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Thermochemical Study on Ternary Complexes of Dysprosium with Aromatic Acids and Phenanthroline

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Three ternary Dy(III) complexes were synthesized with aromatic acids (*p*-nitrobenzoic acid, *m*-nitrobenzoic acid, and *o*-chlorobenzoic acid) as the first ligand and 1,10-phenanthroline as the second ligand. In accordance with Hess's law, a reasonable thermochemical cycle was designed, and standard molar enthalpies of dissolution for the reactants and products of the coordination reactions in the selected solvent were measured by a solution-reaction isoperibol calorimeter, respectively. In addition, the enthalpy changes of the coordination reactions were determined. Finally, the standard molar enthalpies of formation of the three synthetic coordination complexes were estimated to be $\Delta_f H_m^\theta[[\mathrm{Dy}(p\text{-NBA})_3\mathrm{phen}]_2\cdot 3\mathrm{H_2O(s)}, 298.15\ \mathrm{K}] = -(5177 \pm 8)\ \mathrm{kJ\cdot mol^{-1}}$, $\Delta_f H_m^\theta[[\mathrm{Dy}(m\text{-NBA})_3\mathrm{phen}]_2\cdot 4\mathrm{H_2O(s)}, 298.15\ \mathrm{K}] = -(5452 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}$, and $\Delta_f H_m^\theta[[\mathrm{Dy}(o\text{-ClBA})_3\mathrm{phen}]_2\mathrm{(s)}, 298.15\ \mathrm{K}] = -(5317 \pm 7)\ \mathrm{kJ\cdot mol^{-1}}$.

Introduction

Some rare earth complexes which have excellent luminescent properties may be used for the preparation of organic light-emitting devices that have high brightness, high efficiency, and low voltage DC drive, are easy to match with the IC, and easily achieve a large area color flat panel display.[1] Therefore, the synthesis of the rare earth complexes for the preparation of excellent performance light-emitting devices has become one of the most interesting topics in the study of rare earth chemistry in recent years. The luminescent properties of complexes of rare earths with aromatic carboxylic acids have been reported in the literature.[2] However, the thermodynamic properties of these complexes have not aroused sufficient attention. In this paper, a series of complexes of dysprosium with aromatic carboxylic acids and 1,10-phenanthroline have been synthesized and their thermodynamic properties calculated.

Reagents and Instruments

Reagents: $\mathrm{Dy_2O_3}$ (> 99.9 %, produced by the Chengdu Feitian Co., Ltd.); $\mathrm{DyCl_3\cdot 6H_2O}$ (synthesized by the reaction of $\mathrm{Dy_2O_3}$ with 6.0 $\mathrm{mol\cdot L^{-1}}$ HCl followed by water bath evaporation); *p*-HNBA (> 99.5 %, A.R.); *m*-HNBA (> 99.5 %, A.R.); *o*-HClBA (> 99.5 %, A.R.); *o*-phenanthroline monohydrate (phen·$\mathrm{H_2O}$, > 99.5 %, A.R., recrystallized with anhydrous ethanol); cyclohexanone (CYC, A.R.); dimethyl sulfoxide (DMSO, A.R.); *N*,*N*-dimethylformamide (DMF, A.R.); methanol (MeOH, A.R.); ethanol (EtOH, A.R.); NaOH (A.R.); HCl (A.R.); KCl (calorimetric primary standard) of purity greater than 99.99 % was dried in a vacuum oven for 6 h at 135 °C.

The instrumentation used included the following: ultraviolet−visible spectrophotometry (U-3010, HITACHI, Japan); Abbe refractometer (WAY, Shanghai, China); conductometer (DDS-12A, Shanghai, China). The dissolution enthalpies were determined by solution-reaction isoperibol calorimetry (SRC-100, constructed by the thermochemical laboratory of Wuhan University, China). The principle and structure of the calorimeter have been reported in detail in the literature.[3,4] The volume of the reaction vessel was 100 $\mathrm{cm^3}$, and the precision of the test temperature and control temperature was ± 0.001 K and ± 0.0001 K, respectively. The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of trihydroxymethyl aminomethane (THAM, NBS 742a, USA) in 0.0001 $\mathrm{mol\cdot cm^{-3}}$ HCl and KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies were $-(29776 \pm 16)\ \mathrm{J\cdot mol^{-1}}$ for THAM and $(17597 \pm 17)\ \mathrm{J\cdot mol^{-1}}$ for KCl, which agree with published data, $-(29766 \pm 31.5)\ \mathrm{J\cdot mol^{-1}}$ for THAM and $(17536 \pm 9)\ \mathrm{J\cdot mol^{-1}}$ for KCl.[5,6] The eventual error was less than 0.5 %.

Synthesis and Calorimetric Experiment

Preparation and Characterization of the Complexes. According to references 7 and 8, the methods of preparation and characterization of the complexes are very similar. Taking the synthesis and analysis of the complex $[\mathrm{Dy}(m\text{-NBA})_3\mathrm{phen}]_2\cdot 4\mathrm{H_2O(s)}$ as an example:

$\mathrm{DyCl_3\cdot 6H_2O}$, *m*-HNBA, and phen·$\mathrm{H_2O}$ were dissolved in 95 % ethanol in a molar ratio of 1:3:1, respectively. The pH value of the *m*-HNBA was adjusted to 6 to 7 by adding 1.0 $\mathrm{mol\cdot L^{-1}}$ NaOH solution. The ethanol solution of two ligands was mixed and then added dropwise to the ethanolic $\mathrm{DyCl_3\cdot 6H_2O}$ solution. At once, a large white precipitate formed. The mixture solution was stirred for 8 h at room temperature and then deposited for 12 h. Subsequently, the precipitate was filtrated and washed several times with 95 % ethanol. The product was dried under vacuum at 298.15 K until the weight of the crystals become constant. Finally, the white powdery complex was obtained in 90.84 % yield. The chemical composition of the synthetic sample was determined by elemental analysis for C, H, and N, by EDTA titration for $\mathrm{Dy^{3+}}$, and by TG-DTG analysis for $\mathrm{H_2O}$. The analysis results proved that the composition of the complex was $[\mathrm{Dy}(m\text{-NBA})_3\mathrm{phen}]_2\cdot 4\mathrm{H_2O(s)}$, and its purity was greater than 99.0 %.

Calorimetric Experiment and Its Results. Generally, there are some difficulties in determining the thermal effects of solid

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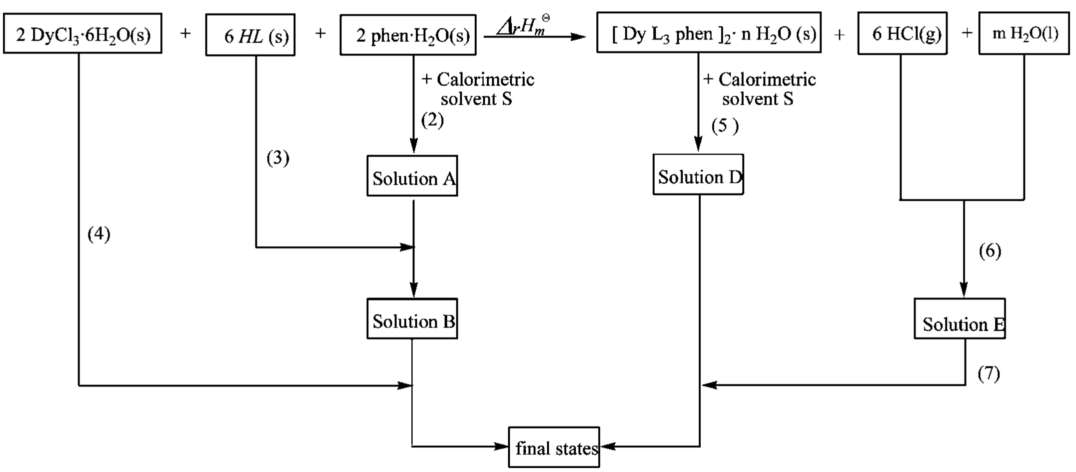

Figure 1. Thermochemical cycle of the coordination reaction.

Table 1. Dissolution Enthalpies of [6*p*-HNBA(s)], [2phen·H_2O(s)], [2$DyCl_3$·6H_2O(s)], and [Dy(*p*-NBA)$_3$phen]$_2$·3H_2O(s) in the Calorimetric Solvent at 298.15 K

		$\Delta_s H_m^\theta$ (kJ·mol^{-1})					
samples	solvent	1	2	3	4	5	mean
2phen·H_2O(s)	solvent S_1	30.6838	31.4254	31.1163	30.8889	31.4041	(31.10 ± 0.32)
6*p*-HNBA(s)	solution A	75.1369	74.9041	74.9776	75.4443	75.8689	(75.27 ± 0.40)
2$DyCl_3$·6H_2O(s)	solution B	−246.10478	−245.4996	−245.8815	−245.6104	−246.4023	−(245.91 ± 0.37)
[Dy(*p*-NBA)$_3$phen]$_2$·3H_2O(s)	solvent S_1	46.0212	46.1053	46.3718	46.1548	45.4833	(46.03 ± 0.33)
solution E	solution D	−349.2112	−348.0837	−348.7105	−348.0459	−348.7165	−(348.55 ± 0.49)

state coordination reactions, but we can find an appropriate solvent that can dissolve the reactants and products and measure the dissolution enthalpies of the substances. According to Hess's law, the thermochemical cycle of the coordination reaction was designed as shown in Figure 1.

In Figure 1, HL stands for aromatic carboxylic acids (*p*-HNBA, *m*-HNBA, and *o*-ClHBA). When HL = *p*-HNBA, $n = 3$ and $m = 11$; HL = *m*-HNBA, $n = 4$ and $m = 10$; and HL = *o*-HClBA, $n = 0$ and $m = 14$. The equations of the three coordination reactions are as follows.

$$2DyCl_3\cdot 6H_2O(s) + 6p\text{-HNBA}(s) + 2\text{phen}\cdot H_2O(s) \rightarrow [Dy(p\text{-NBA})_3\text{phen}]_2\cdot 3H_2O(s) + 6HCl(g) + 11H_2O(l) \quad (I)$$

$$2DyCl_3\cdot 6H_2O(s) + 6m\text{-HNBA}(s) + 2\text{phen}\cdot H_2O(s) \rightarrow [Dy(m\text{-NBA})_3\text{phen}]_2\cdot 4H_2O(s) + 6HCl(g) + 10H_2O(l) \quad (II)$$

$$2DyCl_3\cdot 6H_2O(s) + 6o\text{-HClBA}(s) + 2\text{phen}\cdot H_2O(s) \rightarrow [Dy(o\text{-ClBA})_3\text{phen}]_2(s) + 6HCl(g) + 14H_2O(l) \quad (III)$$

Choice of the Calorimetric Solvent. It is very important to choose the calorimetric solvent which must dissolve the chemicals in the sample cell completely and very rapidly. The test screening, the mixture solvent S_1 of dimethyl sulfoxide and methanol (V_{DMSO}:V_{MeOH} = 2:1), is the most appropriate solvent for reaction I, the mixture solvent S_2 of *N*,*N*-dimethylformamide and methanol (V_{DMF}:V_{MeOH} = 2:1) for reaction II, and the mixture solvent S_3 of *N*,*N*-dimethylformamide, cyclohexanone, and 2 mol·L^{-1} HCl (V_{DMF}:V_{CYC}:V_{HCl} = 2:1:2) for reaction III.

Determination of Dissolution Enthalpies of the Reactants. Both the calorimeter's calibration and enthalpy of dissolution of the sample were determined under the same conditions. The experimental temperature was 298.15 K; the current was 11.760 mA; and the resistance of the heater was 1251.6 Ω.

Taking the coordination reaction I as an example:

The phen·H_2O(s) was grinded in an agate mortar, and a sample (0.050 g) was placed into the sample container of the calorimeter. The calorimetric solvent S_1 (100 mL) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K, and then the sample was added into the reaction vessel and the dissolution enthalpy measured. After five experiments, the result obtained for $\Delta_s H_m^\theta(2)$ was (31.10 ± 0.32) kJ·mol^{-1}. According to the same experimental methods and procedures above, a sample of 0.125 g of *p*-HNBA powder was dissolved in the mixed solution A of the thermochemical cycle, and the dissolution enthalpy was measured. The result shown was $\Delta_s H_m^\theta(3) = (75.27 \pm 0.40)$ kJ·mol^{-1}. Finally, a sample of 0.091 g of $DyCl_3\cdot 6H_2O$(s) powder was dissolved in the mixed solution B of the thermochemical cycle, and the dissolution enthalpy was also measured. The result was shown to be $\Delta_s H_m^\theta(4) = (245.91 \pm 0.37)$ kJ·mol^{-1}. The experimental results of the above steps are listed in Table 1.

Determination of Dissolution Enthalpies of the Products. The coordination complex was grinded in an agate mortar, and a sample (0.127 g) was placed into the sample container of the calorimeter. The calorimetric solvent S_1 (100 mL) was added into the reaction vessel. The calorimeter was adjusted to a constant temperature of 298.15 K, and then the sample was added into the reaction vessel and the dissolution enthalpy measured. After five experiments, the result obtained for $\Delta_s H_m^\theta(5)$ was (46.03 ± 0.33) kJ·mol^{-1}. At the same time, a mass of 0.75 mmol of HCl(g) was dissolved into 1.375 mmol of H_2O(l) to give solution E. Subsequently, solution E was added into the mixed solution D of the thermochemical cycle, and the dissolution enthalpy was measured. The result shown was $\Delta_s H_m^\theta(7) = -(348.55 \pm 0.49)$ kJ·mol^{-1}. The experimental results of the above steps are listed in Table 1.

The methods of determination for reaction II and reaction III are the same as that mentioned above. The results are listed in Table 2 and Table 3.

Results and Discussion

Data Treatment of the Calorimetric Experiment. Evaluation of $\Delta_d H_m^\Theta(6)$ of Reaction I. According to reaction I

Table 2. Dissolution Enthalpies of [2phen·H$_2$O(s)], [6*m*-HNBA(s)], [2DyCl$_3$·6H$_2$O(s)], and [Dy(*m*-NBA)$_3$phen]$_2$·4H$_2$O(s) in the Calorimetric Solvent at 298.15 K

		$\Delta_s H_m^\theta$ (kJ·mol^{-1})					
samples	solvent	1	2	3	4	5	mean
2phen·H$_2$O(s)	solvent S$_2$	21.3786	21.4203	21.9205	22.0667	21.8973	(21.74 ± 0.32)
6*m*-HNBA(s)	solution A	15.1560	15.5081	15.3299	15.6668	15.1566	(15.36 ± 0.22)
2DyCl$_3$·6H$_2$O(s)	solution B	−203.5124	−203.4946	−203.2074	−203.6499	−203.8014	−(203.53 ± 0.22)
[Dy(*m*-NBA)$_3$phen]$_2$·4H$_2$O(s)	solvent S$_2$	53.7956	53.4022	53.3544	53.5419	53.8884	(53.60 ± 0.24)
solution E	solution D	−317.3866	−317.6632	−317.8988	−317.4408	−317.3439	−(317.55 ± 0.23)

Table 3. Dissolution Enthalpies of [6*o*-HClBA(s)], [2phen·H$_2$O(s)], [2DyCl$_3$·6H$_2$O(s)], and [Dy(*o*-ClBA)$_3$phen]$_2$(s) in the Calorimetric Solvent at 298.15 K

		$\Delta_s H_m^\theta$ (kJ·mol^{-1})					
samples	solvent	1	2	3	4	5	mean
2phen·H$_2$O(s)	solvent S$_3$	−2.1095	−2.3864	−1.9973	−2.1628	−2.2088	−(2.17 ± 0.08)
6*o*-HClBA(s)	solution A	122.1406	121.1722	121.0399	120.9866	121.5358	(121.38 ± 0.48)
2DyCl$_3$·6H$_2$O(s)	solution B	−102.1577	−102.4955	−101.8902	−102.6777	−102.0489	−(102.25 ± 032)
[Dy(*o*-ClBA)$_3$phen]$_2$(s)	solvent S$_3$	−24.6656	−24.8004	−24.7220	−24.6424	−24.6773	−(24.70 ± 0.06)
solution E	solution D	−127.9590	−129.6405	−129.0452	−128.7812	−128.7243	−(128.82 ± 0.60)

$$6\text{HCl(g)} + 11\text{H}_2\text{O(l)} \rightarrow \text{solution E}$$

The molality of solution E is 30.28 mol·kg^{-1}. According to the relationship between the enthalpy of dilution and the dissolution enthalpy[9]

$$\Delta_d H_m^\theta = \Delta_s H_m^\Theta(\text{diluted}) - \Delta_s H_m^\Theta(\text{concentrated})$$

So that

$$\Delta_d H_m^\Theta = \Delta_s H_m^\Theta\,(m = 1.00\ \text{mol·kg}^{-1}) - \Delta_s H_m^\Theta\,(m = 30.28\ \text{mol·kg}^{-1})$$

According to the data in ref 10, the enthalpy of extremely diluted HCl(g) is

$$\Delta_d H^\theta_{(30.28\rightarrow 0)} = -\Phi_{L(30.28\rightarrow 0)} = -28.472\ \text{kJ·mol}^{-1}$$

According to the relationship between the apparent molar enthalpy and integration enthalpy of an extremely diluted solution: $\Delta_d H^\theta_{c\rightarrow 0} = -\Phi_{L2}$.

According to the data in ref 10

$$\Delta_s H_m^\Theta(\text{HCl(g)}, 298.15\ \text{K}) = -74.84\ \text{kJ·mol}^{-1}$$

$$\Delta_d H^\theta_{(1.000\rightarrow 0)} = -\Phi_{L(1.000\rightarrow 0)} = -1.695\ \text{kJ·mol}^{-1}$$

So that

$$\Delta_d H^\theta_{(30.28\rightarrow 1.000)} = \Delta_d H^\theta_{(30.28\rightarrow 0)} - \Delta_d H^\theta_{(1.000\rightarrow 0)} = \Phi_{L(30.28\rightarrow 0)} + \Phi_{L(1.000\rightarrow 0)} = -28.472 + 1.695 = -26.77\ \text{kJ·mol}^{-1}$$

and

$$\Delta_s H_m^\theta(6) = \Delta_s H_m^\theta\,(m = 30.28\ \text{mol·kg}^{-1}) = \Delta_s H_m^\theta\,(m = 1.000\ \text{mol·kg}^{-1}) - \Delta_d H^\theta_{m(30.28\rightarrow 1.000)} = [-74.843 - (-26.777)]\ \text{kJ·mol}^{-1} = -48.07\ \text{kJ·mol}^{-1}$$

By the same token, we can calculate that the $\Delta_s H_m^\theta(6)$ of reaction II is −45.33 kJ·mol^{-1} and that the $\Delta_s H_m^\theta(6)$ of reaction III is −53.32 kJ·mol^{-1}.

Standard Molar Enthalpies Change of the Coordination Reactions. According to Hess's law, the standard molar reaction enthalpies of the coordination reactions are obtained from

$$\begin{aligned}\Delta_r H_m^\theta(\text{I}) &= \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) + \Delta_s H_m^\theta(4) - \Delta_s H_m^\theta(5) - \Delta_s H_m^\theta(6) - \Delta_s H_m^\theta(7)\\ &= [31.10 + 75.27 - 245.91 - 46.03 + 48.07 + 348.55]\\ &\pm \left[\sqrt{0.32^2 + 0.40^2 + 0.37^2 + 0.33^2 + 0.49^2}\right]\\ &= (211.05 + 0.87)\ \text{kJ·mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H_m^\theta(\text{II}) &= \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) + \Delta_s H_m^\theta(4) - \Delta_s H_m^\theta(5) - \Delta_s H_m^\theta(6) - \Delta_s H_m^\theta(7)\\ &= [21.74 + 15.36 - 203.53 - 53.60 + 45.33 + 317.55]\\ &\pm \left[\sqrt{0.32^2 + 0.22^2 + 0.22^2 + 0.24^2 + 0.23^2}\right]\\ &= (142.85 + 0.56)\ \text{kJ·mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H_m^\theta(\text{III}) &= \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) + \Delta_s H_m^\theta(4) - \Delta_s H_m^\theta(5) - \Delta_s H_m^\theta(6) - \Delta_s H_m^\theta(7)\\ &= [121.38 - 102.25 - 2.17 + 24.70 + 53.33 + 128.82]\\ &\pm \left[\sqrt{0.48^2 + 0.32^2 + 0.08^2 + 0.06^2 + 0.60^2}\right]\\ &= (223.81 \pm 0.84)\ \text{kJ·mol}^{-1}\end{aligned}$$

Standard Molar Enthalpies of Formation of the Coordination Complexes According to Hess's law

$$\begin{aligned}\Delta_r H_m^\theta(\mathrm{I}) \quad & \Delta_f H_m^\theta[[\mathrm{Dy}(p\text{-NBA})_3\mathrm{phen}]_2\cdot 3\mathrm{H_2O(s)},\\ & 298.15\ \mathrm{K}] + 6\Delta_f H_m^\theta[\mathrm{HCl(g)},\ 298.15\ \mathrm{K}] +\\ & 11\Delta_f H_m^\theta \mathrm{H_2O(l)},\ 298.15\ \mathrm{K}] - 2\Delta_f H_m^\theta[\mathrm{DyCl_3}\cdot\\ & 6\mathrm{H_2O(s)},\ 298.15\ \mathrm{K}] -\\ & 6\Delta_f H_m^\theta[p\text{-HNBA(s)},\ 298.15\ \mathrm{K}] -\\ & 2\Delta_f H_m^\theta[\mathrm{phen}\cdot \mathrm{H_2O(s)},\ 298.15\ \mathrm{K}]\end{aligned}$$

According to refs 11 to 15

$$\Delta_f H_m^\theta[\mathrm{HCl(g)},\ 298.15\ \mathrm{K}] = -(92.31 \pm 0.10)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\ominus[\mathrm{H_2O(l)},\ 298.15\ \mathrm{K}] = -(285.83 \pm 0.04)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\theta[\mathrm{DyCl_3\cdot 6H_2O(s)},\ 298.15\ \mathrm{K}] = -2870\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\theta[p\text{-HNBA(s)},\ 298.15\ \mathrm{K}] = -(427.2 \pm 0.8)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\theta[m\text{-HNBA(s)},\ 298.15\ \mathrm{K}] = -(414.0 \pm 0.4)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\theta[o\text{-HClBA(s)},\ 298.15\ \mathrm{K}] = -(405.1 \pm 0.5)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\begin{aligned}\Delta_f H_m^\theta[\mathrm{phen\cdot H_2O(s)},\ 298.15\ \mathrm{K}] &=\\ &-(391.34 \pm 2.98)\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

So that

$$\begin{aligned}&\Delta_f H_m^\theta[[\mathrm{Dy}(p\text{-NBA})_3\mathrm{phen}]_2\cdot 3\mathrm{H_2O(s)},\ 298.15\ \mathrm{K}]\\ &= [211.05 - 6\cdot(-92.31) - 11\cdot(-285.83) + 2\cdot(-2870) +\\ &\qquad 6\cdot(-427.2) + 2\cdot(-391.34)]\\ &\pm\left[\sqrt{0.87^2 + (6\cdot 0.10)^2 + (11\cdot 0.04)^2 + (6\cdot 0.8)^2 + (2\cdot 2.98)^2}\right]\\ &= -(5177 \pm 8)\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

By the same token

$$\begin{aligned}&\Delta_f H_m^\ominus[[\mathrm{Dy}(m\text{-NBA})_3\mathrm{phen}]_2\cdot 4\mathrm{H_2O(s)},\ 298.15\ \mathrm{K}]\\ &= [142.85 - 6\cdot(-92.31) - 10\cdot(-285.83) + 2\cdot(-2870) +\\ &\qquad 6\cdot(-414.0) + 2\cdot(-391.34)]\\ &\pm\left[\sqrt{0.56^2 + (6\cdot 0.10)^2 + (10\cdot 0.04)^2 + (6\cdot 0.4)^2 + (2\cdot 2.98)^2}\right]\\ &= -(5452 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

and

$$\begin{aligned}&\Delta_f H_m^\theta[[\mathrm{Dy}(o\text{-ClBA})_3\mathrm{phen}]_2\mathrm{(s)},\ 298.15\ \mathrm{K}]\\ &= [224.09 - 6\cdot(-92.31) - 14\cdot(-285.83) + 2\cdot(-2870) +\\ &\qquad 6\cdot(-405.1) + 2\cdot(-391.34)]\\ &\pm\left[\sqrt{0.84^2 + (6\cdot 0.10)^2 + (14\cdot 0.04)^2 + (6\cdot 0.5)^2 + (2\cdot 2.98)^2}\right]\\ &= -(5317 \pm 7)\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

Experimental Discussion. When we calculated the standard molar enthalpies of formation of the complexes, we made the following approximations: (1) Compared with the dissolution enthalpy, it is feasible to ignore the small difference between the actual atmospheric pressure and standard atmospheric pressure in the course of determining $\Delta_r H_m^\theta$. (2) In the processes of estimating $\Delta_s H_m^\ominus(6)$ and measuring $\Delta_s H_m^\ominus(7)$, we neglected a very small amount of HCl volatilization, which is also feasible.

In this work, we determined the UV spectrum and refractive indexes of the final solution of the reactants and the final solution of the products; the experimental results suggested that both of them have similar UV spectra and equal refractive indexes. It proves that they have the same thermodynamics state and that the thermochemical cycle of the coordination reactions designed is reliable.

Conclusion

Dissolution calorimetry is a classical calorimetric method. As long as an appropriate calorimetric solvent is chosen, generally we can obtain a series of reliable data. In this work, the dissolution enthalpies of relevant substances were determined by a solution-reaction isoperibol calorimeter at 298.15 K, respectively. The calculated results based on experimental data indicated the standard molar enthalpy changes of reactions of the synthesis of the complexes were determined to be $\Delta_r H_m^\theta(\mathrm{I}) = (211.05 \pm 0.87)\ \mathrm{kJ\cdot mol^{-1}}$, $\Delta_r H_m^\theta(\mathrm{II}) = (142.85 \pm 0.56)\ \mathrm{kJ\cdot mol^{-1}}$, and $\Delta_r H_m^\theta(\mathrm{III}) = (223.81 \pm 0.84)\ \mathrm{kJ\cdot mol^{-1}}$, and the standard molar enthalpies of formation of the synthetic coordination compounds were estimated to be $\Delta_f H_m^\theta[[\mathrm{Dy}(p\text{-NBA})_3\mathrm{phen}]_2\cdot 3\mathrm{H_2O(s)},\ 298.15\ \mathrm{K}] = -(5177 \pm 8)\ \mathrm{kJ\cdot mol^{-1}}$, $\Delta_f H_m^\theta[[\mathrm{Dy}(m\text{-NBA})_3\mathrm{phen}]_2\cdot 4\mathrm{H_2O(s)},\ 298.15\ \mathrm{K}] = -(5452 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}$, and $\Delta_f H_m^\theta[[\mathrm{Dy}(o\text{-ClBA})_3\mathrm{phen}]_2\mathrm{(s)},\ 298.15\ \mathrm{K}] = -(5317 \pm 7)\ \mathrm{kJ\cdot mol^{-1}}$.

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