Thermochemistry on Coordination Behavior of Praseodymium Chloride Hydrate with Diethylammonium Diethyldithiocarbamate

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The complex of praseodymium 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 $Et_2NH_2[Pr(S_2CNEt_2)_4]$ by chemical and elemental analyses, the bonding characteristics of which were characterized by IR spectrum. The enthalpy of solution for praseodymium chloride hydrate and D-DDC in absolute alcohol at 298.15 K, and the enthalpy changes of liquid-phase reaction of formation for $Et_2NH_2[Pr(S_2CNEt_2)_4]$ 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 praseodymium chloride hydrate, diethylammonium diethyldithiocarbamate (D-DDC), microcalorimetry, thermochemistry

Introduction

Coordination compounds containing lanthanide-sulfur bonds have 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 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 of nanocrystallites of lanthanide sulfide, the decomposition of complex precursors containing lanthanide-sulfur would be regarded as an efficient synthetic route. Clearly, to expound on the study of the complexes containing "RE—S" bonds is of substantially practical, as well as theoretical significance.

In this paper, the complex of praseodymium and diethyldithiocarbamate $Et_2NH_2[Pr(S_2CNEt_2)_4]$ has been synthesized in absolute alcohol and dry N_2 atmosphere by praseodymium 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

Praseodymium chloride lower hydrate, $PrCl_3 \cdot 3.75H_2O$ was prepared in our experiment, the purity of which was attested by GC. Diethylammonium diethyldithiocarbamate (D-DDC), absolute ethanol and acetonitrile are of analytical grade from Xi'an chemical reagent company.

Analyses methods

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

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Equipment and experimental method

The calorimetric experiment was performed using an RD496-III type microcalorimeter.[18] The calorimetric constants at 298.15, 301.15, 304.15 and 307.15 K were determined by the Joule effect before experiment, which are (63.901 ± 0.030), (64.000 ± 0.026), (64.075 ± 0.038) and (64.203 ± 0.043) $\mu V \cdot mW^{-1}$. The enthalpy of solution in deionized water of KCl (spectral purity) was measured to be (17.238 ± 0.048) $kJ \cdot mol^{-1}$, which is in good agreement with the value of (17.241 ± 0.018) $kJ \cdot mol^{-1}$ in Ref. 19. 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 (Fig. 1),[20] respectively. After equilibrium, the containers of sample and reference were pushed down simultaneously. As a result, the two liquids were mixed and the thermogram was recorded.

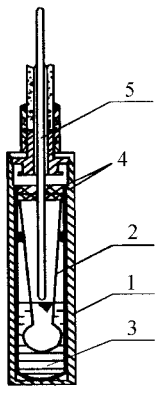

Fig. 1 Sketch used for study of the formation reaction. (1) Calorimetric cell; (2) solution of $PrCl_3 \cdot 3.75H_2O$ in absolute ethanol; (3) solution of D-DDC in absolute ethanol; (4) silicone rubber cover; (5) glass rod.

Synthesis of the complex

$PrCl_3 \cdot 3.75H_2O$ 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 resolving-crystallization in air. With the aid of Bucher funnel, the fine crystal was obtained and followed by three times of washing with a small mount of absolute ethanol, and the crystal product was kept *in vacuo* over P_4O_{10} to dryness for being used.

Results and discussion

Composition analysis of the complex

The elemental analysis result of the title complex is as follows: *w* (calcd): Pr 17.44%, C 35.67%, H 6.48%, N 8.66%, S 31.70%; *w* (found): Pr 17.44%, C 35.45%, H 6.37%, N 8.64%, S 31.68%, which is identified as the formula of $Et_2NH_2[Pr(S_2CNEt_2)_4]$.[6]

IR *spectrum of the complex*

In the IR spectrum of the title complex the single band $\gamma(C\cdots N)$ due to the stretching vibration of the complex appears in the region of 1510 cm^{-1}, and is shifted to the higher wavenumber compared with that 1490 cm^{-1} of the free ligand. One strong $\gamma(C\cdots S)$ band in the region of 979 cm^{-1} indicates that the dithiocarbamate behaves as a bidentate ligand in the complex.[21]

Calculation of the enthalpy 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 $PrCl_3 \cdot 3.75H_2O$ and D-DDC in 6 and 8 mL of anhydrous ethanol are given in Tables 1 and 2, respectively. They can be considered as alcoholic compound. The dilution heat of Q_1 of the alcoholic praseodymium chloride (0.20 mL) in 1.60 mL of absolute alcohol and that of Q_2 of the ligand alcoholic solution (1.60 mL) in 0.20 mL of absolute alcohol, and the enthalpy changes $\Delta_r H_m^\theta(3)$ (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.

$$\begin{aligned}\Delta_r H_m^\theta(4) &= \Delta_{sol}H_m^\theta(1) + 4\Delta_{sol}H_m^\theta(2) + \Delta_r H_m^\theta(3) \\ &= [(-23.626 \pm 0.102) + 4 \times (50.280 \pm 0.151) + (-18.982 \pm 0.077)]\ kJ \cdot mol^{-1} \\ &= (158.512 \pm 0.617)\ kJ \cdot mol^{-1}\end{aligned}$$

Table 1 Molar enthalpy of solution of $PrCl_3 \cdot 3.75\ H_2O$ in absolute alcohol ($c = 0.0400\ mol \cdot L^{-1}$) at 298.15 K

No.	m/mg	Q/mJ	$\Delta_{sol}H_m^\theta(1)$ ($kJ \cdot mol^{-1}$)
1	75.56	−5721.305	−23.836
2	75.51	−5729.245	−23.887
3	75.58	−5589.976	−23.306
4	75.58	−5698.334	−23.736
5	75.56	−5636.917	−23.486
6	75.58	−5642.197	−23.502
Mean			−23.626 ± 0.102

Table 2 Molar enthalpy of solution of D-DDC in absolute alcohol ($c = 0.0200\ \mathrm{mol \cdot L^{-1}}$) at 298.15 K

No.	m (mg)	Q (mJ)	$\Delta_{sol}H_m^\theta(2)$ ($\mathrm{kJ \cdot mol^{-1}}$)
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			50.280 ± 0.151

Calculation of the thermodynamic parameters of liquid phase reaction

Table 4 indicates that the liquid phase reaction is an 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.

$$\ln\left(\frac{1}{H}\frac{\mathrm{d}H_i}{\mathrm{d}t}\right) = \ln k + n\ln\left(1 - \frac{H_i}{H_0}\right) \quad (1)$$

$$\ln k = \ln A - \frac{E}{RT} \quad (2)$$

$$\Delta G_{\neq}^{\theta} = RT\ln\frac{RT}{Nhk} \quad (3)$$

$$\ln\frac{k}{T} = -\frac{\Delta H_{\neq}^{\theta}}{RT} + \frac{\Delta S_{\neq}^{\theta}}{R} + \ln\frac{k_B}{h} \quad (4)$$

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); $\mathrm{d}H_i/\mathrm{d}t$, 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.

Table 3 Heat of dilution of praseodymium chloride alcoholate (Q_1), that of ligand alcoholate (Q_2) in absolute ethanol and enthalpy change of liquid-phase reaction (Q_3) at 298.15 K

No.	Q_1 (mJ)	Q_2 (mJ)	Q_3 (mJ)	$\Delta_r H_m^\theta(3)$ ($\mathrm{kJ \cdot mol^{-1}}$)
1	− 165.062	173.161	− 152.984	− 19.123
2	− 163.296	172.443	− 150.454	− 18.806
3	− 164.450	171.783	− 150.083	− 18.760
4	− 165.669	175.730	− 153.581	− 19.198
5	− 161.872	174.205	− 152.045	− 19.006
6	− 163.891	172.375	− 151.983	− 18.998
Mean	− 164.040 ± 0.605	173.283 ± 0.652	− 151.855 ± 0.613	− 18.982 ± 0.077

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

	Reaction	ΔH_m^θ ($\mathrm{kJ \cdot mol^{-1}}$)
1	$PrCl_3 \cdot 3.75\ H_2O\ (s) + xC_2H_5OH\ (l) = (PrCl_3 \cdot 3.75\ H_2O) \cdot xC_2H_5OH\ (l)$	− 23.626 ± 0.102
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	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2] \cdot yC_2H_5OH\ (l) + (PrCl_3 \cdot 3.75H_2O) \cdot xC_2H_5OH\ (l) = NH_2(C_2H_5)_2[Pr((C_2H_5)_2NCS_2)_4]\ (s) + 3[NH_2(C_2H_5)_2Cl] \cdot (x + y - z)C_2H_5OH\ (l) + 3.75H_2O \cdot zC_2H_5OH\ (l)$	− 18.982 ± 0.077
4	$4[(C_2H_5)_2NCS_2NH_2(C_2H_5)_2]\ (s) + PrCl_3 \cdot 3.75H_2O\ (s) + (x + y)C_2H_5OH\ (l) = NH_2(C_2H_5)_2[Pr((C_2H_5)_2NCS_2)_4]\ (s) + 3[NH_2(C_2H_5)_2Cl] \cdot (x + y - z)C_2H_5OH\ (l) + 3.75H_2O \cdot zC_2H_5OH\ (l)$	158.512 ± 0.617

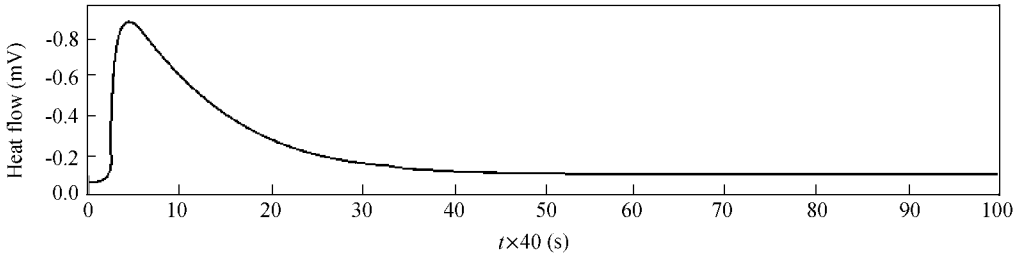

Fig. 2 Thermokinetic curve of the liquid-phase reaction at 298.15 K.

Table 5 Thermokinetical data of liquid-phase reaction[a]

298.15 K			301.15 K			304.15 K			307.15 K		
t (s)	H_i/H_0	dH/dt ($\times 10^4$ J·s)	t (s)	H_i/H_0	dH/dt ($\times 10^4$ J·s)	t (s)	H_i/H_0	dH/dt ($\times 10^4$ J·s)	t (s)	H_i/H_0	dH/dt ($\times 10^4$ J·s)
50	0.2251	8.9200	70	0.2447	8.1094	60	0.2512	8.5837	50	0.3526	4.0652
55	0.2537	8.7323	75	0.2681	7.9688	65	0.2809	8.4276	55	0.4026	3.9095
60	0.2819	8.5758	80	0.2911	7.8594	70	0.3100	8.2560	60	0.4512	3.7381
65	0.3097	0.3880	85	0.3138	7.7031	75	0.3385	8.0531	65	0.4980	3.5512
70	0.3369	8.2315	90	0.3361	7.5781	80	0.3664	7.8970	70	0.5427	3.3643
75	0.3635	8.0593	95	0.3580	7.4375	85	0.3934	7.7409	75	0.5853	3.1930
80	0.3895	7.9185	100	0.3794	7.3125	90	0.4197	7.5536	80	0.6259	3.0528
85	0.4148	7.7307	105	0.4003	7.1875	95	0.4451	7.3820	85	0.6641	2.8659
90	0.4395	7.5429	110	0.4207	7.0469	100	0.4697	7.2259	90	0.7000	2.6790
95	0.4634	7.3864	115	0.4407	6.9219	105	0.4934	7.0542	95	0.7338	2.5388
									100	0.7655	2.3675

[a] $H_0 = 0.1530$ (298.15 K), 0.1045 (301.15 K), 0.0791 (304.15 K) and 0.0305 (307.15 K) J.

Table 6 Kinetic and thermodynamic parameters of liquid-phase reaction

T (K)	Eq. (1)			Eq. (2)			Eq. (3)	Eq. (4)		
	k ($\times 10^{-3}$ 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)	$\Delta S^\theta_{\neq}$ (J·mol^{-1}·K^{-1})	r^a
298.15	6.634	0.509	0.999	79.40	27.01	0.999	85.45	76.88	−28.76	0.999
301.15	8.999	0.527	0.999				85.57			
304.15	12.57	0.504	0.999				85.61			
307.15	16.84	0.535	0.999				85.73			

[a] Correlation coefficient.

Conclusion

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 praseodymium chloride lower hydrate. The decomposition of the title complex demonstrates that the complex can be used as precursor of nanocrystlline praseodymium sulfide, which is performed in our experiment and the TEM image pattern of Pr_2S_3 nanoparticle is shown in Fig. 3.

Fig. 3 TEM image pattern of Pr_2S_3 nanoparticle.

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-DDC 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-DDC 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 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 litter higher than the activation energy 63 $kJ \cdot mol^{-1}$, of which the reaction occurs spontaneously at room temperature, showing that the title reaction proceeds feasibly in ethanol solution.

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