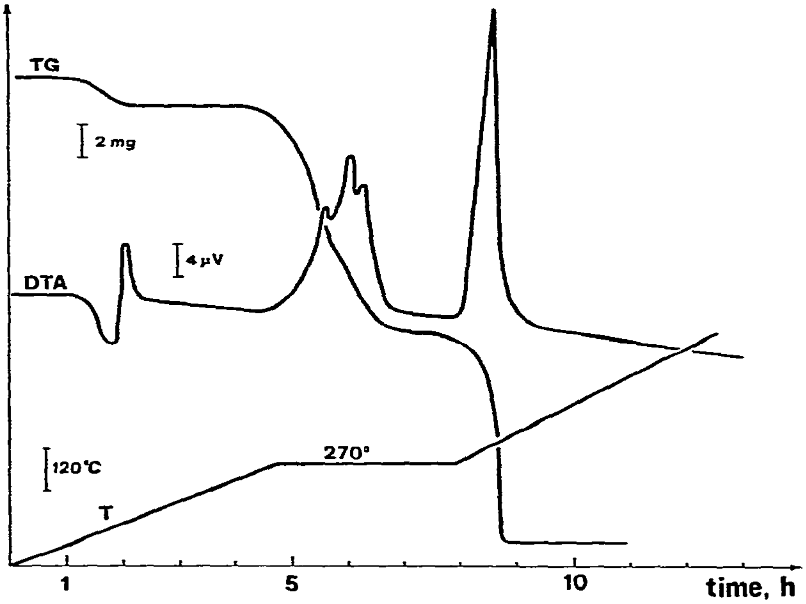

Fig. 1. TG and DTA curves of $Cu(1,3PS)Dy(NO_3)_3 \cdot 2H_2O$ under high vacuum and in isothermal and non-isothermal conditions.

always observed. This fact precludes any information being drawn from the thermoanalytical curves in order to evaluate kinetic parameters. However, because under these experimental conditions some of the neutral Cu(1,3PS) ligand was always found condensed on the surroundings of the sample-holder, it can be argued that this thermal reaction involves, even using the slower heating rate, two simultaneous processes: the sublimation of the neutral ligand, whether partial or complete, and the decomposition of the lanthanoid nitrate salts.

Thermal decomposition in isothermal conditions

In order to separate the two processes mentioned above, still simultaneous even at the slowest heating rate, the thermal decomposition was carried out under isothermal conditions. The temperature (T_{is}) for both the anhydrous trinuclear and the dehydrated binuclear complexes, was kept near the value where the complexes begin to decompose in non-isothermal conditions. The decomposition reaction of the dehydrated complexes (C) fit well into the scheme

$$Cu(1,3PS)\ Ln(NO_3)_3\ (s) \rightarrow Ln(NO_3)_3\ (s) + Cu(1,3PS)\ (v) \qquad (2)$$

The obtained $Ln(NO_3)_3$ salt decomposes further at slightly higher temperature.

In Fig. 1, the thermal behaviour of the Dy complex is shown. The various steps of the whole process are clearly separated along the TG curve:

(i) the initial release of the two water molecules (heating rate $\phi = 1\ °C\ min^{-1}$);

(ii) the exothermic reaction (2) (isothermal conditions);

(iii) the decomposition of the lanthanide salt (again at $\phi = 1\ °C\ min^{-1}$).

The release of the Cu(1,3PS) ligand was confirmed through a separate experiment on a vacuum line by heating each complex in analogous conditions to that described for the isothermal experiments; the ligand was always found on the cold finger. Its nature was confirmed through physico-chemical parameters.

In the case of the trinuclear complexes (A), the release of the first molecule of ligand produces a stable product

$$[\mathrm{Cu(1,3PS)}]_2\mathrm{Ln(NO_3)_3}\ (\mathrm{s}) \rightarrow \mathrm{Cu(1,3PS)\ Ln(NO_3)_3}\ (\mathrm{s}) + \mathrm{Cu(1,3PS)}\ (\mathrm{v}) \qquad (3)$$

Before this reaction is complete (60% conversion) the binuclear complex formed decomposes further

$$\mathrm{Cu(1,3PS)\ Ln(NO_3)_3}\ (\mathrm{s}) \rightarrow \mathrm{Ln_2O_3} + \text{other gaseous products} \qquad (4)$$

It is worth noting that these latter binuclear complexes undergo a different decomposition path to that of the corresponding binuclear complexes (C) of the heavier lanthanoid(III) ions. In this case, in both non-isothermal and isothermal conditions, loss of the ligand molecule with the complete breakdown of the species takes place according reaction (4). This fact can possibly be explained by considering that these binuclear species are formed along with reaction (2) at a temperature (T_{is}) higher then that found for the corresponding complexes of the heavier lanthanoids. Under these conditions, both the binuclear complexes and the lanthanoid salts, $\mathrm{Ln(NO_3)_3}$, are unstable and quickly decompose.

Both the initial decomposition reactions (2) and (3), even though endothermic in principle, are experimentally exothermic processes (Fig. 1). This means that the release of the neutral ligand Cu(1,3PS) does not involve a single process. The release of the ligand, in fact, leaves the lanthanoid ion coordinatively unsaturated. Consequently, structural rearrangements in the solid state can be expected in order to achieve a new stable structure. This structural change will account for the observed exothermal effects.

The weight loss vs. time curves for reactions (2) and (3), in isothermal conditions, yielded the values of the degree of conversion of the initial solid component.

The best reaction order, n, was obtained from the general equation

$$\mathrm{d}x/\mathrm{d}t = K(1 - X)^n$$

The values found for all the complexes lie near $n = 2/3$. This indicates that, under high vacuum, the dissociation reactions are essentially chemically controlled processes, even if surface adsorption phenomena cannot be ruled out.

The "activation energy" (kcal mole^{-1}) of the dissociation reaction was calculated through the relation

$$\log \frac{K_2}{K_1} = \frac{E_a^*}{2.3\ RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and all the values are reported in Table 1.

Due to the variation along the lanthanoid series of the composition of the polynuclear complexes in question, a meaningful relation between the E_a^* values and the lanthanoid ion radius cannot be drawn. However, such a relation can be made for that species having the same composition, namely for the trinuclear complexes (A) (reaction 2) and for the binuclear complexes (B) (reaction 3). The trend in the E_a^* values of the lighter lanthanoid complexes (A), where the NO_3^- groups always behave as bidentate, parallels those observed in other lanthanoid derivatives already studied[3-5].

On the contrary, the E_a^* values related to the complexes of the heavier lanthanoid complexes (from Eu to Lu) do not fit a reliable relation even if these complexes have the same composition.

In this respect, it should be remembered that in these complexes the coordination number of the central atom varies as its ionic radius becomes smaller. IR studies[6], in fact, indicated that in the Tm(III). Yb(III) and Lu(III) binuclear complexes, due to the reduced ionic radius of the metal atom, the steric crowding of the ligands causes some NO_3^- groups to behave as monodentate. Therefore, the non-isostructural characteristics of these latter complexes could explain the anomalous trend in their E_a^* values with respect to other series of isostructural complexes.

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