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PREPARATION AND MECHANISM OF THERMAL DECOMPOSITION OF SOLID COMPLEXES OF RE(NO_3)$_3$(Sm, Tb) WITH ASPARTIC ACID

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Abstract

Solid complexes of RE(NO_3)$_3$(Sm, Tb) and aspartic acid were prepared for the first time in aqueous solution. Based on chemical analysis, elemental analysis and IR spectra, the formulae of the complexes were determined as RE(NO_3)$_3$(Asp)$_2$·2H_2O (*RE*=Sm or Tb, *Asp*=Aspartic acid). Their thermal decomposition mechanism were studied from ambient temperature to 700°C using a linear heating program. The study indicates that the courses of thermal decomposition of the two complexes are very similar.

Keywords: aspartic acid, IR, rare earth nitrates, thermal decomposition

Introduction

Although the preparation and properties of the solid complexes of rare earths and amino acids have been widely studied [1–3], no report has appeared on the coordination behaviour and thermal decomposition of rare earth nitrates and aspartic acid in aqueous solution. By such studies, the field of application of the complexes can be widened, and the thermal stabilities can be compared. Much work is still to be done to explore the thermal and chemical behaviour of rare earth elements in the functioning of living organisms.

Experimental

Reagents

Sm(NO_3)$_3$·6H_2O and Tb(NO_3)$_3$·6H_2O were prepared by methods described in the literature [4]. Chemical analysis, IR spectra and X-ray powder diffraction studies prove that the samples correspond to the above formula. Aspartic acid was purchased from Shanghai Kangda Amino Acid Factory. Other reagents were A. R. grade.

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Instruments

Elemental analysis: Italian model 1106. IR spectra; Alpha Centavri FTIR spectrometer. TG-2 thermogravimetric analysis: Perkin-Elmer, USA. Sample mass ca 4 mg. Heating rate 10 deg·min^{-1}. Data and drafting system, Perkin-Elmer, USA. All glass vessels were calibrated.

Preparations

Weigh $RE(NO_3)_3 \cdot 6H_2O$ and aspartic acid in a molar ratio of 1:2 and dissolve them in distilled water. Adjust the *pH* of the solution to 4–5 by adding aqueous sodium hydroxide. Allow the reactants to react for 6 h with continuous stirring at 75–80°C. Filter and concentrate the solution till crystal films appear. After cooling, store the solution in a desiccator containing concentrated H_2SO_4 for five days, when crystals appear. The crystals of the complex are washed with acetone and ether and dried to constant weight in a P_4O_{10} vacuum desiccator.

Results and discussion

Analysis of the complexes

EDTA titration was used to determine the amounts of the rare earths, elemental C, H and N were determined with an elemental analyser. The compositions of the complexes were determined as $RE(NO_3)_3(Asp)_2 \cdot 2H_2O$ (*RE*=Sm or Tb, *Asp*=Aspartic acid). Table 1 shows the composition of the complexes.

Table 1 Composition of the complexes

Complexes	RE /%		C /%		H /%		N /%	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$Sm(NO_3)_3(Asp)_2 \cdot 2H_2O$	23.52	23.37	14.86	15.03	2.58	2.82	10.72	10.96
$Tb(NO_3)_3(Asp)_2 \cdot 2H_2O$	24.23	24.49	14.61	14.83	2.22	2.58	10.98	10.81

The complexes are readily soluble in water, less soluble in alcohol, but they are difficult to dissolve in other organic solvents like acetone, ether and carbon tetrachloride.

IR spectra of the complexes

The IR spectra of the two complexes studied are similar. Compared with the IR spectrum of aspartic acid, the displacement of some major peaks may be observed and the relative intensities also change. This proves that the coordination occurs between the rare earth ion and aspartic acid molecule. The existence of characteristic peaks of NH_5^- and COO^- groups in the complexes shows that aspartica acid in the complexes retains its molecular structure. The displacements of $\gamma^{s}_{COO^-}$ and $\gamma^{as}_{COO^-}$ bands obviously indicate the COO^- takes part in coordination. The wide peak appearing near 3400 cm^{-1} shows that water molecules exist in the complexes.

Thermal analysis of the complexes

The attached figure shows the thermal analysis curve of $Tb(NO_3)_3(Asp)_2 \cdot 2H_2O$. The curve of $Sm(NO_3)_3(Asp)_2 \cdot 2H_2O$ is very similar. The curves show that the thermal decomposition process consists of four stages for both complexes. In the first stage, a mass loss occurs at about 160°C. From this it may be assumed that the complex loses of crystallization on heating. The water lost by the complex is, to a great extent, coordination water. After the mass loss peak in the first stage, further three peaks connected with a mass loss each appear as the temperature rises. The thermal behaviour of the terbium complex, at 160–487°C shows that after losing two crystal water molecules, the complex loses mass rapidly as the temperature increases. In the second stage, a peak appears at 295°C and in the third stage, a further peak appears near 348°C. We assume that the latter two peaks indicate the disappearance of the coordination bond between the aspartic acid molecule and the rare earth ion. The two ligands breaking off from the central ion are not under the same condition. Meanwhile, by analysis of mass losses at the corresponding temperatures, was have found that the actually determined mass loss is higher than the theoretical value. This is because the ligand does not break away completely from the central rare earth ion. In the fourth stage, the mass loss of the complex, occurs at 451–700°C, with the peak at 689°C. This stage may be assumed to be due to the thermal decomposition of $Tb(NO_3)_3$. The fact that the theoretical mass loss agrees with the value determined shows that the decomposition of $Tb(NO_3)_3$ is nearly complete at this stage. Table 2 gives the weight losses in the different stages.

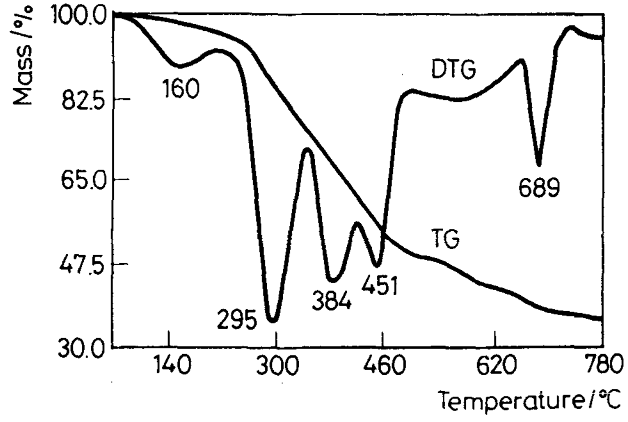

Fig. 1 TG and DTG curves for $Tb(NO_3)_3(Asp)_2 \cdot 2H_2O$

Table 2 Thermal decomposition stages and mass loss data of $Tb(NO_3)_3(Asp)_2{\cdot}2H_2O$

Peak temperature /°C	Found	Calcd.	Product of decomposition
160	4.98	5.55	$Tb(NO_3)_3(Asp)_2$
295	24.39	25.19	$Tb(NO_3)_3(Asp)$
451	48.03	46.83	$Tb(NO_3)_3$
689	37.22	36.52	$TbONO_3$

According to the figure and the weight loss data in different stages, we can write the thermal decomposition of the complexes as follows:

$$RE(NO_3)_3(Asp)_2{\cdot}2H_2O \rightarrow RE(NO_3)_3(Asp)_2$$
$$\rightarrow RE(NO_3)_3(Asp) \rightarrow RE(NO_3)_3 \rightarrow REONO_3$$

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Zusammenfassung — Erstmals wurden in wäßriger Lösung Feststoffkomplexe von $RE(NO_3)_3$(Sm, Tb) und Asparaginsäure hergestellt. Anhand chemischer Analyse, Elementaranalyse und IR-Spektren wurden die Formeln dieser Komplexe mit $RE(NO_3)_3(Asp)_2{\cdot}2H_2O$ (*RE*= Sm oder Tb, *Asp*= Asparaginsäure) bestimmt. Unter Verwendung eines linearen Aufheizprogrammes wurden deren thermischer Zersetzungsmechanismus zwischen Raumtemperatur und 700°C untersucht. Die Untersuchungen ergaben, daß die Reaktionswege der thermischen Zersetzung für die zwei Komplexe sehr ähnlich sind.