研究简报

Lu(Et₂dtc)₃(phen)的生成反应焓变、摩尔热容和恒容燃烧能测定

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Determination of Enthalpy Change of Reaction of Formation, Molar Heat Capacity and Constant-Volume Combustion Energy of the Ternary Solid Complex Lu(Et₂dtc)₃(phen)

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Abstract: A ternary solid complex Lu(Et₂dtc)₃(phen) has been obtained from the reaction of hydrated lutetium chloride with sodium diethyldithiocarbamate (NaEt₂dtc), and 1,10-phenanthroline (*o*-phen·H₂O) in absolute ethanol. IR spectrum of the complex indicates that Lu³⁺ binds with sulfur atom in the Na (Et₂dtc)₃ and nitrogen atom in the *o*-phen. The enthalpy change of liquid-phase reaction of formation of the complex, $\Delta_r H_m^{\ominus}$ (l), was determined to be (−32.821 ± 0.147) kJ·mol⁻¹ at 298.15 K by an RD-496 Ⅲ type heat conduction microcalorimeter. The enthalpy change of the solid-phase reaction of formation of the complex, $\Delta_r H_m^{\ominus}$ (s), was calculated to be (104.160 ± 0.168) kJ·mol⁻¹ on the basis of an appropriate thermochemistry cycle. The thermodynamics of liquid-phase reaction of formation of the complex was investigated by changing the temperature of liquid-phase reaction. Fundamental parameters, such as the activation enthalpy ($\Delta H_{\neq}^{\ominus}$), the activation entropy ($\Delta S_{\neq}^{\ominus}$), the activation free energy ($\Delta G_{\neq}^{\ominus}$), the apparent reaction rate constant (*k*), the apparent activation energy (*E*), the pre-exponential constant (*A*) and the reaction order (*n*), were obtained by combination the reaction thermodynamic and kinetic equations with the data of thermokinetic experiments. The molar heat capacity of the complex, c_m, was determined to be (82.23 ± 1.47) J·mol⁻¹·K⁻¹ by the same microcalormeter. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as (−17 898.228 ± 8.59) kJ·mol⁻¹ by an RBC-Ⅱ type rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^{\ominus}$, and standard enthalpy of formation, $\Delta_f H_m^{\ominus}$, were calculated to be (−17 917.43 ± 8.11) kJ·mol⁻¹ and (−859.95 ±10.12) kJ·mol⁻¹, respectively.

Key words: Lu(Et₂dtc)₃(phen); enthalpy change of reaction of formation; heat capacity constant-volume combustion energy

0 Introduction

A series of lanthanide sulfide complexes have been largely used for ceramics and thin materials[1] and these complexes could be prepared from precursor compounds containing lanthanide-sulfur bonds[2-4]. Early studies on their preparations and structures helped to understand the characterization of lanthanide series in these compounds and to broaden their applications. The experiments on these complexes were usually performed using anhydrous salts in dry inert gas due to difficulties in preparation and their stabilities under moistures[5]. There was a report on the preparation of the ternary complexes involving the variable-valence transitional elements, that 2,2′-bipyridyl or 1,10-phenanthroline with π donor and dithiocarbamates were selected as ligands, which overcame the drawbacks of the preparation on the duality complexes[6]. In Ref.[7], the complexes of rare earth metal with the mixed ligands of NaEt$_2$dtc and o-phen were characterized. Eu(Et$_2$dtc)$_3$(phen) was structurally determined[8]. The complex of rare earth metal with the ligands of NaEt$_2$dtc and bipy was reported and the crystal structure of Er(Et$_2$dtc)$_3$(bipy) was described[9,10]. However, the preparation and properties of the title complex have not been reported in literature.

In the present study, a novel ternary solid complex Lu(Et$_2$dtc)$_3$(phen) has been synthesized by the reaction of hydrated lutetium chloride with sodium diethyldithiocarbamate (NaEt$_2$dtc), and 1,10-phenanthroline (o-phen·H$_2$O) in absolute ethanol and characterized by chemical analysis, elemental analysis and IR. The enthalpy change of liquid-phase reaction of formation and specific heat capacity of the complex were determined by a microcalormeter. The enthalpy change of the solid-phase reaction has been obtained by an appropriate thermochemistry cycle. On the basis of experimental and calculated results, the thermodynamic and kinetics parameters of liquid-phase reaction of formation of the complex were obtained. These thermodynamic quantities would contribute to the recent computer-aided molecular designs of new materials.

1 Experimental

1.1 Reagents

LuCl$_3$·3.73H$_2$O was prepared according to Ref.[11]. Sodium diethyldithiocarbamate (abbreviated as NaEt$_2$dtc, mass fraction higher than 0.995 0) and 1,10-phenanthroline (abbreviated as o-phen·H$_2$O, mass fraction higher than 0.995 0) were commercially obtained from Shanghai Reagent Factory. They were stored in desiccators over P$_4$O$_{10}$ before the calorimetric measurements. Absolute ethanol and chloroform were of A.R. grade from Xi′an Chemical Reagent Company. Potassium chloride (mass fraction 0.999 9) was purchased from Shanghai No.1 Regent Factory, and dried in a vacuum oven at 900 K for 8 h prior to use. The benzoic acid in this work was commercially obtained from Chengdu Chemical Reagent Company, with a mass fraction purity of 0.999 99, and the value of the isothermal heat of combustion is $(-26 434 \pm 3)$ J·g^{-1} at 298.15 K. Before the experiment the benzoic acid was sublimated for three times and kept in vacuum over P$_4$O$_{10}$ to dryness. Thianthrene purchased from TOKYO KASEI KOGYO CO., LTD. was of GC grade with the purity of 99%, and recrystallized three times to achieve a better purity of 99.9% by HPLC prior to use, and was stored in desiccator over P$_4$O$_{10}$. The gamma aluminum oxide was of spectroscopical purity from Shanghai No.1 Regent Factory, and was transformed to alpha aluminum oxide in muffle at 1 473 K for 8 h and kept in desiccator over P$_4$O$_{10}$ prior to use.

1.2 Analytical methods and Equipments

Lu^{3+} was determined with EDTA by complexometric titration. C, H, N and S content analyses were carried out on an instrument of Vario EL III CHNOS of German. The IR analysis was conducted in the 4 000~400 cm^{-1} region on a BEQ, UZNDX - 550 spectrometer (KBr discs). The calorimetric experiment were performed using an RD496-III type microcalorimeter[12] and an RBC-II type rotating-bomb calorimeter[13]. ICP-AES experiment was carried out on a T. E. IRIS Advantage Inductively Coupled Plasma Atomic Emission Spectrophotometer. The purity of the compound was attested by an HP-1100 type HPLC instrument, and

the solvent was CH_2Cl_2, the eluting reagent was CH_2Cl_2 and the column was contra-phase carbon −18.

1.3 Calorimetric method

All the enthalpies of solutions and enthalpies of reaction of the complex were measured by an RD496-Ⅲ type microcalorimeter. The design, assemblage and test of the microcalorimeter were published in Ref.[12]. The calorimetric constants at 292.15, 295.15, 298.15 and 301.15 K were determined by the Joule effect before experiment, which were (63.691 ± 0.035), (63.799 ± 0.042), (63.901 ± 0.030) and (64.000 ± 0.026) μV·mW^{-1}. The enthalpy of solution of KCl in deionized water was measured to be (17.581 ± 0.039) kJ·mol^{-1}, which is in good agreement with the value of (17.584 ± 0.006 6) kJ mol^{-1} in Ref.[14]. The relative error of the experiment result is 0.02% and the RSD of the calorimeter is 0.3%, which indicates that the calorimetric system is accurate and reliable. The main experimental procedures were described previously[15].

To gain the value of molar heat capacity of the complex, the empty cell (system Ⅰ), the cell containing sample with unknown specific heat c (system Ⅱ), the cell containing first standard substance with known specific heat c_1 (system Ⅲ), and the cell containing second standard substance with known specific heat c_2 (system Ⅳ) were uniformly heated by the same Peltier current for 1 h. When thermal equilibrium of systems Ⅰ~Ⅳ is established, it can be shown that, (a) the temperature is uniform within the cell, and (b) the equilibrium temperature θ is the same for a given Peltier current, whatever the cell contents. When the Peltier current is cut off, the quantities of heat q_0, q, q_1 and q_2 retained by the systems Ⅰ~Ⅳ are given by the following equations.

For system Ⅰ $\quad q_0 = a\theta$ $\qquad\qquad$ (1)

For system Ⅱ $\quad q = (a + mc)\theta$ $\qquad\quad$ (2)

For system Ⅲ $\quad q_1 = (a + m_1c_1)\theta$ $\qquad$ (3)

For system Ⅳ $\quad q_2 = (a + m_2c_2)\theta$ $\qquad$ (4)

where a is the apparent heat capacity of the empty cell in J·K^{-1}, θ is the equilibrium temperature for a given Peltier current, m, m_1 and m_2 are masses of the samples under study, the first standard substance and second standard substance, respectively, in g; c, c_1

and c_2 are molar heat capacity of the sample under study, the first standard substance and second standard substance, respectively, in J·mol^{-1}·K^{-1}; q_0, q, q_1 and q_2 are the quantities of heat retained by the systems Ⅰ~Ⅳ when they are heated up by a given peltier current.

Combination of the Eqs. (1) and (4), the following formula is obtained.

$$c=[(q - q_0) / 2m][m_1c_1 / (q_1 - q_0) + m_2c_2 / (q_2 - q_0)] \qquad (5)$$

The value of c for the sample under study can be obtained from Eq. (5) if the values of c_1 and c_2 of two standard substances are known.

The constant-volume combustion energy of the complex was determined by an RBC-Ⅱ type precise rotating-bomb calorimeter. The main experimental procedures were described previously[13,16]. The cross-sectional view and the bicyclic suppor of the rotating bomb were the same as those in Ref.[16]. The initial temperature was regulated to (25.000 0 ± 0.000 5) ℃ and the initial oxygen pressure was 2.5 MPa. The digital indicator for temperature measurement was used to ensure a better precision and accuracy of the experiment. The correct value of the heat exchange was calculated according to Linio-Pyfengdelel-Wsava formula (6)[17]:

The calorimeter was calibrated with benzoic acid. The calibrated experimental results with an uncertainty of 4.18 × 10^{-4} are summarized in Table 1. The energy equivalent of the rotating-bomb calorimeter was calculated according to Eq. (6),

$$W=\frac{Qa+Gb+5.97c}{\Delta T} \qquad (6)$$

where W is the energy equivalent of the rotating-bomb calorimeter (in J·K^{-1}), Q is the combustion enthalpy of benzoic acid (in J·g^{-1}), a is the mass of determined benzoic acid or flower of sulfur (in g), G is the combustion enthalpy of Ni-Cr wire for ignition (0.9 J·cm^{-1}), b is the length of the actual Ni-Cr wire consumed (in cm), 5.97 is the formation enthalpy and solution enthalpy of the acid corresponding to 1 mL of 0.100 0 mol·L^{-1} solution of NaOH (in J·mL^{-1}), c the volume (in mL) for NaOH (0.100 0 mol·L^{-1} solution) consump-

tion and ΔT is the correct value of the temperature rise. In order to measure the standard energy of combustion for the compound involved sulfur element, the standard energy of combustion of thianthrene was determined as $(-33\,507.76 \pm 14.13)$ J·g^{-1}, as shown in Table 2. The RSD is 4.22×10^{-4} and the relative error is 1.19×10^{-3}, which is in good agreement with $(-33\,468 \pm 4)$ J·g^{-1} [18].

Table 1　Results for calibration of energy equivalent of the rotating-bomb calorimeter at 298.15 K

No. of experiments	Mass of benzoic acid m / g	Calibrated heat of combustion wire q_c / J	Calibrated heat of acid q_N / J	Calibrated ΔT / K	Energy equivalent W / (J·K^{-1})
1	0.997 02	10.35	24.78	1.4834	17 790.45
2	0.789 40	8.10	20.89	1.1746	17 789.88
3	0.830 60	12.60	20.43	1.238 2	17 758.93
4	0.968 69	12.60	17.43	1.441 8	17 780.82
5	0.994 85	12.60	20.80	1.480 0	17 798.18
6	1.123 28	9.09	21.85	1.673 5	17 761.41
7	0.900 36	9.28	21.67	1.342 9	17 745.97
Mean ± SD^a					17 775.09 ± 7.43

^{a} SD$=\sqrt{\dfrac{\Sigma\,(x_1-\overline{x})^2}{n-1}}$

Table 2　Experimental results for the combustion energies of the complex and thianthrene

Compound	No. of experiments	Mass of complex m / g	Calibrated heat of combustion wire Q_c / J	Calibrated heat of acid Q_N / J	Calibrated / K	Combustion energy of complex $-\Delta_c U$ / (J·g^{-1})
Complex	1	0.789 36	11.70	1 598.37	1.0844	22 378.05
	2	0.792 50	12.60	1 604.73	1.089 5	22 395.75
	3	0.793 15	12.60	1 606.05	1.090 9	22 407.10
	4	0.788 71	11.70	1 597.06	1.083 0	22 367.74
	5	0.789 65	10.80	1 698.96	1.083 5	22 351.10
	6	0.790 96	12.60	1 601.61	1.084 8	22 337.68
	Mean ± SD					22 372.90 ± 10.74
Thianthrene	1	0.488 60	12.60	1 383.69	0.999 8	33 514.62
	2	0.488 86	11.70	1 384.41	1.001 5	33 558.98
	3	0.490 11	12.60	1 387.90	1.002 8	33 511.58
	4	0.487 98	12.60	1 381.96	0.997 7	33 484.26
	5	0.488 35	12.60	1 382.99	0.997 7	33 456.78
	6	0.488 23	12.60	1 382.65	0.999 2	335 20.31
	Mean ± SD					33 507.76 ± 14.13

The analytical methods for final products (gas, liquid and solid) were the same as those in Ref.[13]. The analytical results of the final products showed that the combustion reactions were complete.

1.4　Synthesis of the complex

LuCl$_3$·3.73H$_2$O, o-phen·H$_2$O and NaEt$_2$dtc were dissolved in a minimal amount of anhydrous ethanol, respectively, and the salt alcoholic solution was poured into a three-necked round bottle. To the salt alcoholic solution, the ligands of o-phen and NaEt$_2$dtc mixed in mole ratio of 1:3 was dropwise added when keeping electromagnetic stirring. After the addition, the mixture was allowed to stand for overnight and the precipitate was collected by suction filter, then the crude product was purified with CHCl$_3$. The fine crystal was obtained and followed by three small amounts of absolute ethanol portions washing and kept in vacuum over P$_4$O$_{10}$ to dryness prior to use.

2　Results and discussion

2.1　Composition of the complex

The elementary analyses results of the title complex are as follows: w(Calc.): Lu 21.87%, C 40.54%, H 4.79%, N 8.75%, S 24.05%; w(Found): Lu 22.01%, C 40.65%, H 4.64%, N 8.64%, S 24.10%, which is identified as the formula of Lu(Et₂dtc)₃(phen). The complex was checked by HPLC and its purity is excellent (mass fraction 0.999 9).

2.2　IR spectrum of the complex

Compared with the spectra of salt and o-phen·H₂O (3 390 cm⁻¹, 3 388 cm⁻¹), the characteristic absorption of hydroxyl group is not present in the complex, showing that the complex do not consist of water. The peaks of 1 625, 1 590, 1 572, and 1 517 cm⁻¹ are assigned to the skeleton vibration of benzene ring and the peaks of 854 and 730 cm⁻¹ are assigned to the bend vibration of C-H in the complex, which displays certain shifts in contrast with those of (1 617, 1 587, 1 561, 1 504 cm⁻¹) and (854, 739 cm⁻¹) in the ligand. It is thus assumed that two nitrogen atoms in the ligand of o-phen·H₂O coordinate to Lu³⁺. Contrasting with that of 1 477 cm⁻¹ in the ligand of NaEt₂dtc, ν_{CN} of the complex shifts to higher wave number 1 482 cm⁻¹, which can be attributed to that NCS group has two main forms of vibration[19]: (A) and (B)
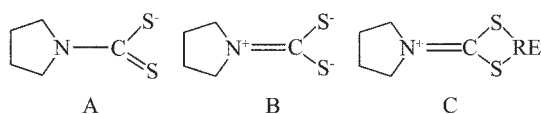
The vibration intensity of the (B) is enhanced when the two sulfur atoms of ligand coordinated to Lu³⁺ to form the new cycle (c), thus ν_{CN} moves to the higher wave number; on the other hand, corresponding to the peak of 986 cm⁻¹ ascribable to the characteristic absorption of -CS in the ligand of NaEt₂dtc, it is found to be spitted into peaks two in the complex. Obviously, this can be due to the new-formed cycle and its formation increases the vibration intensity of ν_{CN}[20]. The changes of ν_{CN} and ν_{CS} indicate that the two sulfur atoms of ligand coordinate to Lu³⁺ in a bidentate manner. The final results demonstrate that it is an octa-coordinated complex, and one pentaatomic ring and three tetraatomic rings are formed.

2.3　Calculation of the enthalpy change of formation of the title solid-phase reaction

The molar enthalpies of solution $\Delta_{sol}H_m^{\ominus}$ (1), $\Delta_{sol}H_m^{\ominus}$ (2), and $\Delta_{sol}H_m^{\ominus}$ (3) of LuCl₃·3.73H₂O, NaEt₂dtc and o-phen·H₂O in absolute alcohol at 298.15 K are given in Table 3, respectively. They can be considered as alcoholic compound. The mixture enthalpies of the alcoholic solutions of two ligands $\Delta_{mix}H_m^{\ominus}$ and the enthalpy changes of the liquid-phase reaction $\Delta_r H_m^{\ominus}$ (l) at 298.15 K are listed in Table 4. The enthalpy of dissolution, $\Delta_{dil}H_m^{\ominus}$ of water in ethanol is so small that it can be regarded as zero.

Therefore, the enthalpy change of formation of solid-phase reaction for the title complex at 298.15 K can be calculated by a thermochemistry cycle in Table 5:

Table 3　Experimental data of $\Delta_{sol}H_m^{\ominus}$ (1), $\Delta_{sol}H_m^{\ominus}$ (2), $\Delta_{sol}H_m^{\ominus}$ (3) at 298.15 K

No.	m / mg	Q / mJ	$\Delta_{sol}H_m^{\ominus}$ (1) / (kJ·mol⁻¹)	m / mg	Q / mJ	$\Delta_{sol}H_m^{\ominus}$ (2) / (kJ·mol⁻¹)	m / mg	Q / mJ	$\Delta_{sol}H_m^{\ominus}$ (3) / (kJ·mol⁻¹)
1	80.91	−9 818.136	−42.313	36.07	7 935.321	45.566	31.71	3 351.540	20.950
2	80.90	−9 796.738	−42.226	36.02	7 916.679	49.518	31.77	3 393.602	21.173
3	80.99	−9 800.901	−42.197	36.09	8 010.432	50.007	31.76	3 343.271	20.866
4	80.90	−9 811.354	−42.289	36.02	7 911.509	49.485	31.73	3 356.008	20.965
5	80.91	−9 819.296	−42.318	36.05	7 968.605	49.806	31.68	3 315.208	20.746
6	80.96	−9 790.770	−42.169	36.04	7 972.883	49.842	31.73	3 379.615	21.123
Mean ± SD			−42.252 ± 0.135			49.703 ± 0.094			20.970 ± 0.071

Table 4　Experimental data of $\Delta_{mix}H_m^{\ominus}$ and $\Delta_rH_m^{\ominus}$ (l) at 298.15 K

No.	Q_1 / mJ	$\Delta_{mix}H_m^{\ominus}$ / (kJ·mol⁻¹)	Q_2 / mJ	$\Delta_rH_m^{\ominus}$/ (kJ·mol⁻¹)
1	73.360	9.170	−261.968	−32.746
2	74.266	9.283	−263.720	−32.965
3	72.746	9.093	−265.296	−33.162
4	73.096	9.137	−257.992	−32.249
5	74.097	9.262	−261.832	−32.729
6	71.842	8.980	−264.552	−32.729
Mean ± SD	72.234 ± 0.401	9.154 ± 0.050	−262.560 ± 1.176	−32.821 ± 0.147

Table 5　Thermochemical cycle and results for $\Delta H_m^{\ominus}$ (298.15 K)

Reaction	$\Delta H_m^{\ominus}$ / (kJ·mol⁻¹)
$LuCl_3 \cdot 3.73H_2O$ (s) + xC_2H_5OH (l) = $[(LuCl_3 \cdot 3.73H_2O) \cdot xC_2H_5OH]$ (l)	−42.252 ± 0.135
$3(NaEt_2dtc)$ (s) + $3yC_2H_5OH$ (l) = $3[(NaEt_2dtc) \cdot yC_2H_5OH]]$ (l)	49.703 ± 0.094
o-phen·H_2O (s) + zC_2H_5OH (l) = $[(o\text{-phen} \cdot H_2O) \cdot zC_2H_5OH]$ (l)	20.970 ± 0.071
$3[(NaEt_2dtc) \cdot yC_2H_5OH]]$ (l) + $[(o\text{-phen} \cdot H_2O) \cdot zC_2H_5OH]$ (l) = $\{[3(NaEt_2dtc) + (o\text{-phen} \cdot H_2O)] \cdot (3y+z)(C_2H_5OH)\}$ (l)	9.154 ± 0.050
$[(LuCl_3 \cdot 3.73H_2O) \cdot xC_2H_5OH]$ (l) + $\{[3(NaEt_2dtc) + (o\text{-phen} \cdot H_2O)] \cdot (3y+z)(C_2H_5OH)\}$ (l) = $Lu(Et_2dtc)_3(phen)$(s) + $3NaCl$(s)+$[(1+3.73)H_2O \cdot (x+3y+z)C_2H_5OH]$ (l)	−32.821 ± 0.147
$(LuCl_3 \cdot 3.73H_2O)$ (s) + $3(NaEt_2dtc)$(s) + $(o\text{-phen} \cdot H_2O)$ (s) = $Lu(Et_2dtc)_3(phen)$(s) + $3NaCl$ (s) + $(1+3.73)$ H_2O (l)	104.160 ± 0.168
$(1+3.73)H_2O$ (l) + $[(x+3y+z)C_2H_5OH]$ (l) = $4.73 \cdot H_2O \cdot (x+3y+z)C_2H_5OH]$ (l)	0

$\Delta_rH_m^{\ominus}$(s) = $\Delta_{sol}H_m^{\ominus}$(1) + $3\Delta_{sol}H_m^{\ominus}$(2) + $\Delta_{sol}H_m^{\ominus}$(3) +

$\Delta_{mix}H_m^{\ominus}$+ $\Delta_rH_m^{\ominus}$ (l) − $\Delta_{dil}H_m^{\ominus}$=

[(−42.252 ± 0.135) + 3(49.703 ± 0.094) + (20.970 ± 0.071) + (9.154±0.050)+ (−32.821±0.147)−0] kJ·mol⁻¹= (104.160 ± 0.168) kJ·mol⁻¹

The final products in the calorimetrical experiments were checked by elemental analysis and ICP-AES experiments, indicating that the final thermodynamic states of the title solid-phase reaction and that of liquid-phase reaction are the same and the designed thermochemistry cycle is reasonable.

2.4 Calculation of the thermodynamic parameters of liquid phase reaction

The synthesis of complex and the thermochemistry cycle indicate the fact that the liquid-phase reaction is of irreversible one. The experimental data from the curves are shown in Table 6. The energy change of the reaction system depends on the reaction progression. Based on the thermodynamic Eq.[7~10,21], the

thermodynamic and kinetic parameters of the liquid reaction are obtained and shown in Table 7.

2.5 Molar heat capacity of the complex

Molar heat capacity of the complex was determined by an RD496-Ⅲ type microcalorimeter just changing the samples in the sample cell. The values of q used to calculate the molar heat capacity of the sample are obtained by the testing method presented as a thermogram in Fig.1. In Fig.3, AG is baseline; at time B, a constant peltier current is generated in the laboratory cell; at CD, the steady state of the system is established; at point D, the Peltier effect is cut off; at
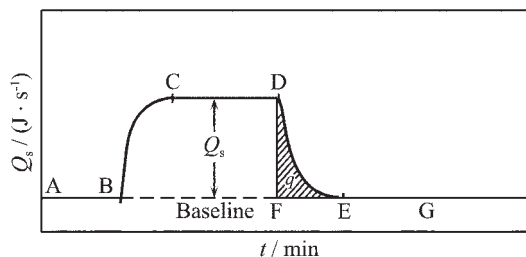

Fig.1　Schematic thermogram of measurement of the molar heat capacity of solid sample

Table 6　Thermokinetical data of liquid-phase reaction

292.15 K			295.15 K			298.15 K			301.15 K		
t / s	H_{ii} / H_0	$\mathrm{d}H_i$ / $\mathrm{d}t$ / (kJ·s⁻¹)	t / s	H_{ii} / H_0	$\mathrm{d}H_i$ / $\mathrm{d}t$ / (kJ·s⁻¹)	t / s	H_{ii} / H_0	$\mathrm{d}H_i$ / $\mathrm{d}t$ / (kJ·s⁻¹)	t / s	H_{ii} / H_0	$\mathrm{d}H_i$ / $\mathrm{d}t$ / (kJ·s⁻¹)
270	0.674 9	4.066 5	180	0.570 2	4.404 5	190	0.743 5	2.785 6	180	0.699 2	2.448 4
275	0.687 5	3.972 3	185	0.585 7	4.310 4	195	0.760 7	2.660 4	185	0.715 8	2.353 1
280	0.700 0	3.878 1	190	0.601 0	4.216 4	200	0.777 4	2.550 8	190	0.731 8	2.275 0
285	0.712 4	3.783 9	195	0.615 9	4.122 3	205	0.793 7	2.441 3	195	0.747 5	2.193 8
290	0.724 5	3.674 0	200	0.630 4	4.028 3	210	0.809 4	2.331 7	200	0.762 8	2.112 5
295	0.736 4	3.579 8	205	0.644 7	3.934 2	215	0.824 7	2.206 5	205	0.777 7	2.034 4
300	0.748 2	3.485 6	210	0.658 5	3.840 2	220	0.839 5	2.097 0	210	0.792 2	1.951 6
305	0.759 7	3.391 4	215	0.672 0	3.746 1	225	0.853 8	1.987 4	215	0.806 4	1.870 3
310	0.771 0	3.297 2	220	0.685 1	3.652 1	230	0.867 6	1.862 3	220	0.820 2	1.790 6
315	0.782 1	3.187 3	225	0.697 9	3.558 0	235	0.881 0	1.752 7	225	0.833 7	1.709 4
320	0.793 0	3.093 1	230	0.710 4	3.479 7	240	0.893 8	1.643 2	230	0.846 7	1.626 6

Table 7　Kinetic, thermodynamic parameters of liquid-phase reaction

T / K	k / ms⁻¹	n	r^{b}	E / (kJ·mol⁻¹)	ln$A$	r^{b}	$\Delta G^{\ominus}_{\neq}$ / (kJ·mol⁻¹)	$\Delta H^{\ominus}_{\neq}$ / (kJ·mol⁻¹)	$\Delta S^{\ominus}_{\neq}$ / (J·mol⁻¹·K⁻¹)	r^{b}
292.15	4.618	0.606 7	0.999 8				84.59			
295.15	5.409	0.602 5	0.999 8	36.29	9.557 3	0.997 5	85.06	33.819 7	−173.718 7	0.997 1
298.15	6.218	0.599 2	0.999 9				85.62			
301.15	7.237	0.601 7	0.999 7				86.14			

ᵇ linear correlation coefficient.

point E, the state of the system returned to the experimental initial state after cutting off the peltier current. q is the total heat, as shown as the shadow area. So the molar heat capacity of the sample is derived from Eq. (**5**). The results of the experiments are shown in Table 8.

Table 8　Raw data used for calculating the values of c

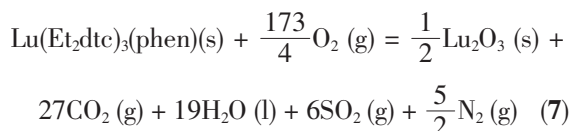| Experimental data	Empty cell	Benzoic acid	α-Al₂O₃	Complex
q / mJ	4 453.908	6 088.611	4 959.916	4 940.285
	4 444.543	6 080.422	4 962.776	4 942.768
	4 432.133	6 094.207	4 977.771	4 941.977
	4 447.035	6 098.640	4 984.568	4 944.232
	4 438.165	6 075.115	4 967.144	4 943.685
	4 450.647	6 073.035	4 983.760	4 943.597
mean ± SD (n = 6)	4 444.405 ± 3.610	6 085.005 ± 4.672	4 972.656 ± 4.824	4 942.741 ± 5.415
RSD (n=6)	8.122 × 10⁻⁴	7.677 × 10⁻⁴	9.701 × 10⁻⁴	1.095 × 10⁻³
m / g		4.514 78	2.684 16	2.369 87
c / (J·mol⁻¹·K⁻¹)		78.707 ± 2.927	145.923 ± 0.562	82.23 ± 1.47
c_0 of lit. / (J·mol⁻¹·K⁻¹)		79.03[22]	145.327[23]	
Relative error		4 × 10⁻³	4 × 10⁻³	

2.6　Combustion energy of the complex

The method for the determination and calculation of the constant-volume combustion energy for the complex are the same as for the calibration of the calorimeter with benzoic acid. The experimental results are given in Table 2.

2.7　Standard combustion enthalpy of complex

The standard combustion enthalpy of the complex, $\Delta_c H_m^{\ominus}$ (complex, s, 298.15 K), refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.

$$Lu(Et_2dtc)_3(phen)(s) + \frac{173}{4}O_2(g) = \frac{1}{2}Lu_2O_3(s) +$$

$$27CO_2(g) + 19H_2O(l) + 6SO_2(g) + \frac{5}{2}N_2(g) \quad (7)$$

The standard combustion enthalpy of the complex is calculated by the following equations:

$$\Delta_c H_m^{\ominus} \text{(complex, s, 298.15 K)} =$$
$$\Delta_c U \text{(complex, s, 298.15K)} + \Delta n\, RT \quad (8)$$

$$\Delta n = n_g \text{(products)} - n_g \text{(reactants)} \quad (9)$$

where n_g is the total amount in mole of gases present as products or as reactants, $R = 8.314$ J·K^{-1}·mol^{-1}, $T = 298.15$ K. Its standard enthalpy of combustion, $\Delta_c H_m^{\ominus}$, is calculated to be (−17 917.43 ± 8.59) kJ·mol^{-1}.

2.8　Standard enthalpy of formation for the complex

The standard enthalpy of formation for the complex, $\Delta_f H_m^{\ominus}$ (complex, s, 298.15 K), is calculated by Hess′s law according to the above thermochemical Eq. (7):

$$\Delta_f H_m^{\ominus}[Lu(Et_2dtc)_3(phen), s] = [\frac{1}{2}\Delta_f H_m^{\ominus}(Lu_2O_3, s) +$$

$$27\Delta_f H_m^{\ominus}(CO_2, g) + 19\Delta_f H_m^{\ominus}(H_2O, l) +$$

$$6\Delta_f H_m^{\ominus}(SO_2, g) + \frac{5}{2}\Delta_f H_m^{\ominus}(N_2, g)] -$$

$$\Delta_f H_m^{\ominus}[Lu(Et_2dtc)_3(phen), s] \quad (10)$$

Where $\Delta_f H_m^{\ominus}$ (Lu$_2$O$_3$, s) = (−1 894.50 ± 7.53); $\Delta_f H_m^{\ominus}$ (CO$_2$, g) = (−393.51 ± 0.13) kJ·mol^{-1}, $\Delta_f H_m^{\ominus}$ (H$_2$O, l) = (−285.830 ± 0.042) kJ·mol^{-1}, $\Delta_f H_m^{\ominus}$ (SO$_2$, g) = (−296.81 ± 0.20) kJ·mol^{-1} [24]. Its standard enthalpy of formation, $\Delta_f H_m^{\ominus}$, is calculated to be (−859.95 ± 10.12) kJ·mol^{-1}.

4　Conclusions

(1) The title ternary complex of Lu(Et$_2$dtc)$_3$(phen) has been synthesized in absolute ethanol by LuCl$_3$· 3.73H$_2$O reacting with the mixed ligands of NaEt$_2$dtc and *o*-phen in the ordinary laboratory atmosphere without any cautions against moisture or air.

(2) A method and calculation formula for determining the molar heat capacity of novel solid complex by use of the Peltier effects is proposed.

(3) The thermodynamics of liquid-phase reaction of formation for the complex Lu(Et$_2$dtc)$_3$(phen) was investigated by changing the temperature of liquid-phase reaction. The thermodynamic and kinetics parameters of the title reaction have been calculated. The apparent activation energy of the reaction is a litter higher than the activation energy 63 kJ·mol^{-1} for a spontaneous reaction at room temperature, showing that the title reaction proceeds feasibly in ethanol solution.

(4) The standard enthalpy of formation of the title complex is (−859.95 ± 10.12) kJ·mol^{-1} and the complex is of certain thermal stability.

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