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THERMOCHEMICAL STUDY OF THE SOLID COMPLEX Ho(PDC)$_3$ (*o*-PHEN)

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A novel solid complex, formulated as Ho(PDC)$_3$ (*o*-phen), has been obtained from the reaction of hydrate holmium chloride, ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (*o*-phen·H$_2$O) in absolute ethanol, which was characterized by elemental analysis, TG-DTG and IR spectrum. The enthalpy change of the reaction of complex formation from a solution of the reagents, $\Delta_r H_m^\theta$(sol), and the molar heat capacity of the complex, c_m, were determined as being –19.161±0.051 kJ mol^{-1} and 79.264±1.218 J mol^{-1} K^{-1} at 298.15 K by using an RD-496 III heat conduction microcalorimeter. The enthalpy change of complex formation from the reaction of the reagents in the solid phase, $\Delta_r H_m^\theta(s)$, was calculated as being (23.981±0.339) kJ mol^{-1} on the basis of an appropriate thermochemical cycle and other auxiliary thermodynamic data. The thermodynamics of reaction of formation of the complex was investigated by the reaction in solution at the temperature range of 292.15–301.15 K. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as being –16788.46±7.74 kJ mol^{-1} by an RBC-II type rotating-bomb calorimeter at 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 –16803.95±7.74 and –1115.42±8.94 kJ mol^{-1}, respectively.

Keywords: *ammonium pyrrolidinedithiocarbamate (APDC), hydrate holmium chloride, 1,10-phenanthroline (o-phen·H$_2$O), thermochemistry*

Introduction

There has been a significant increase interest in research of the complexes containing the bond 'lanthanide-sulfur' over the past decades one part since they have potential applications in the ceramics industry and thin materials [1]. Another reason stems from the challenge that the binary complexes exhibit high sensitivity to moisture, so the syntheses of these complexes should be performed under strongly anhydrous condition [2]. In particular, the class of these complexes can be used as precursors to generate the lanthanide sulfide nanocrystallites via thermodecomposition conveniently [3–5].

As chemical and physical processes are accompanied by heat effects calorimetry represents a unique technique to gather information about thermodynamics and kinetics [6–8]. Reaction calorimetry has a wide application in thermal and kinetic analyses of chemical reactions in the context of thermal process safety and process development. Although there have been reports on these complexes [9–12], both structurally and spectroscopically, experimental data on the thermodynamic behaviors of these coordination compounds are sparse.

As an extension of our previous studies on the complexes of lanthanides with sulfur-containing ligands, it is in the present work that many efforts have been devoted to synthesize a novel complex Ho(PDC)$_3$ (*o*-phen) by the reaction of hydrous holmium chloride with ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (*o*-phen·H$_2$O) in absolute ethanol, and characterize the complex by chemical analysis, elemental analysis, IR spectrum and TG-DTG technique. The enthalpy change of the reaction in solution and the molar heat capacity of the resultant complex at 298.15 K were determined by a microcalorimeter. The enthalpy change of complex formation from the reaction of the reagents in solid phase was derived from a thermochemical cycle. The thermodynamic of the reaction in solution at different temperatures was investigated and the thermochemical 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 activation 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 an RBC-II rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^\theta$, and the standard enthalpies of formation, $\Delta_f H_m^\theta$, were calculated.

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Experimental

Materials

Reagents

$HoCl_3 \cdot 4.56H_2O$ was prepared according to reference [13], the hydration number of which was determined by EDTA titration. Ammonium pyrrolidinedithiocarbamate (abbreviated as APDC, mass fraction higher than 0.9950) and 1,10-phenanthroline (abbreviated as *o*-phen·H_2O, mass fraction higher than 0.9950) were commercially obtained from Shanghai Reagent Factory. They were maintained in desiccators over P_4O_{10} before the calorimetric measurements. Absolute ethanol and dichloromethane are of A. R. grade from Xi'an chemical reagent company. Potassium chloride (mass fraction 0.9999) was purchased from Shanghai No. 1 Reagent Factory, Shanghai, China, and dried in a vacuum oven at 500 K for 8 h prior to use. Thianthrene purchased from Tokyo Kasei Kogyo Co., Ltd is of GC grade with the purity of 99%, which was recrystallized with mass fraction better than 99.99% characterized by HPLC, and was stored in desiccator containing P_4O_{10}. The gamma aluminum oxide are of spectroscopic pure from Shanghai No. 1 Reagent Factory, which was transformed to alpha aluminum oxide in muffle oven at 1473 K prior to use and maintained in desiccator with P_4O_{10}.

The relative atomic masses used were those recommended by IUPAC Commission in 1999 [14].

Synthesis of the complex

A mixture of $HoCl_3 \cdot 4.56H_2O$, *o*-phen·H_2O and APDC in a molar relation salt/phen/APDC of 1/1/3, were dissolved independently in a minimal amount of absolute ethanol. To the mixed ethanolic solution of *o*-phen·H_2O and APDC, the ethanolic solution of salt was slowly drop-wise under electromagnetically stirring. The reaction mixture was allowed to stand for 30 min resulting in the formation of a solid which was filtered, washed with three small portions of absolute ethanol and purified with CH_2Cl_2. The resulting crystals were dried in vacuum and stored in a desiccator over P_4O_{10} ready to be used.

Equipment and methods of analyses

The contents of Ho^{3+} and Cl^{-1} were determined volumetrically with EDTA by complexometric titration and gravimetrically, respectively; C, H, N and S contents were carried out by an instrument of Vario EL III CHNOS of German. Spectra were obtained with samples in KBr matrix for the title complex and ligands. A BEQ UZNDX–550 series FT-IR spectrophotometer in the region of 400–4000 cm^{-1} was used. The TG-DTG tests were performed in a Perkin Elmer thermobalance and under dynamic atmosphere of high purity N_2 (mass fraction 0.9999) with flow rate of 60 cm^3 min^{-1} and a heating rate of 10 K 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 CuK_α radiation. An X-ray power diffractometer typed in D/max-III with CuK radiation was used. The calorimetric experiment were performed using an RD496-III type microcalorimeter and an RBC-II type rotating-bomb calorimeter [15, 16]. The purity of the compound was attested by an HP-1100 type high performance liquid chromatography analyzer, and the solvent is CH_2Cl_2, the rinsing reagent is CH_2Cl_2 and the column is contraphase carbon –18.

RD496-III heat conduction calorimeter

All the enthalpies of solutions and that of reaction were measured by an RD496-III micro-calorimeter as described before [15]. The working temperature of the calorimeter lies in the range of 77.15–473.15 K. The baseline stability was determined at a constant temperature and with a rising temperature at a stated heating rate. Keeping the temperature at 313.15 K for 50 h, the baseline change was less than ±0.2 μV. While raising the temperature from 313.15 to 73.15 K at the speed of 1 K h^{-1}, the stability is 0.4 μV K^{-1}.

The calorimetric constants at 292.15, 295.15, 298.15 and 301.15 K were determined by the Joule effect before experiment, which are 63.691±0.035, 63.799±0.042, 63.901±0.030 and 64.000±0.026 μV mW^{-1}. The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at 298.15 K. The average enthalpy of dissolution of KCl determined from the 6 tests was, $\Delta_s H^0_{m,KCl}$=17.581±0.039 kJ mol^{-1}, which is in agreement with the published value 17.584±0.007 kJ mol^{-1} [8, 17].

RBC-II rotating-bomb combustion calorimeter

The constant-volume combustion energy of the compound was measured by an RBC-type II precision rotating-bomb combustion calorimeter. The structure and principle of the calorimeter have been described in detail previously elsewhere [8, 16]. It is mainly composed of a thermostatic trough with an outer casing, a calorimetric tube and a system for the temperature measurement. The temperature of the thermostatic water in the bath was automatically maintained at 298.15±0.001 K by means of a precise thermistor. The temperature gauge from the digital indicator with integrated circuit was used to measure the temperature of the calorimetric tube. The bicyclic structure of the crucible support in the oxygen bomb was constructed so that the bomb can make a compound rotation about an axis perpendicular to the bomb axis (i.e., end-over-end rotation) and about the bomb axis (axial rotation) at the same time, which assured the complete combustion of the compound.

The temperature rise was corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correction value of the heat exchange was calculated according to [18].

The analyses of the final gas of the combustion reaction were referred to [8, 16]. The amount of $CO_2(g)$ was determined through the mass increment of the tube containing alkali asbestos after absorbing the carbon dioxide. The total amount of acid was obtained through titration with a standard solution of NaOH [8]. The identity of the final solid product was checked by the chemical analysis and XRD. The analyses of the combustion products indicated that the compound was combusted to $CO_2(g)$, $H_2O(l)$, $H_2SO_4(aq)$ and $Ho_2O_3(s)$ under the excess oxygen.

The energy equivalent of the RBC-type II calorimeter was determined from 6 combustion experiments using about 0.8 g of NIST 39i benzoic acid with a certified massic energy of combustion, $\Delta_c U=-26434\pm3$ J g^{-1}, under the same experimental conditions to be of $\varepsilon_{calor}=17775.09\pm7.43$ J K^{-1} [8].

In order to evaluate the precision and the accuracy of the measurement of the standard energy of combustion for the compound involved of sulfur element, the standard energy of combustion of thianthrene was determined by employing our rotating-bomb set, as being -33507.76 ± 14.13 J g^{-1} [19].

Results and discussion

Characterization of the complex

The elemental analyses results of the title complex are as follows: m_{found} Ho 20.95%, C 41.14%, H 3.95%, N 8.81%, S 24.49%; $m_{calculated}$: Ho 21.04%, C 41.37%, H 4.11%, N 8.93%, S 24.54%, which is identified as the formula of Ho(PDC)$_3$(*o*-phen). The complex was checked by HPLC and its purity is excellent (mass fraction 0.9999).

XRD and IR data

The main XRD data of ligands and the complex are shown in Table 1. Clearly, the main XRD data of the complex are very different from that of hydrate holmium chloride (L.C.D.D. card) and ligands, indicating that the complex is a new phase.

The preliminary identification regarding the nature of bonding of the ligands *o*-phen·H_2O and APDC to holmium ion has been obtained from the IR data. Figure 1 shows the IR spectra of hydrate holmium chloride, ligands and the complex. The IR spectra reveal that both ligands *o*-phen·H_2O and APDC are coordinated to the holmium ion [20, 21]. Comparing with the spectra of hydrate holmium chloride (a) and *o*-phen·H_2O (b), the characteristic absorption band attributed to the stretching vibration of the hydroxyl group of water molecules, is observed at 3390 and 3388 cm^{-1}, respectively. The band is not observed in the complex spectrum. The IR spectrum of Ho(PDC)$_3$ (*o*-phen) showed the absorption bands at 1625, 1590, 1573 and 1517 cm^{-1}, which are attributed to the skeleton vibration of the benzene ring when compared with that of free *o*-phen. Absorption bands at 843 and 727 cm^{-1} are attributed to the bend vibration of C–H group in the complex. These vibrations are found to be shifted to higher frequencies in the complex relative to free *o*-phen, suggesting that the two coordination of two nitrogen atoms of *o*-phen to Ho^{3+}. In contrast with the absorption band found at 1417 cm^{-1} in

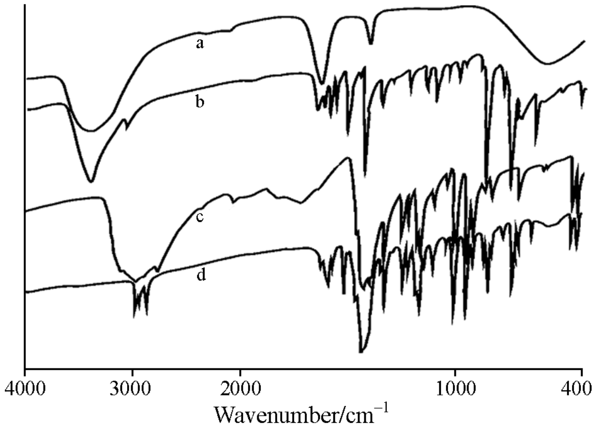
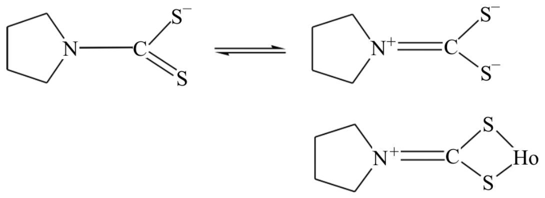


Fig. 1 Comparison of IR spectra of a – $HoCl_3\cdot4.56H_2O$, b – *o*-phen·H_2O, c – APDC and d – Ho(PDC)$_3$ (*o*-phen)

Table 1 Main XRD data of the title complex Ho(PDC)$_3$(*o*-phen), ligands *o*-phen·H_2O and ammonium pyrrolidinedithiocarbamate (APDC)

Compound		Main X-ray powder diffraction data							
APDC	I/I_0	40	100	12	26	62	10	20	13
	d/nm	0.1099	0.5507	0.4736	0.4107	0.3675	0.2877	0.2641	0.2206
o-phen·H_2O	I/I_0	46	26	54	99	72	34	25	33
	d/nm	0.8909	0.6189	0.5169	0.4454	0.3959	0.3847	0.3149	0.2817
Ho(PDC)$_3$(*o*-phen)	I/I_0	57	49	99	56	42	76	61	68
	d/nm	9.839	8.631	7.922	6.702	5.719	4.892	4.211	3.900

the ligand APDC (c), due to the stretching vibration of the group CN (ν_{CN}) shifts to higher frequencies (1425 cm^{-1}), featuring a double bond character of the CN bond. The $C_4H_8NCSS^-$ ion may be represented by resonance hybrid of the structures [10, 22]:



The second structure is favored when the two sulfur atoms of ligand coordinate to Ho^{3+} to form a four-number ring, accordingly ν_{CN} moves to a higher frequency. Additionally, corresponding to the peak of 938 cm^{-1} ascribable to the characteristic absorption of $-CSS^{2-}$ in the ligand of APDC, it spites into two peaks of 1011 and 949 cm^{-1} in the complex. Obviously, the resulting four-number ring increases the vibration intensity of ν_{CN} [21]. The changes of ν_{CN} and ν_{CSS} indicate that the two sulfur atoms of $C_4H_8NCSS^-$ coordinate to Ho^{3+} in a bidentate ligand manner.

Thermostability of $Ho(PDC)_3$ (*o*-phen)

TG-DTG curve of the complex is presented in Fig. 2. The complex is decomposed into the final compounds in one step, which begin at 303.15 and complete 745.15 K, accompanying with the mass loss of 69.60%. In order to explore the decomposition process of the title complex, the final compounds determined by XRD are of the mixture of Ho_2S_3 and deposited carbon in which Ho_2S_3 predominates [23]. Based on the above analyses, the decomposition process is postulated as Eq. (1), where 228°C is the peak value in DTG curve and 30.24% is the calculated value of the mass residual. Clearly, the experimental result is in good agreement with the calculated result.

$$Ho[(C_5H_8NS_2)_3(C_{12}H_8N_2)] \xrightarrow{30°\,C\sim228°\,C\sim472°\,C;\ 30.40\%\ (30.24\%)} 1/2Ho_2S_3+2C \qquad (1)$$

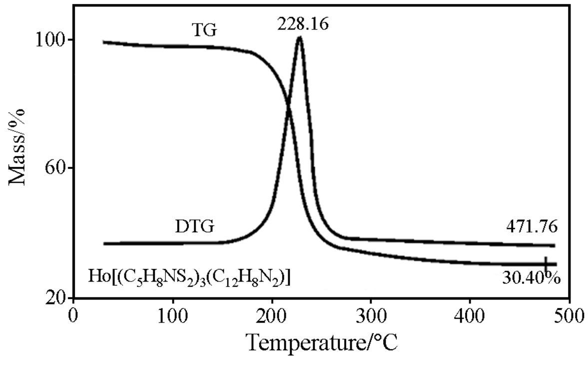


Fig. 2 TG -DTG curve of $Ho(PDC)_3$ (*o*-phen)

Calculation of the standard molar enthalpy change for the reaction in the solid-state

The molar enthalpy of solution $\Delta_{sol}H_m^{\theta}$(1), $\Delta_{sol}H_m^{\theta}$(2) and $\Delta_{sol}H_m^{\theta}$(3) of $HoCl_3\cdot4.56H_2O$, APDC and *o*-phen·H_2O in absolute ethanol at 298.15 K are given in Table 2, respectively. The mixed enthalpy of the mixture of the two ethanolic solutions of the ligands $\Delta_{mix}H_m^{\theta}$ and the enthalpy change for the reaction in solution $\Delta_rH_m^{\theta}$(sol) are listed in Table 3. The enthalpy of dissolution, $\Delta_{sol}H_m^{\theta}$(4)of water in ethanol is so small that it can be regarded as zero.

The application Hess' law to the series of equations shown in Table 4 gives a thermochemical cycle, from which the enthalpy change of the reaction in the solid-state is derived as being 23.981±0.339 kJ mol^{-1} according to Eq. (2), where the uncertainty is given as the standard deviation of the mean.

$$\begin{gathered}\Delta_rH_m^{\theta}(s)=\Delta_{sol}H_m^{\theta}(1)+3\Delta_{sol}H_m^{\theta}(2)+\Delta_{sol}H_m^{\theta}(3)\\+\Delta_{mix}H_m^{\theta}+\Delta_rH_m^{\theta}(l)-\Delta_{sol}H_m^{\theta}(4)=\\ [(-47.034\pm0.178)+3(19.538\pm0.090)\\+(20.970\pm0.071)+(10.592\pm0.049)\\+(-19.161\pm0.051)-0]\ kJ\ mol^{-1}=\\(23.981\pm0.339)\ kJ\ mol^{-1}\end{gathered} \qquad (2)$$

Some efforts have been devoted to test the reasonability of the thermochemistry cycle. The crude products from liquid-phase reaction were collected and separated by centrifugal effect. The solid crude products was purified and identified as being the same product as that obtained in the direct synthesis. The concentration of Ho^{3+} retained in the centrifugal liquid was determined as $6\cdot10^{-3}$ μg mL^{-1} by the ICP-AES experiment, indicating that the starting reactants have been transformed fully to the title products, that is, the liquid-phase reaction proceeds in 100%. All of these show that the final thermodynamic states of the title solid-phase reaction and is the same with that of liquid-phase reaction, and the designed thermochemistry cycle is correct.

Calculation of the thermodynamic parameters for the reaction in the liquid-state

The calorimetric experiment showed that this reaction is an exothermic one. Based on thermokinetic data of the reaction in solution at different temperatures as shown in Table 5, and the thermodynamic equations [6], the thermodynamic parameters and kinetic parameters of the reaction in solution are obtained and shown in Table 6.

Molar heat capacity of $Ho(PDC)_3$ (*o*-phen)

To gain the value of molar heat capacity of the solid compound, the empty cell (system I), the cell containing sample with unknown specific heat *c* (system II), the

Table 2 Enthalpies of solution of $HoCl_3·4.56H_2O$, ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (o-phen·H_2O) in absolute ethanol at 298.15 K

No.	m/ mg	Q/ mJ	$\Delta_{sol}H^{\theta}_{m}(1)$/ kJ mol^{-1}	m/ mg	Q/ mJ	$\Delta_{sol}H^{\theta}_{m}(2)$/ kJ mol^{-1}	m/ mg	Q/ mJ	$\Delta_{sol}H^{\theta}_{m}(3)$/ kJ mol^{-1}
1	80.61	–11333.968	–47.213	26.29	3099.238	19.368	31.71	3351.540	20.950
2	80.60	–11222.976	–46.756	26.25	3121.801	19.539	31.77	3393.602	21.173
3	80.59	–11390.995	–47.461	26.27	3171.104	19.832	31.76	3343.271	20.866
4	80.60	–11161.595	–46.500	26.24	3082.010	19.297	31.73	3356.008	20.965
5	80.61	–11389.102	–47.448	26.33	3157.941	19.705	31.68	3315.208	20.746
6	80.56	–10234.888	–46.827	26.28	3117.297	19.488	31.73	3379.615	21.123
$(\bar{x}\pm\sigma_a)^a$			–47.034±0.178			19.538±0.090			20.970±0.071

$\Delta_{sol}H^{\theta}_{m}(1)$ represents the enthalpy of solution of $HoCl_3·4.56H_2O$ in absolute ethanol; $\Delta_{sol}H^{\theta}_{m}(2)$ represents the enthalpy of solution of APDC in absolute ethanol; $\Delta_{sol}H^{\theta}_{m}(3)$ represents the enthalpy of solution of o-phen·H_2O in absolute ethanol; $^a\sigma_a=\sqrt{\sum_{i=1}^{6}(x_i-\bar{x})^2/n(n-1)}$ where n is the experimental number; x_i, a simple value in a set of measurements; $\bar{x}$, the mean value of a set of measurement results.

Table 3 The mixed enthalpy of the ethanolic solution of APDC and o-phen·H_2O, and the enthalpy change of the reaction in liquid-state $\Delta_rH^{\theta}_{m}$(sol) $(HoCl_3·4.56H_2O)·xC_2H_5OH(l)$+[3APDC·$yC_2H_5OH(l)$+[($o$-phen·$H_2O$)·$zC_2H_5OH(l)$]= Ho(PDC)$_3$($o$-phen)($s$)+3$NH_4Cl(s)$+5.56$H_2O·(x+3y+z)C_2H_5OH(l)$, at 298.15 K

No.	Q_1/mJ	$\Delta_{mix}H^{\theta}_{m}$/kJ mol^{-1}	Q_2/mJ	$\Delta_rH^{\theta}_{m}$/kJ mol^{-1}
1	84.809	10.601	–153.693	–19.212
2	86.293	10.787	–153.012	–19.127
3	84.231	10.529	–154.456	–19.307
4	86.064	10.508	–152.574	–19.072
5	83.987	10.498	–152.032	–19.004
6	85.006	10.626	–153.965	–19.246
$(\bar{x}\pm\sigma_a)^a$	85.065±0.421	10.592±0.049	–153.289±0.407	–19.161±0.051

$\Delta_{mix}H^{\theta}_{m}$ is the mixed enthalpy of the ethanolic solution of APDC and o-phen·H_2O; and $\Delta_rH^{\theta}_{m}(l)$ is the enthalpy change of the liquid-phase reaction $(HoC_3·4.56H_2O)·xC_2H_5OH(l)$+3APDC·$yC_2H_5OH(l)$+[($o$-phen·$H_2O$)·$zC_2H_5OH(l)$]= Ho(PDC)$_3$($o$-phen)($s$)+3$NH_4Cl(s)$+5.56$H_2O·(x+3y+z)C_2H_5OH(l)$; $^a\sigma_a=\sqrt{\sum_{i=1}^{6}(x_i-\bar{x})^2/n(n-1)}$ where n is the experimental number; x_i, a simple value in a set of measurements; $\bar{x}$, the mean value of a set of measurement results.

Table 4 Thermochemical cycle and results for ΔH^{θ}_{m}

	Reaction	ΔH^{θ}_{m}/kJ mol^{-1}
1	$HoCl_3·4.56H_2O(s)+xC_2H_5OH(l)=(HoCl_3·4.56H_2O)·xC_2H_5OH(l)$	–47.034±0.178
2	3APDC(s)+$yC_2H_5OH(l)$=3(APDC·yC_2H_5OH)(l)	19.538±0.090
3	o-phen·$H_2O(s)$+$zC_2H_5OH(l)$=(o-phen·H_2O)·$zC_2H_5OH(l)$	20.970±0.071
4	[3APDC·$yC_2H_5OH(l)$]+[(o-phen·H_2O)·$zC_2H_5OH(l)$]=(3APDC)(o-phen·H_2O)·$(y+z)(C_2H_5OH)(l)$	10.592±0.049
5	[$(HoCl_3·4.56H_2O)·xC_2H_5OH(l)$+3APDC·$yC_2H_5OH(l)$+[($o$-phen·$H_2O$)·$zC_2H_5OH(l)$]= Ho(PDC)$_3$($o$-phen)($s$)+3$NH_4Cl(s)$+5.56$H_2O·(x+3y+z)C_2H_5OH(l)$	–19.161±0.051
6	5.56$H_2O+(x+3y+z)C_2H_5OH(l)$=5.56$H_2O·(x+3y+z)C_2H_5OH(l)$	0
7	$HoCl_3·4.56H_2O(s)$+3APDC(s)+o-phen·$H_2O(s)$=Ho(PDC)$_3$(o-phen)(s)+3$NH_4Cl(s)$+5.56H_2O	23.981±0.339

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 I) are 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 Eqs (3)–(6).

Table 5 Thermokinetic data of liquid-phase of formation reaction $(HoCl_3\cdot 4.56H_2O)\cdot xC_2H_5OH(l)+[3APDC\cdot yC_2H_5OH(l)]+[(o\text{-phen}\cdot H_2O)\cdot zC_2H_5OH(l)]=Ho(PDC)_3(o\text{-phen})(s)+3NH_4Cl(s)+5.56H_2O\cdot(x+3y+z)C_2H_5OH(l)$

t/s	292.15 K		t/s	295.15 K		t/s	298.15 K		t/s	301.15 K	
	H_i/H_0	dH_i/dt/ 10^{-4} J s^{-1}		H_i/H_0	dH_i/dt/ 10^{-4} J s^{-1}		H_i/H_0	dH_i/dt/ 10^{-4} J s^{-1}		H_i/H_0	dH_i/dt/ 10^{-4} J s^{-1}
200	0.5821	5.4168	120	0.3328	7.0221	85	0.2631	6.4788	145	0.5972	3.0469
205	0.5948	5.3226	125	0.3494	6.9123	90	0.2820	6.3849	150	0.6157	2.9688
210	0.6074	5.2127	130	0.3657	6.8183	95	0.3007	6.2753	155	0.6338	2.8750
215	0.6197	5.1185	135	0.3819	6.7086	100	0.3191	6.1814	160	0.6514	2.7969
220	0.6318	5.0243	140	0.3978	6.5832	105	0.3373	6.0562	165	0.6686	2.7188
225	0.6437	4.9301	145	0.4134	6.5048	110	0.3551	5.9780	170	0.6852	2.6250
230	0.6553	4.8201	150	0.4288	6.3951	115	0.3726	5.8841	175	0.7014	2.5469
235	0.6667	4.7259	155	0.4439	6.2854	120	0.3898	5.7902	180	0.7170	2.4688
240	0.6779	4.6317	160	0.4588	6.1913	125	0.4067	5.6963	185	0.7323	2.3906
245	0.6888	4.5375	165	0.4734	6.0816	130	0.4233	5.6024	190	0.7470	2.3125

H_0=0.2683 J (292.15 K), 0.2164 J (295.15 K), 0.1537 J (298.15 K) and 0.0846 J (301.15 K); t – time

Table 6 Kinetic, thermodynamic parameters of liquid-phase reaction $(HoCl_3\cdot 4.56H_2O)\cdot xC_2H_5OH(l)+[3APDC\cdot yC_2H_5OH(l)]+[(o\text{-phen}\cdot H_2O)\cdot zC_2H_5OH(l)]=Ho(PDC)_3\ (o\text{-phen})(s)+3NH_4Cl(s)+5.56H_2O\cdot(x+3y+z)C_2H_5OH(l)$

Temperature/ K	$k\cdot 10^3$/ s^{-1}	n	r	E/ kJ mol^{-1}	ln$A$	r	$\Delta G^{\theta}_{\neq}$/ kJ mol^{-1}	$\Delta H^{\theta}_{\neq}$/ kJ mol^{-1}	$\Delta S^{\theta}_{\neq}$/ J mol^{-1} K^{-1}	r
292.15	3.4156	0.6023	0.9998	48.32	5.677	0.9996	85.30	45.8525	–135.0436	0.9995
295.15	4.1469	0.6056	0.9994				85.72			
298.15	5.0498	0.5936	0.9991				86.13			
301.15	6.1926	0.5957	0.9998				86.51			

r – linear correlation coefficient

For system I $\quad q_0=a\theta \quad$ (3)

For system II $\quad q=(a+mc)\theta \quad$ (4)

For system III $\quad q_1=(a+m_1c_1)\theta \quad$ (5)

For system IV $\quad q_2=(a+m_2c_2)\theta \quad$ (6)

where a (in J K^{-1}) is the apparent heat capacity of the empty cell, θ (in K) is the equilibrium temperature for a given Peltier current, m (in g), m_1 (in g) and m_2 (in g) are masses of the investigated sample, the first standard substance and second standard substance, respectively; c (in J mol^{-1} K^{-1}), c_1(in J mol^{-1} K^{-1}) and c_2 (in J mol^{-1} K^{-1}) are molar heat capacity of the investigated sample, the first standard substance and second standard substance, respectively; q_0 (in J), q (in J), q_1 (in J) and q_2 (in J) are the quantities of heat retained by the systems I–IV when they were heated up by a given Peltier current.

Combination of the Eqs (3)–(6), Eq. (7) is obtained.

$$c=[(q-q_0)/2m][m_1c_1/(q_1-q_0)+m_2c_2/(q_2-q_0)] \quad (7)$$

The value of c of the investigated sample can be obtained from Eq. (7) if the values of c_1 and c_2 of two standard substances are known.

Molar heat capacity of the complex was determined by an RD496-III type microcalorimeter when changing the samples in the sample cell. The values of q are obtained by the testing method presented as a curve in Fig. 3. 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 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. (7). The results of the experiments are shown in Table 7.

Combustion energy of $Ho(PDC)_3$ (o-phen)

The determination method of combustion energy for the complex was the same as for the calibration of the calorimeter with benzoic acid. The combustion energies of the samples were calculated in accord with [18]. The results of the calculations are given in Table 8.

Standard combustion enthalpy of $Ho(PDC)_3$ (o-phen)

The standard combustion enthalpy of the complex, $\Delta_cH^{\theta}_m$ (complex, s, 298.15 K), refers to the combus-

Table 7 Experimental data used for calculating the molar heat capacity of Ho(PDC)$_3$(*o*-phen), c_m, at 298.15 K

Experimental data	Empty cell	Benzoic acid	α-Al_2O_3	Ho(PDC)$_3$ (*o*-phen)
q/mJ	4453.908 4444.543 4432.133 4447.035 4438.165 4450.647	6088.611 6080.422 6094.207 6098.640 6075.115 6073.035	4959.916 4962.776 4977.771 4984.568 4967.144 4983.760	5008.360 4973.729 4998.337 4994.254 4985.635 4980.327
$(\bar{x}\pm\sigma_a)^a$	4444.405±3.610	6085.005±4.672	4972.656±4.824	4990.107±5.664
precision $(\sigma_a/\bar{x})$	$1.816\cdot10^{-3}$	$1.717\cdot10^{-3}$	$2.169\cdot10^{-3}$	$2.538\cdot10^{-3}$
m/g		4.51478	2.68416	2.75901
c/J mol^{-1} K^{-1}		78.707±2.927	145.923±0.562	79.264±1.218
c_0 of lit./J mol^{-1} K^{-1}		79.03 [24]	145.327 [25]	
accuracy $(c_0-c)/c_0$		$4\cdot10^{-3}$	$4\cdot10^{-3}$	

$^a\sigma_a=\sqrt{\sum_{i=1}^{6}(x_i-\bar{x})^2/n(n-1)}$ where n is the experimental number; x_i, a simple value in a set of measurements; $\bar{x}$, the mean value of a set of measurement results

Table 8 Experimental results for the combustion energy of the complex Ho(PDC)$_3$ (*o*-phen)

Compound	No.	m/g	Q_c/J	Q_N/J	ΔT/K	$-\Delta_cU$/J g^{-1}
Ho(PDC)$_3$(*o*-phen)	1	0.72532	9.90	1484.57	0.9574	21402.14
	2	0.72527	10.80	1484.41	0.9585	21429.56
	3	0.72130	12.60	1476.26	0.9514	21381.34
	4	0.71056	12.60	1474.75	0.9521	21422.66
	5	0.72455	12.60	1482.91	0.9569	21411.18
	6	0.71690	12.60	1467.26	0.9484	21450.74
	$(\bar{x}\pm\sigma_a)^a$					21416.10±9.87

$^a\sigma_a=\sqrt{\sum_{i=1}^{6}(x_i-\bar{x})^2/n(n-1)}$ where n is the experimental number; x_i, a simple value in a set of measurements; $\bar{x}$, the mean value of a set of measurement results; m – mass of complexes, Q_c – calibrated heat of combustion wire, Q_N – calibrated heat of acid, $-\Delta_cU$ – combustion energy of complex

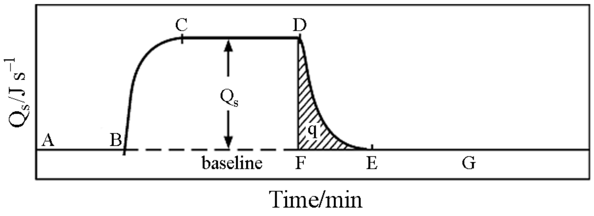


Fig. 3 Curve of measurement of the molar heat capacity of the complex Ho(PDC)$_3$ (*o*-phen)

tion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.

$$\text{Ho(PDC)}_3\ (o\text{-phen})(s)+167/4O_2(g)=1/2Ho_2O_3(s)+27CO_2(g)+16H_2O(l)+6SO_2(g)+5/2N_2(g) \quad (8)$$

The standard combustion enthalpy of the complex calculated by Eqs (9) and (10).

$$\Delta_cH_m^\theta\ (\text{complex}, s, 298.15\ \text{K})=\Delta_cU\ (\text{complex}, s, 298.15\ \text{K})+\Delta nRT \quad (9)$$

$$\Delta n=n_g(\text{products})-n_g(\text{reactants}) \quad (10)$$

where n_g is the total amount in moles of gases present as products or as reactants, R=8.314 J K^{-1} mol^{-1}, T=298.15 K. The standard combustion enthalpy of the complex is of –16803.95±7.74 kJ mol^{-1}.

Standard enthalpy of formation of Ho(PDC)$_3$ (*o*-phen)

The standard enthalpy of formation of the complex, $\Delta_fH_m^\theta$ (complex (s), 298.15 K), is calculated by Hess's law according to the thermochemical equation above.

$$\Delta_fH_m^\theta[\text{Ho(PDC)}_3\ (o\text{-phen})(s)]=[1/2\Delta_fH_m^\theta(Ho_2O_3(s))+27\Delta_fH_m^\theta(CO_2(g))+16\Delta_fH_m^\theta(H_2O(l))+6\Delta_fH_m^\theta(SO_2(g))+5/2\Delta_fH_m^\theta(N_2(g))]-\Delta_cH_m^\theta[\text{Ho(PDC)}_3\ (o\text{-phen})(s)] \quad (11)$$

where $\Delta_f H_m^\theta$ (Ho_2O_3(cr), 298.15 K)=–1883.3 ±8.2 kJ mol^{-1} [24]; $\Delta_f H_m^\theta$ ($CO_2(g)$)=–393.51 ±0.13 kJ mol^{-1}, $\Delta_f H_m^\theta$ ($H_2O(l)$)=–285.830 ±0.042 kJ mol^{-1}, $\Delta_f H_m^\theta$ ($SO_2(g)$)=–296.81 ±0.20 kJ mol^{-1} [26–29]. Its standard enthalpy of formation, $\Delta_f H_m^\theta$, is calculated to be –1115.42±8.94 kJ mol^{-1}.

Conclusions

The ternary complex formulated as $Ho(PDC)_3$ (*o*-phen) has been synthesized in absolute ethanol by $HoCl_3 \cdot 4.56H_2O$ reacting with the mixed ligands of APDC and *o*-phen. The calorimetrical investigation at 298.15 K reflects that the reaction in the liquid-state occurs smoothly while the solid reaction does not.

The molar heat capacity of the complex, c_m, was determined as being 79.264±1.218 J mol^{-1} K^{-1} at 298.15 K by using an RD496-III heat conduction microcalorimeter. Through a designed thermochemical cycle, the standard molar enthalpy of reaction for the title solid-phase reaction was derived as being 23.981±0.339 kJ mol^{-1} at 298.15 K.

Based on thermokinetic data of liquid-phase reaction at different temperatures, the thermodynamic parameters and kinetic parameters of the reaction in the liquid-state are obtained. The apparent activation energy of the reaction is higher than the activation energy 63 kJ mol^{-1} at which the reaction occurs instantaneously at room temperature, showing that the title reaction proceeds feasibly in ethanol solution.

TG-DTG investigations indicate that the title complex is decomposed into Ho_2S_3 and deposited carbon in one step, which provide a probe for the preparation of rare earth chalcogenide sulfide.

The standard enthalpy of formation of the title complex was determined as being –1115.42±8.94 kJ mol^{-1}, showing that the complex is of quite thermal stability.

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