Thermochemistry of Coordination of Terbium Chloride Hydrate with Diethylammonium Diethyldithiocarbamate

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The complex of terbium chloride hydrate with diethylammonium diethyldithiocarbamate (D-DDC) has been synthesized from the mixing of their solutions in absolute alcohol using a dry N_2 atmosphere. The elemental and chemical analyses showed that the complex has the general formula $Et_2NH_2[Tb(S_2CNEt_2)_4]$. It was also characterized by IR spectroscopy. The enthalpies of dissolution of terbium chloride hydrate and D-DDC in absolute alcohol at 298.15 K and the enthalpy changes of liquid-phase reaction of formation for the above complex 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 Gibbs 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 complex formation were obtained. The enthalpy change of the solid-phase complex formation reaction at 298.15 K was calculated by a thermochemical cycle.

Coordination compounds containing lanthanide—sulfur bonds have attracted much attention because of high performance of their biological properties [1] and friction properties [2]. In addition, they have been largely used because of their chemical and physical properties which allow, for instance, to use them as catalysts for vulcanization [3, 4]. There are many studies on the preparations, characterizations, and structures of this kind of compounds in the literature [5—16], which is of great importance for understanding the kind of bonding present in the lanthanide series and increasing of the applications of these compounds. Recently there has been substantial interest in the preparation and characterization of nanocrystalline materials of sulfide [17]. This promising method for the preparation of nanocrystallites of lanthanide sulfide is currently of our great interest. Calorimetry is recognized as an experimentally simple method for the determination of both the thermodynamic and kinetic parameters associated with chemical reaction systems. The developed procedures [18], for maximum utility, enable direct calculation of the required parameters (n, k, ΔH, ΔS, ΔG, and E), which would greatly improve the interpretation of the reaction system.

In this work, the complex of terbium and diethyldithiocarbamate $Et_2NH_2[Tb(S_2CNEt_2)_4]$ has been synthesized from the reaction in absolute ethanol solution of terbium chloride hydrate and diethyldithiocarbamate (D-DDC) in a dry nitrogen atmosphere. 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. Clearly, the present work will assist in going deep into the formation reaction of the complexes containing "RE—S" bonds, and the related thermochemistry study would provide thermodynamic basis for the syntheses and applications of these complexes.

EXPERIMENTAL

Terbium chloride hydrate, $TbCl_3 \cdot 5.35H_2O$ was prepared according to Ref. [19]. Diethylammonium diethyldithiocarbamate (D-DDC), absolute ethanol, and acetonitrile are of A. R. grade from Xi'an chemical reagent company.

Tb^{3+} was determined with EDTA by complexometric titration. The elemental analyses were carried out by an instrument Varian EL III CHNOS (Germany).

All the enthalpies of solutions were measured in

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Table 1. The Molar Enthalpies of Solution of $TbCl_3 \cdot 5.35H_2O$ in Absolute Alcohol ($c = 0.0400$ mol dm^{-3}) at 298.15 K

Exp.	m/mg	Q/mJ	$\Delta_{sol}H_m^o(1)/(\text{kJ mol}^{-1})$
1	86.85	−7117.958	−29.641
2	86.76	−6868.900	−28.633
3	86.80	−7056.672	−29.402
4	86.78	−6921.273	−28.845
5	86.78	−6898.114	−28.748
6	86.76	−6803.592	−28.361
Mean			−28.938 ± 0.217

Table 2. The Molar Enthalpies of Solution of D-DDC in Absolute Alcohol ($c = 0.0200$ mol dm^{-3}) at 298.15 K

Exp.	m/mg	Q/mJ	$\Delta_{sol}H_m^o(2)/(\text{kJ mol}^{-1})$
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	49.986
Mean			50.280 ± 0.151

RD496-III microcalorimeter. The detailed description of the structure and the technical parameters of this calorimeter has been given [20]. An automatic electronic balance (Sartorius, Germany) with a sensibility of 10 μg was employed at the preparation of solutions.

The sensibility of the calorimeter was measured through electrical calibration at 295.15 K, 298.15 K, 301.15 K, 304.15 K, and 307.15 K, respectively. The Joule cell, which has 1000 Ω electrical resistance, was given 100 mW electric power for 100 s at 298.15 K. The corresponding calorimetric constants are (63.799 ± 0.025) μV mW^{-1}, (63.901 ± 0.030) μV mW^{-1}, (64.000 ± 0.026) μV mW^{-1}, (64.075 ± 0.038) μV mW^{-1}, and (64.203 ± 0.043) μV mW^{-1}. The accuracy and precision were determined through chemical calibration at 298.15 K. The enthalpy of solution of KCl in deionized water (spectral purity) at infinite dilution was measured and compared with the literature value. The experimental value of (17.238 ± 0.048) kJ mol^{-1} is in good agreement with that of (17.241 ± 0.018) kJ mol^{-1} reported in Ref. [21]. The accuracy is 0.02 % and the precision is 0.3 %, which indicates that the calorimetric system is accurate and reliable.

Complex

$TbCl_3 \cdot 5.35H_2O$ and D-DDC were dissolved separately in a minimal amount of anhydrous ethanol. The salt alcoholic solution was poured into a three-necked round bottle. To the salt alcoholic solution, the D-DDC alcoholic solution was added dropwise and with keeping electromagnetic stirring in dry N_2 atmosphere. After the addition, the mixture was allowed to stand overnight. The solid formed was filtered using suction. The crude product was purified by crystallization from acetonitrile. The fine crystals obtained were filtered using a Bucher funnel and washed with three small portions of absolute ethanol. The crystals were dried up and stored in a desiccator under vacuum and over P_4O_{10}, ready to be used.

RESULTS AND DISCUSSION

The elemental analysis results of the title complex are as follows: w_i(calc): 19.24 % Tb, 34.89 % C, 6.34 % H, 8.48 % N, 31.00 % S; w_i(found): 19.34 % Tb, 34.92 % C, 6.30 % H, 8.60 % N, 31.11 % S, which matches the general formula $Et_2NH_2[Tb(S_2CNEt_2)_4]$.

The IR spectrum of the complex shows a single band at $\tilde{\nu} = 1520$ cm^{-1} which is attributed to the stretching vibration of the CN group (ν_{CN}). This band is shifted to higher frequencies when compared with its position in the IR spectrum of the free ligand (1490 cm^{-1}). The strong band at 979 cm^{-1} (ν_{CS}) indicates that the dithiocarbamate anion behaves as a bidentate ligand in the complex [22].

The molar enthalpies of solution of $TbCl_3 \cdot 5.35H_2O$ $\Delta_{sol}H_m^o(1)$ and of D-DDC $\Delta_{sol}H_m^o(2)$ in 6 cm^3 and 8 cm^3 of anhydrous ethanol are given in Tables 1 and 2, respectively. They can be considered as alcoholic compounds. The dilution heat Q_1 of the alcoholic terbium chlorides (0.20 cm^3) in 1.60 cm^3 of absolute alcohol and the dilution heat Q_2 of the ligand alcoholic solution (1.60 cm^3) in 0.20 cm^3 of absolute alcohol, and the enthalpy changes $\Delta_r H_m^o(3)$ (including Q_1 and Q_2) of the liquid-phase reaction of complex formation are shown in Table 3. Therefore, the enthalpy change for the solid-phase reaction of complex formation (as defined by eqn (D) in Table 4) at 298.15 K can be calcu-

Table 3. The Heat of Dilution of Terbium 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

Exp.	Q_1/mJ	Q_2/mJ	Q_3/mJ	$\Delta_{sol}H_m^o(3)/(\text{kJ mol}^{-1})$
1	−138.849	173.161	−107.852	−13.482
2	−136.259	172.443	−105.492	−13.186
3	−139.686	171.783	−104.063	−13.008
4	−136.667	175.730	−106.223	−13.278
5	−140.634	174.205	−106.764	−13.346
6	−138.588	172.374	−108.302	−13.538
Mean	−138.447 ± 0.760	173.283 ± 0.652	−106.449 ± 0.697	−13.306 ± 0.087

Table 4. Thermochemical Cycle and Results for ΔH_m^o (298.15 K)

Eqn	Reaction	$\Delta H_m^o/(\text{kJ mol}^{-1})$
(A)	$TbCl_3 \cdot 5.35H_2O$ (s) + xC_2H_5OH (l) = $(TbCl_3 \cdot 5.35H_2O) \cdot xC_2H_5OH$ (l)	−28.938 ± 0.217
(B)	$(C_2H_5)_2NCS_2NH_2(C_2H_5)_2$ (s) + yC_2H_5OH (l) = $[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2] \cdot yC_2H_5OH$ (l)	50.280 ± 0.151
(C)	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2] \cdot yC_2H_5OH$ (l) + $(TbCl_3 \cdot 5.35H_2O) \cdot xC_2H_5OH$ (l) = $NH_2(C_2H_5)_2[Tb((C_2H_5)_2NCS_2)_4]$ (s) + $3[NH_2(C_2H_5)_2Cl] \cdot (x+y-z)C_2H_5OH$ (l) + $5.35H_2O \cdot zC_2H_5OH$ (l)	−13.306 ± 0.087
(D)	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2]$ (s) + $TbCl_3 \cdot 5.35H_2O$ (s) + $2xC_2H_5OH$ (l) = $NH_2(C_2H_5)_2[Tb((C_2H_5)_2NCS_2)_4]$ (s) + $3[NH_2(C_2H_5)_2Cl] \cdot (x+y-z)C_2H_5OH$ (l) + $5.35H_2O \cdot zC_2H_5OH$ (l)	158.876 ± 0.648

Table 5. Thermokinetic 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	$\dfrac{dH/dt}{10^{-4} \cdot \text{J s}^{-1}}$	t/s	H_i/H_0	$\dfrac{dH/dt}{10^{-4} \cdot \text{J s}^{-1}}$	t/s	H_i/H_0	$\dfrac{dH/dt}{10^{-4} \cdot \text{J s}^{-1}}$	t/s	H_i/H_0	$\dfrac{dH/dt}{10^{-4} \cdot \text{J s}^{-1}}$	t/s	H_i/H_0	$\dfrac{dH/dt}{10^{-4} \cdot \text{J s}^{-1}}$
75	0.2633	5.7211	60	0.2650	6.9121	100	0.4932	7.3594	50	0.3417	5.7589	75	0.3636	5.0932
80	0.2866	5.6427	65	0.2975	6.7397	105	0.5204	7.1719	60	0.4396	5.2907	80	0.4374	4.7817
85	0.3097	5.5644	70	0.3297	6.5830	110	0.5469	6.9688	70	0.5324	4.8225	85	0.5095	4.4546
90	0.3324	5.4546	75	0.3616	6.4419	115	0.5727	6.7813	80	0.6174	4.3543	90	0.5784	4.1431
95	0.3547	5.3606	80	0.3930	6.2695	120	0.5978	6.5938	90	0.6937	3.8705	95	0.6429	3.8004
100	0.3765	5.2665	85	0.4238	6.1284	125	0.6222	6.4063	100	0.7606	3.4023	100	0.7026	3.4734
105	0.3978	5.1725	90	0.4539	5.9717	130	0.6458	6.2031	110	0.8184	2.9341	105	0.7571	3.1463
110	0.4187	5.0941	95	0.4833	5.8150	135	0.6686	6.0156	120	0.8669	2.4815	110	0.8059	2.8036
115	0.4391	5.0158	100	0.5119	5.6425	140	0.6905	5.8438	130	0.9075	2.0289	115	0.8489	2.4454
120	0.4590	4.9217	105	0.5397	5.4701	145	0.7117	5.6250	140	0.9398	1.6387	120	0.8861	2.1027
125	0.4784	4.8433				150	0.7321	5.4375						

H_0 = 0.1269 J (295.15 K), 0.1068 J (298.15 K), 0.0954 J(301.15 K), 0.0503 J (304.15 K), and 0.0312 J (307.15 K).

lated following a thermochemistry cycle as presented in Table 4.

$$\Delta_r H_m^o(4) = \Delta_{sol} H_m^o(1) + 4\Delta_{sol} H_m^o(2) + \Delta_r H_m^o(3) =$$
$$= [(-28.938 \pm 0.217) + 4 \times (50.280 \pm 0.151) +$$
$$+ (-13.306 \pm 0.087)] \text{ kJ mol}^{-1} =$$
$$= (158.876 \pm 0.648) \text{ kJ mol}^{-1}$$

The final solutions collected from each experiment are filtered and the precipitant is dried. The analytical results identify that the compound has the composition of $Et_2NH_2[Tb(S_2CNEt_2)_4]$, indicating that the liquid-phase reaction is an irreversible one. The shapes of the thermokinetic (T/K) curves at all studied temperatures are similar and the reaction is an exothermic one. The experimental data from the curves are presented in Table 5. The energy change of the reaction system depends on the reaction progression. Based on the thermodynamic equations [18], the thermodynamic parameters and kinetic parameters of the liquid reaction are obtained and shown in Table 6.

$$\ln\left\{\frac{1}{k} \cdot \frac{1}{H_0}\frac{dH_i}{dt}\right\} = n\ln\left\{1 - \frac{H_i}{H_0}\right\} \qquad (1)$$

Table 6. Kinetic, Thermodynamic Parameters of Liquid-Phase Reaction

T/K	Eqn (1)			Eqn (2)			Eqn (3)	Eqn (4)			
	k $\overline{10^{-3} \cdot \text{s}^{-1}}$	n	r^a	E $\overline{\text{kJ mol}^{-1}}$	$\ln(A/s)$	r^a	$\Delta G^{\text{o}}_{\neq}$ $\overline{\text{kJ mol}^{-1}}$	$\Delta H^{\text{o}}_{\neq}$ $\overline{\text{kJ mol}^{-1}}$	$\Delta S^{\text{o}}_{\neq}$ $\overline{\text{kJ mol}^{-1}}$	r^a
295.15	5.2417	0.490	0.999	84.95	29.374	0.999	85.11	82.45	−9.08	0.999
298.15	7.5199	0.492	0.999				85.14			
301.15	10.638	0.473	0.999				85.16			
304.15	14.339	0.528	0.999				85.27			
307.15	20.585	0.511	0.999				85.32			

a) Linear correlation coefficient.

$$\ln \left\{ \frac{k}{A} \right\} = -\frac{E}{RT} \qquad (2)$$

$$\Delta G^{\text{o}}_{\neq} = RT \ln \frac{RT}{Nhk} \qquad (3)$$

$$\ln \left\{ \frac{k}{T} \cdot \frac{k_{\text{B}}}{h} \right\} = -\frac{\Delta H^{\text{o}}_{\neq}}{RT} + \frac{\Delta S^{\text{o}}_{\neq}}{R} \qquad (4)$$

where H_0 is the total heat of reaction, H_i the reaction heat at the time t, dH_i/dt the rate of heat production at time t, k the rate constant, n reaction order, A pre-exponent, E apparent activation energy, R gas constant, T absolute temperature, N Avogadro's constant, h Planck's constant, $\Delta G^{\text{o}}_{\neq}$ activation Gibbs energy, $\Delta H^{\text{o}}_{\neq}$ activation enthalpy, $\Delta S^{\text{o}}_{\neq}$ activation entropy, k_{B} Boltzmann constant.

CONCLUSION

It is well known that the main difficulty in the method of preparing the complexes containing lanthanide—sulfur bonds in solution is the fact that the complexes exhibit extremely high sensitivity to hydrolysis. 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 terbium chloride hydrate.

The enthalpy change of liquid-phase complex formation is so small that it can be attributed to the fact that the dilution heat Q_2 of the alcoholic solution of D-DDC in absolute ethanol presents the larger positive value.

The liquid-phase reaction is an exothermic one, and the reaction rate increases with the increasing the temperature. The order of the reaction is 0.5. The apparent activation energy of the reaction is a little higher than the activation energy 63 kJ mol^{-1} at which the reaction occurs spontaneously at room temperature, showing that the complex formation reaction proceeds feasibly in ethanol solution.

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