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COORDINATION BEHAVIOR OF ERBIUM CHLORIDE HYDRATE WITH DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE

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Abstract

The complex of erbium chloride lower hydrate with diethylammonium diethyldithiocarbamate (D-DDC) has been synthesized conveniently in absolute alcohol and dry N_2 atmosphere. The title complex was identified as $Et_2NH_2[Er(S_2CNEt_2)_4]$ by chemical and elemental analyses, the bonding characteristics of which was characterized by IR. The enthalpies of solution of erbium chloride hydrate and D-DDC in absolute alcohol at 298.15 K and the enthalpies change of liquid-phase reaction of formation for $Et_2NH_2[Er(S_2CNEt_2)_4]$ at different temperatures were determined by microcalorimetry. On the basis of experimental and calculated results, three thermodynamic parameters (the activation enthalpy, the activation entropy and the activation free energy), the rate constant and three kinetic parameters (the apparent activation energy, the pre-exponential constant and the reaction order) of liquid phase reaction of formation were obtained. The enthalpy change of the solid-phase title reaction at 298.15 K was calculated by a thermochemical cycle.

Keywords: diethylammonium diethyldithiocarbamate (D-DDC), erbium chloride hydrate, microcalorimetric method, thermochemistry

Introduction

Coordination compounds containing lanthanide–sulfur bonds have been attracted much attention because of high performance of biological properties [1] and friction properties [2]. In addition, they have been largely used because of their chemical and physical properties, such as vulcanization accelerator [3, 4]. There have been vast investigations on preparations, characterizations and structures of these compounds [5–16], which is of great importance for illuminating the bonding characterization of lanthanide series and

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enriching the application of these compounds. Recently there has been substantial interest in the preparation and characterization of nanocrystalline materials of sulphide [17]. As a promising method for the preparation nanocrystallites of chalcogenide, the decomposition of complex precursors containing lanthanide – sulfur would be regarded as an efficient synthetic route [18]. Clearly, to expound on the study of the complexes containing 'RE–S' bonds is substantial practical, as well as theoretical, significance.

In this paper, the complex of erbium and diethyldithiocarbamate $Et_2NH_2[Er(S_2CNEt_2)_4]$ has been synthesized in absolute alcohol and dry N_2 atmosphere by erbium chloride lower hydrate reacting with diethylammonium diethyldithiocarbamate (D-DDC). The enthalpy changes of the reaction at different temperatures were measured by a microcalorimeter. The thermodynamic parameters, the rate constant and kinetic parameters were calculated. The related thermochemistry study would provide thermodynamic basis for the synthesis and application of these complexes containing lanthanide–sulfur bonds.

Experimental

Reagents

Erbium chloride lower hydrate, $ErCl_3\cdot3.46H_2O$ were prepared in our experiment, which was attested by chemical analysis. D-DDC, absolute ethanol and acetonitrile are of A.R. grade from Xi'an chemical reagent company.

Analysis method

Er^{3+} was determined with EDTA by complexometric titration. C, H, N and S analyses were carried out by an instrument of Vario EL III CHNOS of Germany. Transmission electron microscopy (TEM) images were taken on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

Equipment and experimental method

The calorimetric experiment was performed using an RD496-III type microcalorimeter [19, 20]. The calorimetric constants at 295.15, 298.15, 301.15, 304.15 and 307.15 K were determined by the Joule effect before experiment, which are 63.799 ± 0.025, 63.901 ± 0.030, 64.000 ± 0.026, 64.075 ± 0.038 and 64.203 ± 0.043 $\mu V\ mW^{-1}$. The enthalpies at solution in deionized water of KCl (spectral purity) was measured to be 17.238 ± 0.048 kJ mol^{-1}, which is in good agreement with the value at 17.241 ± 0.018 kJ mol^{-1} in [21]. The accuracy is 0.02% and the precision is 0.3%, which indicates that the calorimetric system is accurate and reliable. The reaction solution/solvent and the diluent were put into the stainless steel sample cell with the container of 15 mL [22] (Fig. 1), separately. After equilibrium, the containers of sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the curve was recorded.

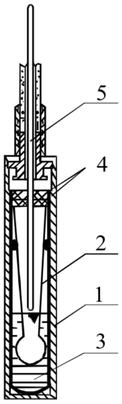

Fig. 1 Sketch used for study of the formation reaction. 1 – Calorimetric cell; 2 – Solution of $ErCl_3{\cdot}3.46H_2O$ in absolute ethanol; 3 – Solution of D-DDC in absolute ethanol; 4 – Silicone rubber cover; 5 – Glass rod

Synthesis of the complex

$ErCl_3{\cdot}3.46H_2O$ and D-DDC 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 D-DDC alcoholic solution was dropwise added in dry N_2 atmosphere when keeping electromagnetic stirring. After the addition, the mixture was allowed to stand for overnight and the precipitant was collected by suction filter, then the crude product was purified with acetonitrile by re-solving – crystallization in air. With the aid of Bucher funnel, the fine crystal was obtained and followed by three small amount of absolute ethanol portions washing; the crystal product was kept in vacuum over P_4O_{10} to dryness for being used.

Results and discussion

Composition analysis of the complex

The elementary analyses result of the title complex are as follows: *w* (calcd.): Er 20.04%, C 34.54%, H 6.28%, N 8.39%, S 30.70%; *w* (found): Er 20.11%, C 34.66%, H 6.32%, N 8.30%, S 30.65%, which is identified as the formula of $Et_2NH_2[Er(S_2CNEt_2)_4]$ [6].

IR spectrum of the complex

In the IR spectrum of the title complex the single band $\gamma(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ due to the stretching vibration of the complex appears in the region 1490 cm^{-1}, and is shifted to the higher wavenumber compared with that 1520 cm^{-1} of the free ligand. One strong $\gamma(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ band in the region 979 cm^{-1} indicates that the dithiocarbamate behaves as a bidentate ligand in the complex [23].

Calculation of the enthalpies change of the title solid phase reaction

The molar enthalpies of solution $\Delta_{sol}H_m^\theta$ (1) and $\Delta_{sol}H_m^\theta$ (2) of $ErCl_3 \cdot 3.46H_2O$ and D-DDC in 6 and 8 mL anhydrous ethanol are given in Tables 1 and 2, respectively. They can be considered as alcoholate compound. The dilution heat of Q_1 of the ethanol erbium chlorides (0.20 mL) in 1.60 mL absolute ethanol and that of Q_2 of the ligand ethanol solution (1.60 mL) in 0.20 mL absolute ethanol, and the enthalpy changes $\Delta_r H_m^\theta$ (including Q_1 and Q_2) of the liquid phase reaction enthalpy change of the title reaction are shown in Table 3. Therefore, the enthalpy change of the title solid phase reaction at 298.15 K can be calculated following a thermochemistry cycle, as presented in Table 4.

$$\Delta_r H_m^\theta\ (4)=\Delta_{sol}H_m^\theta\ (1)+\Delta_{sol}H_m^\theta\ (2)+\Delta_r H_m^\theta\ (3)=$$
$$=[(-45.714\pm0.196)+4(50.280\pm0.151)+(-18.484\pm0.049)]\ \text{kJ mol}^{-1}=$$
$$=(136.992\pm0.637)\ \text{kJ mol}^{-1}$$

Table l The molar enthalpies of solution of $ErCl_3 \cdot 3.46H_2O$ in absolute alcohol (c=0.0400 mol L^{-1}) at 298.15 K

No.	m/mg	Q/mJ	$\Delta_{sol}H_m^\theta$ (1)/kJ mol^{-1}
1	80.66	–10944.216	–45.583
2	80.59	–10870.105	–45.313
3	80.68	–11098.503	–46.214
4	80.63	–11074.625	–46.143
5	80.58	–11005.231	–45.882
6	80.59	–10830.292	–45.147
Mean			–45.714±0.196

Table 2 The molar enthalpies of solution of D-DDC in absolute alcohol (c=0.0200 mol L^{-1}) at 298.15 K

No.	m/mg	Q/mJ	$\Delta_{sol}H_m^\theta$ (2)/kJ mol^{-1}
1	35.25	7902.978	49.862
2	35.24	7952.067	50.186
3	35.30	8057.711	50.766
4	35.31	7997.799	50.374
5	35.28	8012.162	50.508
6	35.24	7919.752	49.982
Mean			50.289±0.151

Table 3 The heat of dilution of erbium chloride alcoholate (Q_1), that of ligand alcoholate (Q_2) in absolute ethanol and enthalpies change of liquid-phase reaction (Q_3) at 298.15 K

No.	Q_1/mJ	Q_2/mJ	Q_3/mJ	$\Delta_r H^{\theta}_{m}$ (3)/kJ mol^{-1}
1	–38.207	173.161	–148.220	–18.528
2	–38.260	172.443	–147.726	–18.466
3	–37.220	171.783	–148.367	–18.546
4	–37.968	175.730	–147.249	–18.406
5	–38.678	174.205	–149.097	–18.637
6	–38.817	172.374	–146.588	–18.324
Mean	–38.192±0.255	173.283±0.652	–147.874±0.396	–18.484±0.049

Calculation of the thermodynamic parameters of liquid phase reaction

Table 4 indicates that the liquid phase reaction is of irreversible one. The typical thermokinetic (T/K) curve at 298.15 K is depicted in Fig. 2, to which the curves in shape at other different temperatures are similar and the reaction is an exothermic one. The experimental data from the curves are shown in Table 5. The energy change of the reaction system depends on the reaction progression. Based on the thermodynamic equations [22], the thermodynamic parameters and kinetic parameters of the liquid reaction are obtained and shown in Table 6.

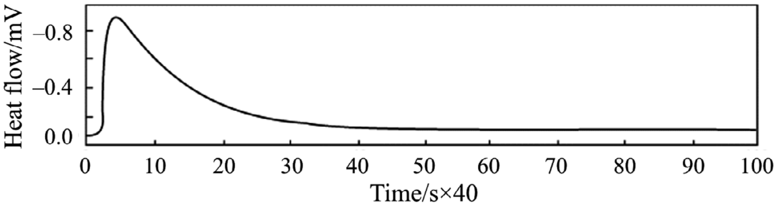

Fig. 2 Thermokinetic curve of the liquid-phase reaction at 298.15 K

$$\ln\left(\frac{1}{H}\frac{dH}{dt}\right)=\ln k+n\ln\left(1-\frac{H_i}{H_0}\right) \tag{1}$$

$$\ln k=\ln A-\frac{E}{RT} \tag{2}$$

$$\Delta G^{\theta}_{\neq}=RT\ln\frac{RT}{Nhk} \tag{3}$$

$$\ln\frac{k}{T}=-\frac{\Delta H^{\theta}_{\neq}}{RT}+\frac{\Delta S^{\theta}_{\neq}}{R}+\ln\frac{k_B}{h} \tag{4}$$

Table 4 Thermochemical cycle and results for ΔH_m^θ (298.15 K)

No.	Reaction	ΔH_m^θ/kJ mol^{-1}
1	$ErCl_3 \cdot 3.46H_2O$ (*s*)+xC_2H_5OH (*l*)=$(ErCl_3 \cdot 3.46H_2O) \cdot xC_2H_5OH$ (*l*)	–45.714±0.196
2	$(C_2H_5)_2NCS_2NH_2(C_2H_5)_2$ (*s*)+yC_2H_5OH (*l*)=$[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2] \cdot yC_2H_5OH$ (*l*)	50.280±0.151
3	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2] \cdot yC_2H_5OH$ (*l*)+$(ErCl_3 \cdot 3.46H_2O) \cdot xC_2H_5OH$ (*l*)= $NH_2(C_2H_5)_2[Er((C_2H_5)_2NCS_2)_4]$ (*s*)+$3[NH_2(C_2H_5)_2Cl] \cdot (x+y-z)C_2H_5OH$ (*l*)+$3.46H_2O \cdot zC_2H_5OH$ (*l*)	–18.484±0.049
4	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2]$ (*s*)+$ErCl_3 \cdot 3.46H_2O$ (*s*)+$(x+y)C_2H_5OH$ (*l*)= $NH_2(C_2H_5)_2[Er((C_2H_5)_2NCS_2)_4]$ (*s*)+$3[NH_2(C_2H_5)_2Cl] \cdot (x+y-z)C_2H_5OH$ (*l*)+$3.46H_2O \cdot zC_2H_5OH$ (*l*)	136.992±0.637

Table 5 Thermokinetical data of liquid-phase reaction

295.15 K			298.15 K			301.15 K			304.15 K			307.15 K		
t/s	H_i/H_0*	dH/dt (10^4 J s^{-1})	t/s	H_i/H_0*	dH/dt (10^4 J s^{-1})	t/s	H_i/H_0*	dH/dt (10^4 J s^{-1})	t/s	H_1/H_0**	dH/dt (10^4 J s^{-1})	t/s	H_i/H_0**	dH/dt (10^4 J s^{-1})
90	0.3777	8.5581	85	0.3921	8.8105	60	0.2801	11.484	70	0.3018	14.171	80	0.4360	1.5576
95	0.4036	8.3544	90	0.4200	8.5914	70	0.3486	10.922	80	0.3629	13.687	85	0.4716	1.5108
100	0.4290	8.1819	95	0.4473	8.3880	80	0.4155	10.313	90	0.4222	12.985	90	0.5062	1.4610
105	0.4539	7.9939	100	0.4740	8.2002	90	0.4797	9.7188	100	0.4790	12.314	95	0.5397	1.4111
110	0.4783	7.8058	105	0.5000	7.9967	100	0.5406	9.1406	110	0.5329	11.611	100	055722	1.3613
115	0.5022	7.6333	110	0.5254	7.7620	110	0.5978	8.5469	120	0.5838	10.956	105	0.6035	1.3084
120	0.5256	7.4609	115	0.5502	7.5586	120	0.6510	7.9219	130	0.6313	10.269	110	0.6336	1.2554
125	0.5484	7.2572	120	0.5742	7.3708	130	0.7002	7.3438	140	0.6756	9.6137	115	0.6624	1.2087
130	0.5706	7.0848	125	0.5975	7.1360	140	0.7451	6.7656	150	0.7164	8.9739	120	0.6899	1.1588
135	0.5922	6.8967	130	0.6202	6.9326	150	0.7859	6.1875	160	0.7540	8.3496	125	0.7162	1.1090
			135	0.6420	6.7292									

*H_0=0.1834 (295.15 K), 0.1477 (298.15 K), 0.1236 (301.15K)
**H_0=0.1099 (304.15 K) and 0.0966 (307.15 K) J

Table 6 Kinetic, thermodynamic parameters of liquid-phase reaction

T/K	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	$k/10^{-3}$ s^{-1}	n	r[a]	E/kJ mol^{-1}	ln$A$	r[a]	$\Delta G^{\theta}_{\neq}$/ kJ mol^{-1}	$\Delta H^{\theta}_{\neq}$/ kJ mol^{-1}	$\Delta S^{\theta}_{\neq}$/ kJ mol^{-1} K^{-1}	r[a]
295.15	5.925	0.506	0.999	82.46	28.441	0.997	84.85	79.96	–16.84	0.997
298.15	7.692	0.510	0.999	–	–	–	85.05	–	–	–
301.15	10.988	0.510	0.999	–	–	–	85.07	–	–	–
304.15	15.634	0.515	0.999	–	–	–	85.09	–	–	–
307.15	21.466	0.497	0.999	–	–	–	85.11	–	–	–

[a] Correlation coefficient.

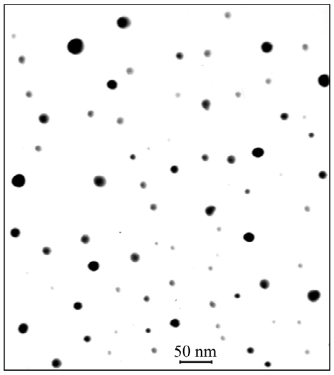

Fig. 3 TEM image pattern of Er_2S_3 nanoparticle

where H_0, the total heat of reaction (corresponding to the area under the T/K curve); H_t, the reaction heat at some time t (corresponding to the area under the curve at time t); dH_i/dt, the rate of heat production at time t; k – rate constant; n – reaction order; A – pre-exponent; E – apparent activation energy; R – gas constant; T – absolute temperature; N – Avogadro constant; h – Planck constant; $\Delta G_{\neq}^{\theta}$ – activation Gibbs energy; $\Delta H_{\neq}^{\theta}$ – activation enthalpy; $\Delta S_{\neq}^{\theta}$ – activation entropy; k_B – Boltzmann constant.

Conclusions

- It is well known that the main difficulty in the method of preparing the complexes containing lanthanide–sulfur bonds in solution is due to the fact that the complexes exhibit extremely high sensitivity to hydrolysis, and the synthesis should be performed under strongly anhydrous conditions. In this paper, a new very simple method for the synthesis of the complexes containing lanthanide–sulfur bonds is developed with erbium chloride lower hydrate. The decomposition of the title complex demonstrates that the complex can be used as precursor of nanocrystlline erbium sulfide, which is performed in our experiment and the TEM image pattern of Er_2S_3 nanoparticle is shown in Fig. 3.
- The enthalpy change of liquid phase is so small, which is attributed to the fact that the dilution heat Q_2 of the alcohol D-DDT in absolute ethanol presents the larger positive value. The large magnitude and the positive sign of the solution enthalpy $\Delta_{sol}H_m^{\theta}$ (2) of the alcohol D-DDT indicates that the enthalpy change of the solid phase reaction has a more positive value and the solid phase reaction occurs unfeasibly.
- Liquid phase reaction is of an exothermic one, and the reaction rate increases with increasing the reaction temperature. The order of the reaction is 0.5. The apparent activation energy of the reaction is a litte higher than the activation energy 63 kJ mol^{-1} of which the reaction occurs spontaneously at room temperature, showing that the title reaction proceeds feasibly in ethanol solution.

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