研究简报

RE(Et$_2$dtc)$_3$(phen)(RE=La,Pr,Nd,Sm)的恒容燃烧能测定

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Determination of Constant-volume Combustion Energies for Complexes of RE(Et$_2$dtc)$_3$(phen) (RE=La, Pr, Nd, Sm)

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Four ternary solid complexes were synthesized with sodium diethyldithiocarbamate ($NaEt_2dtc$) (**b**), 1,10-phenanthroline (*o*-phen) (**c**) and hydrated lanthanide chlorides in absolute ethanol by an improved reported method. The complexes were identified as the general formula of RE(Et$_2$dtc)$_3$(phen) (RE=La, Pr, Nd, Sm) by chemical and elemental analyses. IR spectra of the complexes showed that the RE^{3+} was coordinated with sulfur atoms of $NaEt_2dtc$ and nitrogen atoms of *o*-phen. The constant-volume combustion energies of complexes, Δ_cU, were determined by a precise rotating-bomb calorimeter at 298.15 K. The standard enthalpies of combustion, $\Delta_cH_m^{\ominus}$, and standard enthalpies of formation, $\Delta_fH_m^{\ominus}$, were calculated for these complexes, respectively.

Keywords: **RE(Et$_2$dtc)$_3$(phen)** **combustion energies** **standard enthalpies of formation** **standard enthalpies of combustion**

0 Introduction

The series of complexes lanthanide sulfide have been largely used for the precursors of ceramics and thin film materials[1-4]. For instance, the complexes synthesized with $[(alkyl)_2dtc]^-$, *o*-phen·H_2O and lanthanide salts have been utilized as the volatile precursors for preparing lanthanide sulfide. Preparation of the complexes Ln(Et$_2$dtc)$_3$(phen) and the crystal structure of Eu(Et$_2$dtc)$_3$(phen) were investigated[5,6]. In addition, the friction properties of the complexes in lubricant were reported[7]. To our best knowledge, however, no investigation has been carried out concerning the thermochemical properties for these complexes.

Thermodynamic data could offer better interpretation to the essence of lanthanide-sulfide bonds and stability of this series of complexes. We report here the standard enthalpies of combustion and standard enthalpies of formation for the above mentioned complexes calculated from the data of the constant-volume

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energies combustion for these complexes. The results offer theoretical basis for extending the application range of the complexes.

1 Experimental

1.1 Reagents

Lanthanide chloride hydrate, $RECl_3 \cdot xH_2O$ (**h**) (RE=La, Pr, Nd, Sm; x=3~4) was prepared according to Ref.[8]. $NaEt_2dtc \cdot 3H_2O$ (**b**) was of A.R. grade from Shanghai Reagent Company, *o*-phen·H_2O (**c**), absolute ethanol and $CHCl_3$ were of A.R. grade from Xi'an Chemical Reagent Company.

1.2 Preparation and Composition of the Complexes

The complexes have been synthesized according to the following chemical equation:

$$RECl_3 \cdot xH_2O + 3NaEt_2dtc \cdot 3H_2O + o\text{-phen} \cdot H_2O \xrightarrow{C_2H_5OH} RE(Et_2dtc)_3(phen) + 3NaCl + (10+x)H_2O \quad (\mathbf{1})$$

(RE=La, Pr, Nd, Sm)

8 mmol $RECl_3 \cdot xH_2O$, 24 mmol $NaEt_2dtc \cdot 3H_2O$ and 8 mmol *o*-phen·H_2O were dissolved in a minimal amount of absolute ethanol, respectively, then the alcoholic solutions of *o*-phen and $NaEt_2dtc$ were mixed together. The salt alcoholic solution was added to the above mixture dropwise under electromagnetic stirring. After the addition, the mixture was allowed to stand 30 min and filtered. The crude product was rinsed three times by a small amount of absolute ethanol, followed by purification with $CHCl_3$. The fine crystal obtained was stored in a vacuum desiccator over P_4O_{10} to dryness.

RE^{3+} was determined with EDTA by complexometric titration; C, H, N and S analyses were carried out by a Vario EL Ⅲ CHNOS instrument made in German. The final results are showed in Table 1. The complexes were $La(Et_2dtc)_3(C_{12}H_8N_2)$ (**d**), $Pr(Et_2dtc)_3(C_{12}H_8N_2)$ (**e**), $Nd(Et_2dtc)_3(C_{12}H_8N_2)$ (**f**), $Sm(Et_2dtc)_3(C_{12}H_8N_2)$ (g), respectively.

1.2 Apparatus and Experimental Conditions

The constant-volume combustion energies of the complexes were determined by a precise rotating-bomb calorimeter (RBC-type Ⅱ)[9]. The main experimental procedures were described previously[9]. Cross-sectional view of the rotating bomb was showed in Fig. 1. The bicyclic support showed in Fig.2 was used as the holder for the crucible in the oxygen bomb to maintain the crucible position stable relative to the bomb when the bomb was rotating horizontally and vertically, thus assuring the completion of the combustion reaction and the stable final state in a short time.

The initial temperature was regulated to (25.000 0 ± 0.000 5) ℃ and the initial oxygen pressure was 2.5

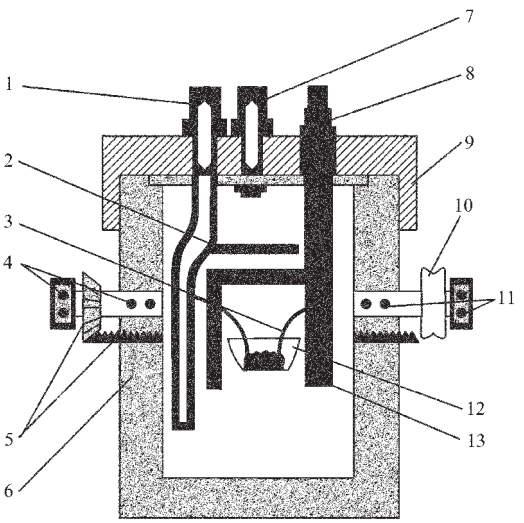


Fig.1 A cross-sectional view of the rotating bomb
1. gas-filled valve; 2. flame baffle; 3. Ni-Cr wire for ignition; 4. ball; 5. bevel gear; 6. bomb body; 7. exhaut valve ; 8. electrode; 9. bomb cover; 10. pulley; 11. ball bearing; 12. crucible; 13. crucible support.

Table 1 Analytical Results Related to the Composition of the Complexes

complexes	RE / %	S / %	C / %	N / %	H / %
d	18.21(18.18)	25.07(25.18)	42.53(42.45)	9.09(9.17)	4.87(5.01)
e	18.30(18.40)	25.07(25.12)	42.23(42.36)	9.10(9.14)	4.79(5.00)
f	18.59(18.75)	24.87(25.01)	42.08(42.16)	9.01(9.10)	4.69(4.98)
g	19.42(19.39)	24.79(24.82)	41.78(41.82)	9.00(9.03)	5.00(4.94)

[a] The data in brackets are calculated values.

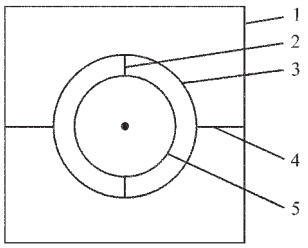


Fig.2　Bicycle structure of the crucible support in the oxygen bomb

1. support; 2. *x*-axle; 3. outside ring; 4. *y*-axle; 5. inside ring.

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:

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{\bar{T}_n - \bar{T}_0}\left(\frac{T_0 + T_n}{2} + \sum_{i=i}^{n-1} - n\bar{T}_0\right) \qquad (2)$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n is the number of readings for the main (or reaction) period, V_0 and V_n are the rate of temperature change at the initial and final stages, respectively (V is positive when temperature decreased), $\bar{T}_0$, $\bar{T}_n$ are the average temperature of calorimeter at the initial and final stages, respectively (the average temperature for first and last reading), T_0 is the last reading of the initial stage, T_n is the first reading of the final stage, $\sum_{i=i}^{n-1} T_i$ is the sum of all the readings, except for the last one of the main period, is a constant.

The calorimeter was calibrated with benzoic acid of 99.999% purity (Chengdu Chemical Reagent Company) with an isothermal heat of combustion of −26 434 J·g^{-1} at 25 ℃. The calibrated experimental results with an uncertainty of 4.18×10^{-4} are summarized in Table 2. The energy equivalent of the rotating-bomb calorimeter was calculated according to the following equation:

$$W = \frac{Qa + Gb + 5.97c}{\Delta T} \qquad (3)$$

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 (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) consumption and ΔT is the correct value of the temperature rise.

The analytical methods for final products (gas, liquid and solid) were the same as those in Ref[10]. The analytical results of the final products showed that the combustion reactions were complete.

2　Results and Discussion

2.1　IR spectra of the Complexes

IR spectra of the complexes are similar because of their similar structure. Taking the complex d for example, and referring to the literature[11,12], IR spectra of salt (**a**) , NaEt$_2$dtc·3H$_2$O **b**, *o*-phen·H$_2$O *c* and the complex **d** in Fig.3 are assigned as follows: compared with the spectra of salt **a**, ligand **b** and ligand **c**

Table 2　Results for Calibration of Energy Equivalent of the Rotating-bomb Calorimeter at 298.15 K

No.	mass of complex m / g	calibrated heat of combustion Q_c wire / 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	1.483 4	17 790.45
2	0.789 40	8.10	20.89	1.174 6	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					17 775.09 ± 7.43

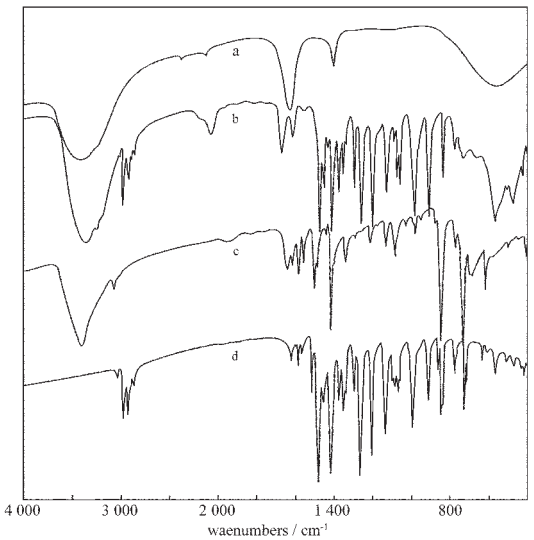
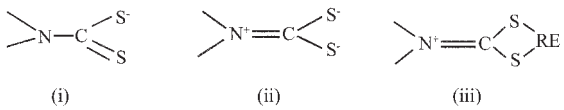


Fig.3 IR spectra of the ligands and the complex
a: $LaCl_3 \cdot 3.94H_2O$, b: $NaEt_2dtc \cdot 3H_2O$, c: *o*-phen·H_2O, d: $La(Et_2dtc)_3$(phen)

(3 390, 3 366 and 3 388 cm^{-1}), the characteristic absorption of hydroxyl group is not present in the complex **d**, showing that the complex **d** does not contain water. The bands at 1 624, 1 588, 1 572 and 1 516 cm^{-1} assigned to the skeleton vibration and the bands of 848 and 729 cm^{-1} assigned to the $\nu_{C\text{-}H}$ bend vibration of benzene ring in the complex **d** shift to higher wave number compared to that of the free ligand **c**, suggesting that *o*-phen behaves as bidentate ligand in the complex. In contrast to that of 1 477 cm^{-1} in the ligand **b**, ν_{CN} of the complex shift to higher wave number and present a double-bond character in the complex. This can be attributed to two main forms of vibration in the NCS_2^- group[13]: (i) and (ii). The vibration intensity of the later will be enhanced when the two sulfur atoms of ligand **b** coordinates to RE^{3+} to form the new cycle (iii), thus ν_{CN} moves to a higher wave number.



On the other hand, an increase in wave number of νcss stretching vibration was observed compared with that of ligand **b**. Obviously, this can be due to the new formed cycle because its formation increases the vibration intensity of ν_{CN}[12]. The changes in ν_{CN} and ν_{CSS} indicate that the sulfur atoms of ligand **b** coordinate to RE^{3+} in a bidentate manner. The final results demonstrate that it is an octahedral-coordinated complex and one penta-atomatic ring and three tetra-atomatic rings are formed. As for the other complexes, the detailed data are listed in Table 3.

2.2 Combustion Energies of the Complexes

The methods of determination and calculation of the constant-volume combustion energies for complexes are the same as for the calibration of the calorimeter with benzoic acid. The values are calculated by means of equation (**4**):

$$\Delta_c U(\text{complex, s}) = \frac{W\Delta T - bG - Q_N}{m} \qquad (4)$$

where $\Delta_c U$(complex, s) denotes the constant-volume combustion energies of the complexes, Q_N is the calibrated heat of acids, m is the mass in g of the complexes, the other symbols are the same as in equation (**3**). The results are given in Table 4.

2.3 Standard Combustion Enthalpies of Complexes

The standard combustion enthalpies of the complexes, $\Delta_c H_m^{\ominus}$ (complex, s, 298.15 K), refer to the combustion enthalpy changes of the following ideal

Table 3 Data of IR Absorption for Main Groups of Ligands and Complexes cm^{-1}

complexes	$\nu(OH^{-1})$	ν(C=C)	ν(C-H)	ν(CN)	ν(CSS)
h	3 347~3 435				
b	3 366			1 477	986
c	3 388	1 617, 1 587, 1 561, 1 504	854, 739		
d	—	1 624, 1 588, 1 572, 1 516	848, 729	1 480, 1 516	995
e	—	1 622, 1 589, 1 570, 1 515	851, 730	1 480, 1 515	993
f	—	1 624, 1 589, 1 572, 1 516	851, 730	1 482, 1 516	997
g	—	1 623, 1 589, 1 571, 1 516	852, 730	1 481, 1 516	996

Table 4　Experimental Results for the Combustion Energies of the Complexes

complexes	No.	mass of complexes m / g	calibrated heat of combustion wire Q_c / J	calibrated heat of acid Q_N / J	calibrated ΔT / K	combustion energy of complexes $\Delta_c U$ / (J·g^{-1})
d	1	0.706 95	12.60	1 405.38	0.990 0	22 886.14
	2	0.700 30	12.60	1 392.16	0.977 9	22 815.22
	3	0.701 26	12.60	1 394.07	0.980 9	22 857.31
	4	0.700 02	12.60	1 391.61	0.979 6	22 868.30
	5	0.710 33	12.60	1 412.10	0.992 9	22 840.35
	6	0.702 58	12.60	1 396.70	0.981 8	22 833.39
	mean ± SD					22 850.12 ± 10.44
e	1	0.742 85	9.90	1 505.69	1.060 2	23 328.48
	2	0.707 80	9.90	1 434.65	1.006 4	23 232.98
	3	0.720 60	12.60	1 460.59	1.028 1	23 315.32
	4	0.725 32	12.60	1 470.16	1.034 3	23 302.84
	5	0.726 21	12.60	1 471.96	1.035 0	23 288.94
	6	0.720 36	12.60	1 460.10	1.026 6	23 287.26
	mean ± SD					23 292.64 ± 13.55
m	1	0.756 80	12.60	1 476.62	1.116 7	24 260.34
	2	0.763 21	12.60	1 489.13	1.127 4	24 289.39
	3	0.745 35	12.60	1 454.28	1.099 7	24 257.58
	4	0.752 37	12.60	1 467.98	1.109 6	24 246.93
	5	0.723 58	12.60	1 411.81	1.068 4	24 277.20
	6	0.737 70	12.60	1 439.36	1.0910	24 319.73
	mean ± SD					24 275.20 ± 10.83
n	1	0.731 60	12.60	1 445.54	1.005 8	22 444.02
	2	0.725 98	11.70	1 434.44	0.998 4	22 453.11
	3	0.732 15	11.70	1 446.63	1.008 4	22 490.02
	4	0.726 00	12.60	1 434.48	0.999 4	22 475.68
	5	0.724 55	12.60	1 431.61	0.994 7	22 409.32
	6	0.713 29	12.60	1 409.36	0.979 8	22 422.96
	mean ± SD					22 449.18 ± 12.50

combustion reaction at 298.15 K and 100 kPa.

$$RE(Et_2dtc)_3(phen)(s)+\frac{173}{4}O_2(g)$$
$$=\frac{1}{2}RE_2O_3(s)+27CO_2(g)+19H_2O+6SO_2(g)+\frac{5}{2}N_2(g) \quad (\mathbf{5})$$

(RE=La, Pr, Nd, Sm)

The standard combustion enthalpies of the complexes are calculated by the following equations:

$$\Delta_c H_m^{\ominus}(\text{complex, s, 298.15 K})$$
$$= \Delta_c U(\text{complex, s, 298.15K}) + \Delta n\, RT \quad (\mathbf{6})$$
$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (\mathbf{7})$$

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. The results of the calculations are given in Table 5.

2.4　Standard Enthalpies of Formation of the Complexes

The standard enthalpies of formation of the complexes, $\Delta_f H_m^{\ominus}$ (complex, s, 298.15 K), are calculated by Hess's law according to the above thermochemical equation (**5**).]

$$\Delta_f H_m^{\ominus}(RE(Et_2dtc)_3(phen), s)$$
$$= [\frac{1}{2}\Delta_f H_m^{\ominus}(RE_2O_3, s) + 27\Delta_f H_m^{\ominus}(CO_2, g)$$
$$+ 19\Delta_f H_m^{\ominus}(H_2O, l) + 6\Delta_f H_m^{\ominus}(SO_2, g) + \frac{5}{2}\Delta_f H_m^{\ominus}(N_2, g)]$$
$$- \Delta_c H_m^{\ominus}(RE(Et_2dtc)_3(phen), s) \quad (\mathbf{8})$$

Table 5 Combustion Energies, Standard Combustion Enthalpies and Standard Enthalpies of Formation of the Complexes at 298.15 K

complexes	$\Delta_c U$ / (kJ·mol^{-1})	$\Delta_c H_m^{\ominus}$/ (kJ·mol^{-1})	$\Delta_f H_m^{\ominus}$/ (kJ·mol^{-1})
d	−17 455.98 ± 7.98	−17 475.19 ± 7.98	−1 257.78 ± 8.84
e	−17 840.67 ± 10.38	−17 859.88 ± 10.38	−888.22 ± 11.55
f	−18 674.22 ± 8.33	−18 693.43 ± 8.33	−47.03 ± 9.17
g	−17 406.90 ± 9.69	−17 426.11 ± 9.69	−1 317.99 ± 10.45

where $\Delta_f H_m^{\ominus}(La_2O_3, s)$ = (−1 793.14 ± 0.79) kJ·mol^{-1}; $\Delta_f H_m^{\ominus}(Pr_2O_3, s)$ = (−1 823.39 ± 6.69) kJ·mol^{-1}; $\Delta_f H_m^{\ominus}(Nd_2O_3, s)$ = (−1 808.12 ± 1.00) kJ·mol^{-1}; $\Delta_f H_m^{\ominus}(Sm_2O_3, s)$ = (−1 808.12 ± 1.00) kJ·mol^{-1}, $\Delta_f H_m^{\ominus}(CO_2, g)$ = (−393.51 ± 0.13) kJ·mol^{-1}, $\Delta_f H_m^{\ominus}(H_2O, l)$ = (−285.830 ± 0.042) kJ·mol^{-1}, $\Delta_f H_m^{\ominus}(SO_2, g)$ = (−296.81 ± 0.20) kJ·mol^{-1} [14,15]. The results of calculation are also listed in Table 5.

In Fig.4, $\Delta_f H_m^{\ominus}$ and $\Delta_c H_m^{\ominus}$ of the complexes are plotted against the atomic numbers of light rare earth elements.

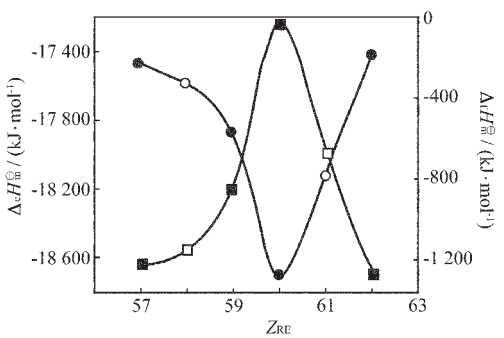


Fig.4 Plot of $\Delta_f H_m^{\ominus}$ and $\Delta_c H_m^{\ominus}$ against the atomic numbers (ZRE) of light rare earth elements for the complexes
●: $\Delta_f H_m^{\ominus}$; ■: $\Delta_c H_m^{\ominus}$; ○, □: the estimated values

Obviously, they appear as a curve relationship not a linear one, suggesting that a certain amount of covalence is present in the chemical bonding between the RE^{3+} and ligands, which is in agreement with Nephelauxetic effect of 4*f* electrons of rare earth ions. And On the basis of Fig.3, the standard enthalpies of formation of unstudied $Ce(Et_2dtc)_3(phen)$ and $Pm(Et_2dtc)_3(phen)$ could be estimated as −1 180 and −700 kJ·mol^{-1}, the standard enthalpies of combustion are as −17 590 and −18 120 kJ·mol^{-1}, respectively.

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