Thermochemistry of the ternary complex Eu(Et$_2$dtc)$_3$(phen)

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Abstract

A ternary solid complex Eu(Et$_2$dtc)$_3$(phen) has been obtained from the reaction of sodium diethyldithiocarbamate (NaEt$_2$dtc), 1,10-phenanthroline (phen) and hydrated europium chloride in absolute ethanol. The title complex was described by chemical and elemental analyses, TG-GTG and IR spectrum. The enthalpy change of liquid-phase reaction of formation of the complex, $\Delta_r H_m^\theta$ (l), was determined as $-(13.481 \pm 0.0314)$ kJ $\cdot$ mol^{-1} at $T = 298.15$ K by a RD-496 III heat conduction microcalorimeter. The enthalpy change of the solid-phase reaction of formation of the complex, $\Delta_r H_m^\theta$ (s), was calculated as (152.317 ± 0.542) kJ $\cdot$ mol^{-1} on the basis of a designed thermochemical cycle and other auxiliary thermodynamic qualities. The thermodynamics of reaction of formation of the complex was investigated by changing the temperature of liquid-phase reaction. Fundamental parameters, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_{\neq}^\theta$), the activation entropy ($\Delta S_{\neq}^\theta$), the activation free energy ($\Delta G_{\neq}^\theta$) and the enthalpy ($\Delta_r H_{\neq}^\theta$), were obtained combination the reaction thermodynamic and kinetic equations with the data of thermokinetic experiments. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as $-(17410.63 \pm 8.95)$ kJ $\cdot$ mol^{-1} by a RBC-Π rotating-bomb calorimeter at $T = 298.15$ K. Its standard enthalpy of combustion, $\Delta_c H_m^\theta$, and standard enthalpy of formation, $\Delta_f H_m^\theta$, were calculated to be $-(17429.84 \pm 8.95)$ kJ $\cdot$ mol^{-1} and $-(1231.76 \pm 9.92)$ kJ $\cdot$ mol^{-1}, respectively.
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1. Introduction

The prospect of generating new materials used for the precursors of ceramics and film [1–4] provides significant motivation for the research interest in coordination compounds containing lanthanide–sulfur bonds. Many investigations on the preparations, characterizations and structures of these kinds of compounds have been documented [5–7]. As part of our interests in the thermochemistry of complexes containing lanthanide–sulfur bonds, we have recently finished thermodynamic studies of reactions of rare earths with diethyldithiocarbamate [8], which is of great importance for understanding the

driving forces in the coordination reaction systems and the energetic associated with the reaction processes in the formation of coordination compounds.

Calorimetry is a universal technique widely used for the measurements of enthalpies of reactions, dissolution, dilution, mixing, adsorption, formation, and excess enthalpies in a thermochemistry laboratory, which are involved in physical changes, chemical reactions and living biochemical metabolisms. The datum of the standard molar enthalpy of formation plays an important role in theoretical study, application development and industrial production of a compound as a basis of theoretical analysis. In spite of that, to our best knowledge, there is little reliable experimental data available for these complexes containing lanthanide–sulfur bonds.

In the present study, a novel ternary solid complex Eu(Et$_2$dtc)$_3$(phen) has been synthesized from the

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reactions ofeuropium chloride hydrate with sodium diethyldithiocarbamate (NaEt$_2$dtc) and 1,10-phenanthroline (phen) in absolute ethanol. The complex was characterized by chemical and elemental analyses, TG-DTG and IR technique. The enthalpy change of the liquid-phase reaction $\Delta_r H_m^\theta$ (l) at $T = 298.15$ K was measured by a RD-496 III heat conduction microcalorimeter and that of solid-phase $\Delta_r H_m^\theta$ (s) was derived from a thermochemical cycle. The thermodynamics of the liquid-phase reaction at different temperatures were investigated, and fundamental parameters, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_{\neq}^\theta$), the activation entropy ($\Delta S_{\neq}^\theta$), the activation free energy ($\Delta G_{\neq}^\theta$) and the enthalpy ($\Delta_r H_{\neq}^\theta$), were obtained on the basis of reaction thermodynamic and kinetic equations. The constant-volume combustion energy, $\Delta_c U$, of the complex was measured by a RBC-Π rotating-bomb calorimeter at $T = 298.15$ K. Its standard enthalpy of combustion, $\Delta_c H_m^\theta$, and standard enthalpies of formation, $\Delta_f H_m^\theta$, were calculated.

2. Experimental

2.1. Chemicals

The EuCl$_3 \cdot 3.94$H$_2$O was prepared according to reference [9], sodium diethyldithiocarbamate hydrate (abbreviated as NaEt$_2$dtc $\cdot 3$H$_2$O, mass fraction higher than 0.995) and 1,10-phenanthroline (abbreviated as phen $\cdot$ H$_2$O, mass fraction higher than 0.995) were commercially obtained from Shanghai Regent Factory. They were maintained in desiccators over phosphorus pentoxide or silica gel before the calorimetric measurements. Absolute ethanol (analytical grade) from Xi'an Chemical Reagent Company was used to prepare all of the calorimetric solvents. Potassium chloride (mass fraction 0.9999) was purchased from Shanghai No. 1 Regent Factory, Shanghai, China, and dried in a vacuum oven at $T = 500$ K for 8 h prior to use.

The relative atomic masses used were those recommended by IUPAC Commission in 1999 [10].

2.2. Equipments and analyses methods

Spectra were obtained with samples in KBr matrix for the title complex and ligands. A BEQ UZNDX-550 series FT-IR spectrophotometer in the 4000–400 cm^{-1} region was used. The Eu^{3+} and Cl^{-} were determined volumetrically with EDTA by complexometric titration and gravimetrically; C, H, N and S contents were carried out by an instrument of Vario EL III CHNOS of German. The TG-DTG tests were performed in a Perkin–Elmer thermobalance and under dynamic atmosphere of high purity N$_2$(mass fraction 0.99999) with flow rate of 60 cm$^3 \cdot$ min^{-1} and a heating rate of 10 K $\cdot$ min^{-1}. The ICP-OES spectroscopy was carried out for checking the progress of the reaction occurring in the calorimetric experiments using a Perkin–Elmer ICP Liberty 150 instrument. The phase structure of the solid combustion product was identified by a Rigua D/max-IIIC X-ray diffractometer using Cu Kα radiation.

2.3. RD496-III heat conduction calorimeter

All the enthalpies of solutions and that of reaction were measured by an RD496-IIImicro-calorimeter [11]. The heat conduction microcalorimeter is mainly composed of the precision temperature controlling system, the electric energy calibration system, the constant temperature thermostat and the data processing system. The working temperature of the calorimeter lies in the range of $T = (77.15$ to $473.15)$ K. It equips a 16 cm^3 sample cell and 16 cm^3 reference cell. The thermal effect can be determined through a thermoelectric pile composed of 496 thermocouples, which is converted to thermal electric potential. The thermal electric potential is amplified through a microvolt amplifier, converted by modulus, collected and processed by a computer. The functions of controlling the temperature of the system, running on chemical and electrical calibrations, having the sensitivity calibrated, measuring the thermal effect, and picking up and saving the results are achieved by a program under a Window system designed by ourselves.

The baseline stability was determined at a constant temperature and with a rising temperature at a stated heating rate. Keeping the temperature at $T = 313.15$ K for 50 h, the baseline change was less than ± 0.2 μV. While raising the temperature from $T = 313.15$ to $T = 373.15$ K at the speed of 1 K $\cdot$ h^{-1}, the stability is 0.4 μV $\cdot$ K^{-1}.

The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. According to the molar ratio of KCl to water, $n_{KCl} : n_{H_2O} \approx 1 : 500$, a certain amount of KCl is dissolved in double distilled water at $T = (298.15 \pm 0.001)$ K. The average enthalpy of dissolution of KCl determined from the 6 tests was, $\Delta_s H_{m,KCl}^\theta = (17.581 \pm 0.039)$ kJ $\cdot$ mol^{-1}, as shown in table 1, which is in agreement with the published value (17.584 ± 0.007) kJ $\cdot$ mol^{-1} [12].

2.4. RBC-Π rotating-bomb combustion calorimeter

The constant-volume combustion energy of the compound was measured by a RBC-type II precision rotating bomb combustion calorimeter [13]. It mainly