

THERMOCHEMISTRY OF EUROPIUM AND DITHIOCARBAMATE COMPLEX $\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$

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A solid complex $\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$ has been obtained from reaction of hydrous europium chloride with ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (*o*-phen·H₂O) in absolute ethanol. IR spectrum of the complex indicated that Eu³⁺ in the complex coordinated with sulfur atoms from the APDC and nitrogen atoms from the *o*-phen. TG-DTG investigation provided the evidence that the title complex was decomposed into EuS.

The enthalpy change of the reaction of formation of the complex in ethanol, $\Delta_r H_m^0(l)$, as $-22.214 \pm 0.081 \text{ kJ mol}^{-1}$, and the molar heat capacity of the complex, c_m , as $61.676 \pm 0.651 \text{ J mol}^{-1} \text{ K}^{-1}$, at 298.15 K were determined by an RD-496 III type microcalorimeter. The enthalpy change of the reaction of formation of the complex in solid, $\Delta_r H_m^0(s)$, was calculated as $54.527 \pm 0.314 \text{ kJ mol}^{-1}$ through a thermochemistry cycle. Based on the thermodynamics and kinetics on the reaction of formation of the complex in ethanol at different temperatures, fundamental parameters, including the activation enthalpy ($\Delta_r H_a^0$), the activation entropy ($\Delta_r S_a^0$), the activation free energy ($\Delta_r G_a^0$), the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A) and the reaction order (n), were obtained. The constant-volume combustion energy of the complex, $\Delta_c U$, was determined as $-16937.88 \pm 9.79 \text{ kJ mol}^{-1}$ by an RBC-II type rotating-bomb calorimeter at 298.15 K. Its standard enthalpy of combustion, $\Delta_c H_m^0$, and standard enthalpy of formation, $\Delta_f H_m^0$, were calculated to be -16953.37 ± 9.79 and $-1708.23 \pm 10.69 \text{ kJ mol}^{-1}$, respectively.

Keywords: ammonium pyrrolidinedithiocarbamate (APDC), hydrous europium chloride, 1,10-phenanthroline (*o*-phen·H₂O), thermochemistry

Introduction

Dithiocarbamate and xanthate lanthanide complexes have been widely used for ceramics and thin materials [1]. Owing to the volatility at the low temperatures, these complexes hold promise as precursor for the preparation of lanthanide chalcogenides [2–4]. Previously, the preparations for the duality complexes were usually performed using anhydrous salts in dry inert gas because the complexes exhibited sensitive to moisture [5]. When π donor like 2,2'-bipyridyl or 1,10-phenanthroline (abbreviated as *o*-phen) as ancillary ligand was incorporated, the ternary complexes were readily synthesized [6]. The series of complexes of general formula $\text{Ln}(\text{Et}_2\text{dtc})_3\text{L}$ [$L=2,2'$ -bipyridine (abbreviated as bipy) or *o*-phen] have been synthesized [7, 8]. Two structures $\text{Eu}(\text{Et}_2\text{dtc})_3(\text{phen})$ and $\text{Er}(\text{Et}_2\text{dtc})_3(\text{bipy})$ were reported [9, 10].

We are interested in determining 'thermal effects' in the process of the preparations for dithiocarbamate and lanthanide [11, 12], which would help further understanding of these complexes and provide a numeric basis for the computer-aided molecular designs of drugs and new materials. In the present study, a novel complex $\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$ has been

synthesized by reaction of hydrous europium chloride with ammonium pyrrolidinedithiocarbamate (abbreviated as APDC) and *o*-phen·H₂O in absolute ethanol, and characterized by chemical analysis, elemental analysis, IR and TG-DTG. The enthalpy change of liquid-phase reaction of formation and specific heat capacity of the complex were determined by microcalorimetry. 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.

Experimental

Materials

Reagents

$\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}$ was prepared according to [13]. Ammonium pyrrolidinedithiocarbamate (abbreviated as APDC, mass fraction higher than 0.9950) and *o*-phen·H₂O (mass fraction higher than 0.9950) were commercially obtained from Shanghai Regent Fac-

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tory. They were maintained in desiccators over P_4O_{10} before the calorimetric measurements. Absolute ethanol and dichloromethane were of A. R. grade from Xi'an chemical reagent company. Potassium chloride (mass fraction 0.9999) 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 with a purity of 0.99999 (mass fraction) in this work was commercially obtained from Chengdu chemical reagent company. Before the experiment the benzoic acid is sublimated for three times and kept in vacuum over P_4O_{10} to dryness. Thianthrene purchased from Tokyo Kasei Kogyo Co. Ltd. was of GC grade with the purity of 99%, which was recrystallized three times with the purity better than 99.99% characterized by HPLC, and was stored in desiccator containing P_4O_{10} prior to use. The gamma aluminum oxide were of spectroscopically pure from Shanghai No. 1 Regent Factory, which was transformed to alpha aluminum oxide in muffle at 1473 K for 8 h prior to use and kept in desiccator with P_4O_{10} .

Synthesis of the complex

$EuCl_3 \cdot 3.46H_2O$, *o*-phen- H_2O and APDC in a molar relation salt/phen/APDC of 1/1/3, were dissolved independently in the least quantity 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.

Methods

Analytical methods and equipments

Eu^{3+} was determined with EDTA by complexometry. C, H, N and S analyses were carried out by an instrument of Vario EL III CHNOS of German.

The TG-DTG experiments for the title compound were conducted on a P. E. 2100 Company thermal analyzer in a 60 mL min^{-1} N_2 atmosphere (mass fraction 0.99999), the heating rate of TG-DTG was $10^\circ\text{C min}^{-1}$ and the mass of the sample about 1 mg. The IR analysis was conducted on a BEQ, UZNDX-550 spectrometer (KBr discs). 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 [14, 15]. 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 high performance liquid chromatography analyzer, and the solvent was CH_2Cl_2 , the rinsing reagent was CH_2Cl_2 and the column was contra-phase carbon-18.

Calorimetric methods

All the enthalpies of solutions and enthalpies of reaction of the complex were measured by an RD496-III type microcalorimeter. The design, assemble and test of the microcalorimeter were published in [14]. 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 $64.000 \pm 0.026 \mu\text{V mW}^{-1}$. The enthalpy of solution of KCl in deionized water was measured to be $17.581 \pm 0.039 \text{ kJ mol}^{-1}$ [16].

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 [15].

The calorimeter was calibrated with benzoic acid [11, 15]. In addition, the standard energy of combustion for the reference compound thianthrene was determined as $-33507.76 \pm 14.13 \text{ J g}^{-1}$ [17, 18].

The analytical methods for final combustion products (gas, liquid and solid) were the same as those in [15]. In order to determine the amount of SO_2 formed in the combustion products, the final bomb solution was treated with $0.001 \text{ mol dm}^{-3}$ $BaCl_2$. The mass of the precipitate $BaSO_4$ was weighted and listed in Table 1. The amount of CO_2 during the combustion reaction was determined through the mass increase in the tube filled with alkali asbestos after absorbing CO_2 , which is also presented in Table 1. The analytical results of the final products showed that the combustion reactions were completed.

Results and discussion

Composition and XRD analysis of the complex

The elementary analyses result of the title complex are as follows: *w* (Calc.): Eu 19.71%, C 42.06%, H 4.18%, N 9.08%, S 24.96%; *w* (Found): Eu 19.97%, C 41.98%, H 3.99%, N 8.99%, S 25.01%, which is identified as the formula of $Eu(C_5H_8NS_2)_3(C_{12}H_8N_2)$. The purity of the complex was checked up to 0.9999 (mass fraction) by HPLC. XRD patterns of ligands and the complex are shown in Fig. 1. Clearly, the complex is a new phase.

Table 1 Experimental results for the combustion energy of the complex

Complex	No. of experiments	Mass of complexes m/g	Calibrated heat of combustion wire Q_c/J	Calibrated heat of acid Q_N/J	Calibrated $\Delta T/K$	Mass of CO ₂ formed in the combustion reaction m/g	Mass of BaSO ₄ m/g	Combustion energy of complex/J g ⁻¹
Eu(PDC) ₃ (<i>o</i> -phen)	1	0.72130	12.60	1488.89	0.9778	1.10189(1.11175) ^a	1.30240(1.31020) ^b	22014.41
	2	0.72527	10.80	1497.04	0.9795	1.10764(1.11787)	1.30891(1.31741)	21926.81
	3	0.72158	11.70	1489.37	0.9763	1.10283(1.11218)	1.30191(1.31071)	21969.50
	4	0.71065	12.60	1466.81	0.9625	1.08556(1.09534)	1.28226(1.29085)	21992.70
	5	0.71893	12.60	1483.90	0.9719	1.09820(1.10810)	1.29831(1.30589)	21948.05
	6	0.72001	12.60	1486.13	0.9742	1.09954(1.10977)	1.29955(1.30785)	21968.85
								21970.05±12.70

$${}^a\sigma_a = \sqrt{\frac{\sum_{i=1}^6 (x_i - \bar{x})^2}{n(n-1)}}$$

^a σ_a is the experimental number; x_i , a simple value in a set of dissolution measurements; \bar{x} , the mean value of a set of measurement results,

^bThe values in brackets are the calculated amount of CO₂ when all carbon atoms in the complex are transformed to CO₂

^cThe values in brackets are the calculated amount of BaSO₄ when all sulfur atoms are transformed to SO₄²⁻

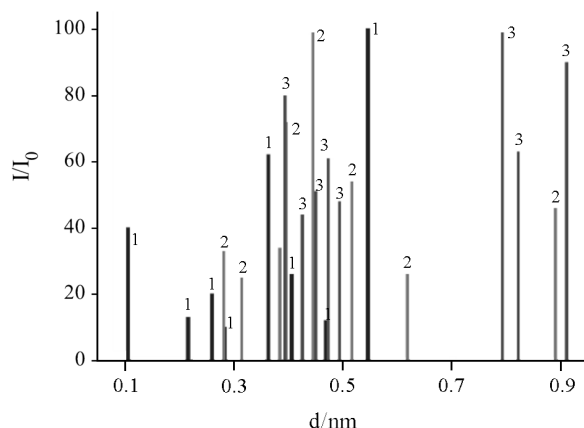


Fig. 1 XRD patterns of 1 – APDC, 2 – *o*-phen and 3 – the complex $\text{Eu}(\text{PDC})_3(\textit{o}\text{-phen})$

IR spectrum of the complex

Comparison of IR spectra of salt, ligands and the complex is depicted in Fig. 2. Compared with the spectra of salt and *o*-phen- H_2O ($3390, 3388 \text{ cm}^{-1}$), the characteristic absorption of hydroxyl group is not present in the complex, showing that the complex do not consist of water. The peaks of $1624, 1589, 1573,$ and 1516 cm^{-1} are assigned to the skeleton vibration of benzene ring and the peaks of 844 and 727 cm^{-1} are assigned to the bend vibration of C–H in the complex, which display certain shifts in contrast with those of $1617, 1587, 1561, 1504 \text{ cm}^{-1}$ and $854, 739 \text{ cm}^{-1}$ in the ligand. It is thus assumed that two nitrogen atoms in the ligand of *o*-phen- H_2O coordinate to Eu^{3+} . Contrasting with that of 1417 cm^{-1} in the ligand of APDC, ν_{CN} of the complex shifts to higher wave number 1424 cm^{-1} , which can be attributed to the two sulfur atoms from NCS_2^- group coordinated to Eu^{3+} [19]. On the other hand, the peak of 938 cm^{-1} ascribable to the characteristic absorption of –CS in the ligand of

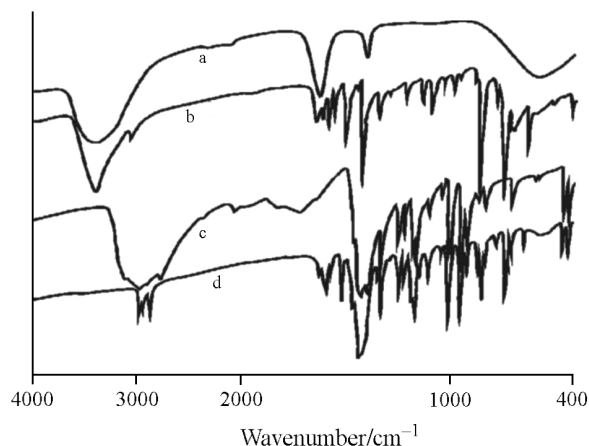


Fig. 2 IR spectra of a – hydrous europium chloride, b – *o*-phen- H_2O , c – APDC and d – the complex $\text{Eu}(\text{PDC})_3(\textit{o}\text{-phen})$

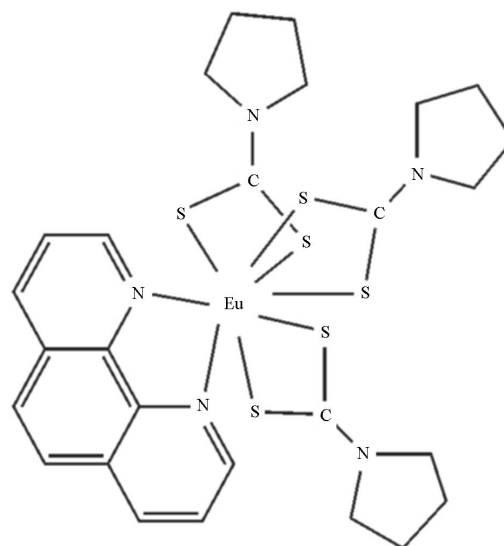


Fig. 3 Presumed structure of the complex $\text{Eu}(\text{PDC})_3(\textit{o}\text{-phen})$

APDC, is splitted into two peaks of 1009 and 948 cm^{-1} in the complex, which is an indication of the two sulfur atoms from NCS_2^- group coordination with Eu^{3+} [20]. Consulting [21], the structure of the title complex is presumed as Fig. 3.

TG-DTG of the complex

TG-DTG curve of the complex is presented in Fig. 4. The complex is decomposed into EuS in one step, which begin at 30 and complete 463°C , with the mass loss of 70.20% . The final residual are determined as EuS by XRD [22, 23].

Calculation of the enthalpy change of formation of the reaction of formation of the complex in solid

The molar enthalpies of solution $\Delta_{\text{sol}} H_m^0(1)$, $\Delta_{\text{sol}} H_m^0(2)$ and $\Delta_{\text{sol}} H_m^0(3)$ of $\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}$, APDC and *o*-phen- H_2O in absolute alcohol at

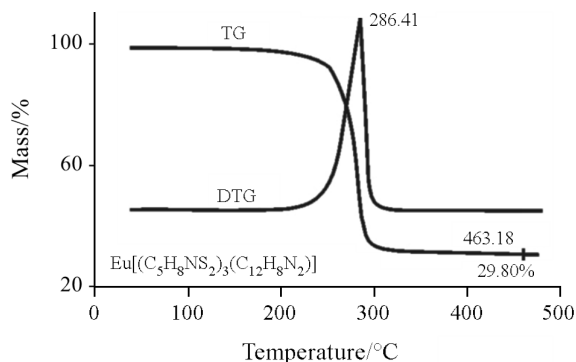


Fig. 4 TG-DTG curves of the complex $\text{Eu}(\text{PDC})_3(\textit{o}\text{-phen})$

Table 2 The experimental data of $\Delta_{\text{sol}}H_m^\theta$ (1), $\Delta_{\text{sol}}H_m^\theta$ (2) and $\Delta_{\text{sol}}H_m^\theta$ (3) at 298.15 K

No.	<i>m</i> / mg	<i>Q</i> / mJ	$-\Delta_{\text{sol}}H_m^\theta$ (1)/ kJ mol ⁻¹	<i>m</i> / mg	<i>Q</i> / mJ	$\Delta_{\text{sol}}H_m^\theta$ (2)/ kJ mol ⁻¹	<i>m</i> / mg	<i>Q</i> / mJ	$\Delta_{\text{sol}}H_m^\theta$ (3)/ kJ mol ⁻¹
1	87.72	3206.978	13.369	26.29	3099.238	19.369	31.71	3351.540	20.950
2	87.79	3307.909	13.779	26.25	3121.801	19.539	31.77	3393.602	21.173
3	87.74	3149.542	13.127	26.27	3171.104	19.832	31.76	3343.271	20.866
4	87.76	3223.853	13.434	26.24	3082.010	19.297	31.73	3356.008	20.965
5	87.74	3274.025	13.646	26.33	3157.941	19.705	31.68	3315.208	20.746
6	87.76	3180.979	13.255	26.28	3117.297	19.488	31.73	3379.615	21.123
$(\bar{x} \pm \sigma_a)$			13.435±0.108			19.538±0.090			20.970±0.071

$\Delta_{\text{sol}}H_m^\theta$ (1) represents the enthalpy of solution of $\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}$ in ethanol; $\Delta_{\text{sol}}H_m^\theta$ (2) represents the enthalpy of solution of APDC in ethanol; $\Delta_{\text{sol}}H_m^\theta$ (3) represents the enthalpy of solution of *o*-phen· H_2O in ethanol

Table 3 The experimental data of $\Delta_{\text{mix}}H_m^\theta$ and $\Delta_rH_m^\theta$ (l) at 298.15 K

No.	<i>Q</i> ₁ /mJ	$\Delta_{\text{mix}}H_m^\theta$ /kJ mol ⁻¹	<i>Q</i> ₂ /mJ	$\Delta_rH_m^\theta$ /kJ mol ⁻¹
1	84.809	10.601	-177.746	-22.218
2	86.293	10.787	-176.511	-22.064
3	84.231	10.529	-180.553	-22.569
4	86.064	10.508	-177.124	-22.141
5	83.987	10.498	-176.998	-22.125
6	85.006	10.626	-177.335	-22.167
$(\bar{x} \pm \sigma_a)$	85.065±0.421	10.592±0.049	-177.711±0.648	-22.214±0.081

$\Delta_{\text{mix}}H_m^\theta$ is the mixed enthalpy of the ethanolic solution of APDC and *o*-phen· H_2O ; and $\Delta_rH_m^\theta$ (l) is the enthalpy change of the liquid-phase reaction $(\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}) \cdot x\text{C}_2\text{H}_5\text{OH} (l) + 3\text{APDC} \cdot y\text{C}_2\text{H}_5\text{OH} (l) + [(o\text{-phen} \cdot \text{H}_2\text{O}) \cdot z\text{C}_2\text{H}_5\text{OH} (l) = \text{Eu}(\text{PDC})_3(o\text{-phen}) (s) + 3\text{NH}_4\text{Cl} (s) + 4.46\text{H}_2\text{O} \cdot (x+3y+z)\text{C}_2\text{H}_5\text{OH} (l)$

298.15 K are given in Table 2, respectively. The mixture enthalpies of the alcoholic solutions of two ligands, $\Delta_{\text{mix}}H_m^\theta$, the enthalpy change of the reaction in alcoholic solution at 298.15 K are listed in Table 3. The enthalpy of dissolution, $\Delta_{\text{sol}}H_m^\theta$ (4) of water in ethanol is so small that it can be regarded as zero.

The application of Hess' law to the series of equations shown in Table 4 gives a thermochemical cycle, from which the enthalpy change of the reaction in solid state is derived as being 54.527±0.314 kJ mol⁻¹ according to Eq. (1), where the uncertainty is given as the standard deviation of the mean.

$$\begin{aligned} \Delta_rH_m^\theta (s) &= \Delta_{\text{sol}}H_m^\theta (1) + 3\Delta_{\text{sol}}H_m^\theta (2) + \Delta_{\text{sol}}H_m^\theta (3) + \\ &+ \Delta_{\text{mix}}H_m^\theta + \Delta_rH_m^\theta (l) - \Delta_{\text{sol}}H_m^\theta (4) = \\ &= [(-13.435 \pm 0.108) + 3(19.538 \pm 0.090) + \\ &+ (20.970 \pm 0.071) + (10.592 \pm 0.049) + \\ &+ (-22.214 \pm 0.081) - 0] \text{ kJ mol}^{-1} = \\ &= (54.527 \pm 0.314) \text{ kJ mol}^{-1} \end{aligned} \quad (1)$$

The precipitation from the reaction in ethanol was identified as the compound $\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$

by chemical and elemental analyses (*w* (Calc.): Eu 19.71%, C 42.06%, H 4.18%, N 9.08%, S 24.96%; *w* (Found): Eu 19.85%, C 42.01%, H 4.11%, N 9.00%, S 24.98%), and the concentration of Eu^{3+} occurred in ethanol was determined as $6 \cdot 10^{-3} \mu\text{g mL}^{-1}$ by the ICP-AES experiment, indicating that the designed thermochemistry cycle is reasonable.

Calculation of the thermodynamic parameters of the reaction of formation of the complex in ethanol

Based on the thermodynamic equations [24] and thermokinetic data of the reaction of formation of the complex listed in Table 5, the thermodynamic parameters and kinetic parameters of the irreversible reaction in ethanol are obtained and shown in Table 6.

Molar heat capacity of the complex

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 cell containing first standard substance with known specific heat *c*₁ (system III), and the cell containing second standard substance with known spe-

Table 4 Thermochemical cycle and results for ΔH_m^0 at 298.15 K

	Reaction	$\Delta H_m^0/\text{kJ mol}^{-1}$
1	$\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}(s) + x\text{C}_2\text{H}_5\text{OH}(l) = (\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}) \cdot x\text{C}_2\text{H}_5\text{OH}(l)$	-13.435 ± 0.108
2	$3\text{APDC}(s) + y\text{C}_2\text{H}_5\text{OH}(l) = 3(\text{APDC} \cdot y\text{C}_2\text{H}_5\text{OH})(l)$	19.538 ± 0.090
3	$o\text{-phen} \cdot \text{H}_2\text{O}(s) + z\text{C}_2\text{H}_5\text{OH}(l) = (o\text{-phen} \cdot \text{H}_2\text{O}) \cdot z\text{C}_2\text{H}_5\text{OH}(l)$	20.970 ± 0.071
4	$[3\text{APDC} \cdot y\text{C}_2\text{H}_5\text{OH}(l)] + [(o\text{-phen} \cdot \text{H}_2\text{O}) \cdot z\text{C}_2\text{H}_5\text{OH}(l)] =$ $= (3\text{APDC})(o\text{-phen} \cdot \text{H}_2\text{O}) \cdot (y+z)(\text{C}_2\text{H}_5\text{OH}(l))$	10.592 ± 0.049
5	$[(\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}) \cdot x\text{C}_2\text{H}_5\text{OH}(l)] + 3\text{APDC} \cdot y\text{C}_2\text{H}_5\text{OH}(l) +$ $+ [(o\text{-phen} \cdot \text{H}_2\text{O}) \cdot z\text{C}_2\text{H}_5\text{OH}(l)] = \text{Eu}(\text{PDC})_3(o\text{-phen})(s) + 3\text{NH}_4\text{Cl}(s) +$ $+ 4.46\text{H}_2\text{O} \cdot (x+3y+z)\text{C}_2\text{H}_5\text{OH}(l)$	-22.214 ± 0.081
6	$4.46\text{H}_2\text{O} + (x+3y+z)\text{C}_2\text{H}_5\text{OH}(l) = 4.46\text{H}_2\text{O} \cdot (x+3y+z)\text{C}_2\text{H}_5\text{OH}(l)$	0
7	$\text{EuCl}_3 \cdot 3.46\text{H}_2\text{O}(s) + 3\text{APDC}(s) + o\text{-phen} \cdot \text{H}_2\text{O}(s) =$ $= \text{Eu}(\text{PDC})_3(o\text{-phen})(s) + 3\text{NH}_4\text{Cl}(s) + 4.46\text{H}_2\text{O} \cdot (x+3y+z)\text{C}_2\text{H}_5\text{OH}(l)$	54.527 ± 0.314

Table 5 Thermokinetical data of the reaction of formation of the complex in ethanol

292.15 K			295.15 K			298.15 K			301.15 K		
t/s	H_i/H_0	$dH_i/dt/10^{-4} \text{ J s}^{-1}$	t/s	H_i/H_0	$dH_i/dt/10^{-4} \text{ J s}^{-1}$	t/s	H_i/H_0	$dH_i/dt/10^{-4} \text{ J s}^{-1}$	t/s	H_i/H_0	$dH_i/dt/10^{-4} \text{ J s}^{-1}$
130	0.3565	9.2164	405	0.8121	4.1066	150	0.5171	6.8700	340	0.8888	1.5469
135	0.3718	9.0751	410	0.8191	4.0126	155	0.5351	6.7292	345	0.8958	1.4844
140	0.3869	8.9495	415	0.8260	3.9186	160	0.5527	6.5570	350	0.9026	1.4375
145	0.4018	8.8396	420	0.8328	3.8245	165	0.5699	6.4005	355	0.9092	1.3750
150	0.4165	8.7139	425	0.8394	3.7305	170	0.5867	6.2440	360	0.9155	1.3125
155	0.4310	8.5726	430	0.8459	3.6364	175	0.6031	6.0875	365	0.9215	1.2656
160	0.4453	8.4470	435	0.8523	3.5424	180	0.6191	5.9467	370	0.9273	1.2031
165	0.4593	8.3214	440	0.8585	3.4797	185	0.6346	5.8059	375	0.9328	1.1406
170	0.4731	8.1801	445	0.8646	3.3700	190	0.6498	5.6494	380	0.9382	1.0938
175	0.4867	8.0388	450	0.8705	3.2759	195	0.6645	5.5085	385	0.9433	1.0313

$H_0 = 0.2974 \text{ J (292.15 K)}, 0.2281 \text{ J (295.15 K)}, 0.1775 \text{ J (298.15 K)}$ and $0.0776 \text{ J (301.15 K)}$; t – time

Table 6 Kinetic, thermodynamic parameters of the reaction of formation of the complex in ethanol

T/K	$k \cdot 10^3/\text{s}^{-1}$	n	r	$E/\text{kJ mol}^{-1}$	$\ln A$	r	$\Delta G_m^0/\text{kJ mol}^{-1}$	$\Delta H_m^0/\text{kJ mol}^{-1}$	$\Delta S_m^0/\text{J mol}^{-1} \text{ K}^{-1}$	r
292.15	4.0340	0.5968	0.9991				84.89			
295.15	4.9178	0.6013	0.9992	49.886	15.019	0.9993	85.30	47.420	-128.31	0.9992
298.15	6.0222	0.6089	0.9998				85.69			
301.15	7.4585	0.6000	0.9993				86.04			

r – linear correlation coefficient

cific 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 (2)–(5).

$$\text{For system I} \quad q_0 = a\theta \quad (2)$$

$$\text{For system II} \quad q = (a + mc)\theta \quad (3)$$

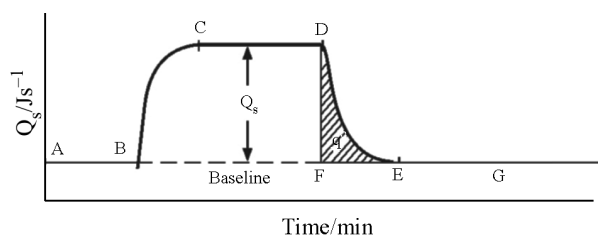
$$\text{For system III} \quad q_1 = (a + m_1c_1)\theta \quad (4)$$

$$\text{For system IV} \quad q_2 = (a + m_2c_2)\theta \quad (5)$$

where a (J K^{-1}) is the apparent heat capacity of the empty cell, θ (K) is the equilibrium temperature for a given Peltier current, m (g), m_1 (g) and m_2 (g) are masses of the investigated sample, the first standard substance and second standard substance, respectively; c ($\text{J mol}^{-1} \text{ K}^{-1}$), c_1 ($\text{J mol}^{-1} \text{ K}^{-1}$) and c_2 ($\text{J mol}^{-1} \text{ K}^{-1}$) are of the molar heat capacity of the

Table 7 Experimental data used for calculating the molar heat capacity of the complex, c_m , at 298.15 K

Experimental data	Empty cell	Benzoic acid	α -Al ₂ O ₃	Eu(PDC) ₃ (<i>o</i> -phen)
	4453.908	6088.611	4959.916	5037.728
	4444.543	6080.422	4962.776	5030.006
	4432.133	6094.207	4977.771	5040.812
q/mJ	4447.035	6098.640	4984.568	5045.962
	4438.165	6075.115	4967.144	5051.083
	4450.647	6073.035	4983.760	5033.461
$(\bar{x} \pm \sigma_a)$	4444.405 ± 3.610	6085.005 ± 4.672	4972.656 ± 4.824	5039.842 ± 3.502
precision/ (σ_a/\bar{x})	1.816 · 10 ⁻³	1.717 · 10 ⁻³	2.169 · 10 ⁻³	1.554 · 10 ⁻³
m/g		4.51478	2.68416	3.86897
$c/J \text{ mol}^{-1} \text{ K}^{-1}$		78.707 ± 2.927	145.923 ± 0.562	61.676 ± 0.651
$c_{0 \text{ lit}}/J \text{ mol}^{-1} \text{ K}^{-1}$		79.03 [26]	145.327 [27]	
accuracy $(c_0 - c)/c_0$		4 · 10 ⁻³	4 · 10 ⁻³	

**Fig. 5** Curve of measurement of the molar heat capacity of the complex Eu(PDC)₃(*o*-phen)

investigated sample, the first standard substance and second standard substance, respectively; q_0 (J), q (J), q_1 (J) and q_2 (J) are of the quantities of heat retained by the systems I–IV when they were heated up by a given Peltier current.

Combination of the Eqs (2)–(5), Eq. (6) is obtained.

$$c = [(q - q_0)/2m][m_1c_1/(q_1 - q_0) + m_2c_2/(q_2 - q_0)] \quad (6)$$

The value of c of the investigated sample can be obtained from Eq. (6) if the values of c_1 and c_2 of two standard substances are known [25].

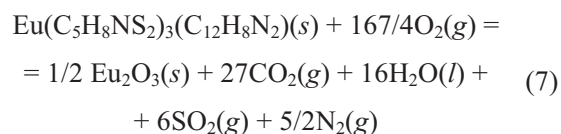
Molar heat capacity of the complex is determined by an RD496-III type microcalorimeter when changing the samples in the sample cell. The values of q are obtained by the testing method presented as a curve in Fig. 5. In Fig. 5, AG is baseline; at time B, a constant Peltier current is generated in the 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. (6). The results of the experiments are shown in Table 7.

Combustion energy of the complex

The methods of 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 [15]. The experimental results of combustion energy of the complex are given in Table 1.

Standard combustion enthalpy of complex

The standard combustion enthalpy of the complex, $\Delta_c H_m^0$ (complex, *s*, 298.15 K), refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.



The standard combustion enthalpy of the complex is calculated by Eqs (8)–(9):

$$\Delta_c H_m^0(\text{complex}, \text{s}, 298.15 \text{ K}) = \quad (8)$$

$$= \Delta_c U(\text{complex}, \text{s}, 298.15 \text{ K}) + \Delta nRT$$

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

where n_g is the total amount in mole of gases present as products or as reactants, $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T=298.15 \text{ K}$. Its standard enthalpy of combustion, $\Delta_c H_m^0$, is calculated to be $-16953.37 \pm 9.79 \text{ kJ mol}^{-1}$.

Standard enthalpy of formation of the complex

The standard enthalpy of formation of the complex, $\Delta_f H_m^0$ (complex, *s*, 298.15 K), is calculated by Hess's law according to the above thermochemical Eq. (10):

$$\begin{aligned} & \Delta_f H_m^0 [\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2),s] = \\ & = [1/2\Delta_f H_m^0 (\text{Eu}_2\text{O}_3,s) + 27\Delta_f H_m^0 (\text{CO}_2,g) + \\ & + 16\Delta_f H_m^0 (\text{H}_2\text{O},l) + 6\Delta_f H_m^0 (\text{SO}_2,g) + \\ & + 5/2\Delta_f H_m^0 (\text{N}_2,g)] - \\ & - \Delta_f H_m^0 [\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2),s] \end{aligned} \quad (10)$$

where $\Delta_f H_m^0 (\text{Eu}_2\text{O}_3,s) = -1663.00 \pm 1.62 \text{ kJ mol}^{-1}$ [28]; $\Delta_f H_m^0 (\text{CO}_2,g) = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$, $\Delta_f H_m^0 (\text{H}_2\text{O},l) = -285.830 \pm 0.042 \text{ kJ mol}^{-1}$, $\Delta_f H_m^0 (\text{SO}_2,g) = -296.81 \pm 0.20 \text{ kJ mol}^{-1}$ [29]. The standard enthalpy of formation of the complex, $\Delta_f H_m^0$, is calculated to be $-1708.23 \pm 10.69 \text{ kJ mol}^{-1}$.

Conclusions

The title ternary complex $\text{Eu}(\text{C}_5\text{H}_8\text{NS}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)$ has been synthesized in absolute ethanol without any cautions against moisture or air.

TG-DTG investigations indicate that the title complex is decomposed into EuS in one step, which provide a probe for the preparation of nanocrystalline semiconductor EuS.

The enthalpy change of the reaction of formation in ethanol and the specific heat capacity of the complex were determined by microcalorimetry. 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 the reaction of formation of the complex in ethanol were obtained.

The standard enthalpy of formation of the title complex was determined as $-1708.23 \pm 10.69 \text{ kJ mol}^{-1}$, showing that the complex is of quite thermal stability.

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