

PREPARATION, THERMAL DECOMPOSITION PROCESS AND KINETICS FOR TERBIUM *p*-METHOXYBENZOATE TERNARY COMPLEX WITH 1,10-PHENANTHROLINE

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The complex of $[\text{Tb}_2(p\text{-MOBA})_6(\text{PHEN})_2]$ ($p\text{-MOBA}=\text{C}_8\text{H}_7\text{O}_3$, p -methoxybenzoate; $\text{PHEN}=\text{C}_{12}\text{H}_8\text{N}_2$, 1,10-phenanthroline) was prepared and characterized by elemental analysis and IR spectroscopy. The thermal behavior of $\text{Tb}_2(p\text{-MOBA})_6(\text{PHEN})_2$ in a static air atmosphere was investigated by TG-DTG, DTA, SEM and IR techniques. By the kinetic method of processing thermal analysis data put forward by Malek *et al.*, it is defined that the kinetic model for the first-step thermal decomposition is SB(m,n). The activation energy E for this step reaction is $140.92 \text{ kJ mol}^{-1}$, the enthalpy of activation ΔH^\ddagger is $136.06 \text{ kJ mol}^{-1}$, the Gibbs free energy of activation ΔG^\ddagger is $145.16 \text{ kJ mol}^{-1}$, the entropy of activation ΔS^\ddagger is $-15.53 \text{ J mol}^{-1}$, and the pre-exponential factor $\ln A$ is 29.26. The lifetime equation at mass loss of 10% was deduced as $\ln \tau = -28.72 + 1.943 \cdot 10^4/T$ by isothermal thermogravimetric analysis.

Keywords: lifetime, non-isothermal kinetics, p -methoxybenzoate, terbium complex, thermal decomposition

Introduction

The rare-earth carboxylic acid complexes have many special structure and interesting spectroscopic properties, which is of great interest in extraction, separation, germicide, catalysis, luminescence and functional materials. The preparation, structure and thermal properties of some rare-earth carboxylic acid complex have been studied [1–19]. In this paper, we have prepared the complex of terbium p -methoxybenzoate with 1,10-phenanthroline and discussed its thermal decomposition procedure by TG-DTG, DTA, SEM and IR techniques and the corresponding non-isothermal kinetics in terms of the Malek method [20, 21]. The lifetime equation at mass loss of 10% was obtained by isothermal thermogravimetric analysis. This has some directive significance to the determination of the stability of the title compound in different temperatures, and also provides basis for the preparation of the composite luminous materials with good thermal stability.

Experimental

Preparation of complex $[\text{Tb}_2(p\text{-MOBA})_6(\text{PHEN})_2]$

A stoichiometric amount of p -methoxybenzoic acid was dissolved in 95% $\text{C}_2\text{H}_5\text{OH}$ and its pH was con-

trolled in a range of 6–7 with 1 mol L^{-1} NaOH solution. A quantitative amount 1,10-phenanthroline was also dissolved in 95% $\text{C}_2\text{H}_5\text{OH}$. The two solutions were mixed, and added dropwise into the TbCl_3 solution prepared by dissolving $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ in 95% $\text{C}_2\text{H}_5\text{OH}$. The mixture was heated under reflux with stirring for a few hours. The white precipitate was formed.

Apparatus and measurements

The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba model 1106 elemental analyzer. The metal content was assayed using EDTA titration method.

Infrared spectra were recorded as KBr discs on Bio-Rad FTS-135 spectrometer, between 4000 and 400 cm^{-1} .

The TG and DTG experiments for the title compounds were performed using a Perkin Elmer's TGA7 thermogravimetric analyzer. The heating rate used were 3, 5, 7, $10^\circ\text{C min}^{-1}$ from ambient to 700°C and the sample size was $(3.6 \pm 0.2) \text{ mg}$. Air was used as a static atmosphere.

The DTA curve was carried out on a Perkin Elmer DTA 1700 with a system 7/4 controller. The sample mass was 2.2 mg. The heating rate used were 5°C min^{-1} . Air was used as a static atmosphere.

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Results and discussion

Elemental analyses and infrared spectra

Analytical results for the complex compared with theoretical calculation results from the proposed formulate are given in Table 1. It can be seen that the experimental data agree with values of theoretical calculation.

Table 1 Elemental analyses of the complex

| Complex [Tb ₂ (<i>p</i> -MOBA) ₆ (PHEN) ₂] | Mass fraction/% | | | |
|--|-----------------|------|------|-------|
| | C | H | N | Tb |
| Theoretical values | 54.54 | 3.69 | 3.54 | 20.06 |
| Experimental data | 54.20 | 3.84 | 3.32 | 20.35 |

Frequencies of characteristic absorption bands in IR spectra (cm⁻¹) for ligands and complex are listed in Table 2. The IR spectra of the complex show that the absorption valence band of the C=O group, $\nu_{C=O}$ at 1685 cm⁻¹, disappear, whereas the bands of the asymmetric vibrations $\nu_{as(COO^-)}$ at 1605 cm⁻¹ and of the symmetric vibrations $\nu_{s(COO^-)}$ at 1417 cm⁻¹ are apparent. The values of the splitting for the absorption bands of the valency vibration $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ ($\Delta\nu = \nu_{as} - \nu_s$) is very high ($\Delta\nu = 188$ cm⁻¹). The IR spectra of the complex show that the absorption valency band of the $\nu_{C=N}$ at 1644 cm⁻¹ are observed to move lower wavenumber. The spectroscopy data suggest that the Tb³⁺ is coordinated with N atoms of 1,10-phenanthroline and O atoms of *p*-methoxybenzoate [22, 23].

Thermogravimetric decomposition data

Thermal analytical data measured at $\beta = 5^\circ\text{C min}^{-1}$ for title compound are presented in Table 3. The percent-

Table 2 Frequencies of characteristic absorption bands in IR spectra (cm⁻¹) for ligands, complex and some intermediate products of the thermal decomposition

| Compounds | $\nu_{C=N}$ | $\nu_{C=O}$ | $\nu_{as(COO^-)}$ | $\nu_{s(COO^-)}$ | $\Delta\nu = \nu_{as} - \nu_s$ |
|--|-------------|-------------|-------------------|------------------|--------------------------------|
| PHEN | 1644 | — | — | — | — |
| <i>p</i> -MOBA | — | 1685 | — | — | — |
| Tb ₂ (<i>p</i> -MOBA) ₆ (PHEN) ₂ | 1639 | — | 1605 | 1417 | 188 |
| Intermediate (Tb ₂ (<i>p</i> -MOBA) ₆) | — | — | 1608 | 1422 | 186 |
| End product (Tb ₄ O ₇) | — | — | — | — | — |

Table 3 Thermal decomposition data for Tb₂(*p*-MOBA)₆(PHEN)₂ from TG and DTG analysis ($\beta = 5^\circ\text{C min}^{-1}$)

| Stage | $T_{\text{range}}/^\circ\text{C}$ | DTG peak $T/^\circ\text{C}$ | Mass loss/% | | Probable composition of expelled groups | Intermediate |
|-------|-----------------------------------|-----------------------------|-------------|--------|---|---|
| | | | TG | Theory | | |
| I | 252.83–354.08 | 310.48 | 23.29 | 22.74 | –2PHEN | [Tb ₂ (<i>p</i> -MOBA) ₆] |
| II | 354.08–486.28 | 418.77–451.12 | 28.34 | 28.60 | –3 <i>p</i> -MOBA | [Tb ₂ (<i>p</i> -MOBA) ₃] |
| III | 486.28–659.26 | 524.25–605.82 | 24.58 | 25.07 | –C ₂₄ H ₂₁ O _{5.5} | Tb ₄ O ₇ |

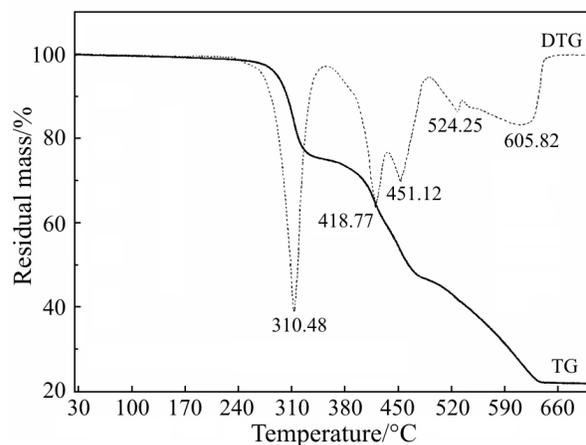


Fig. 1 TG-DTG curves of Tb₂(*p*-MOBA)₆(PHEN)₂ (heating rate of 5°C min⁻¹)

ages of mass loss and probable composition of the expelled groups are also given. TG and DTG curves of Tb₂(*p*-MOBA)₆(PHEN)₂ are shown in Fig. 1. The results of thermal analysis indicate that the thermal decomposition of Tb₂(*p*-MOBA)₆(PHEN)₂ begins at 252.83°C and terminated at 659.26°C. The thermal decomposition process of Tb₂(*p*-MOBA)₆(PHEN)₂ can be divided into three stages, as was observed by the DTG curve (Fig. 1). The first stage starts from 252.83 to 354.08°C with a mass loss 23.29% which corresponds to the loss of 2 mol C₁₂H₈N₂ (theoretical mass loss is 22.74%). The IR spectra of the residue at 354°C shows that the absorption band of C=N disappear at 1639 cm⁻¹. The SEM pictures show that the form of the complex changed from a smooth-surface cylinder to a crackled cylinder (Fig. 2). The second stage in the degradation occurs from 354.08 to 486.28°C. Actually, from DTG curve (Fig. 1), this