1762 *J. Chem. Eng. Data* **2008,** *53,* 1762–1766

Thermochemical Study of the Solid Complexes $Ln[(CH_3)_2NCS_2)]_3(C_{12}H_8N_2)$ (Ln = Eu, Gd, Tb, Dy)

Sanping Chen, Jin He, and Shengli Gao*

Shaanxi key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University,
Xi'an Shaanxi 710069, China

Four solid complexes $Ln(Me_2dtc)_3(phen)$ (Ln = Eu, Gd, Tb, Dy) have been prepared from the reactions of hydrous lanthanide chloride, sodium dimethyldithiocarbamate ($NaMe_2dtc$), and 1,10-phenanthroline ($phen\cdot H_2O$) in anhydrous ethanol. The title complexes were characterized by elemental analysis, IR spectroscopy, TG−DTG−DSC, and X-ray diffraction analysis. Their enthalpy changes of liquid-phase reactions of formation, $\Delta_r H^{\theta}_m(l)$, were determined at 298.15 K by a microcalorimeter, and the enthalpy changes of the solid-phase reactions of formation, $\Delta_r H^{\theta}_m(s)$, were calculated on the basis of a thermochemical cycle. The thermodynamics of reactions of formation of the complexes were studied via the reactions in solution. Combining the thermochemical data of the reactions and kinetic equations with the data of thermokinetic experiments, fundamental thermodynamic and kinetic parameters were achieved. The molar heat capacities of the title complexes were determined using an improved RD496-III type microcalorimeter at 298.15 K.

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1. Introduction

Complexes containing a lanthanide−sulfur bond have been extensively investigated for their favored performance in many paticular fields.[1–5] Many investigations on the preparation, characterization, and structures of these compounds have been documented.[6–9] We recently finished a series of thermodynamic studies of the reactions of rare earths with dimethyldithiocarbamate. This is of great importance in understanding the forces behind the coordination reaction systems and the energy associated with the reaction processes in the formation of coordination compounds.

Calorimetry represents an experimentally simple method for the determination of both the thermodynamic and kinetic parameters associated with chemical reaction systems.[10] The developed procedures 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.[11]

In this study, we describe the syntheses of four solid complexes $Ln(Me_2dtc)_3(phen)$ (Ln = Eu, Tb, Gd, Dy), which can be prepared and investigated using lanthanide chloride hydrate with sodium dimethyldithiocarbamate ($NaMe_2dtc$) and 1,10-phenanthroline ($phen\cdot H_2O$) in anhydrous ethanol. The complexes were characterized by elemental analysis, IR spectrum, TG−DTG−DSC, and X-ray diffraction analysis. The enthalpy changes of the liquid-phase reactions $\Delta_r H^{\theta}_m(l)$ at 298.15 K were measured by a microcalorimeter, and those of solid-phase $\Delta_r H^{\theta}_m(s)$ were obtained according to a designed thermochemical cycle. The thermodynamics of the liquid-phase reactions at four different temperatures were also investigated. On the basis of reaction thermodynamics and kinetic equations, fundamental parameters of the liquid-phase reaction, such as the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H^{\theta}_{\neq}$), the activation entropy ($\Delta S^{\theta}_{\neq}$), and the activation free energy ($\Delta G^{\theta}_{\neq}$), were caculated.

2. Experimental Section

Chemicals. $LnCl_3\cdot nH_2O$ (Ln = Eu, Gd, Tb, Dy; n = 3.94, 3.63, 3.75, 3.74) were prepared following the method developed previously.[12] The hydrated lanthanide trichlorides were prepared by heating the sesquioxides (with the exception that terbium for Tb_4O_7 was used), of 99.99 % purity from Alfa Aesar, with concentrated aqueous HCl. Under cooling with ice, the hydrated lanthanide trichlorides were precipitated with gaseous HCl, sucked off with a glass sinter crucible, and dried in a vacuum dryer over concentrated H_2SO_4. The water content of the hydrated lanthanide trichlorides was controlled by hydration curves with the lanthninde content determined with EDTA. Sodium dimethyldithiocarbamate (abbreviated $NaMe_2dtc$, with a mass fraction higher than 0.9950) and 1,10-phenanthroline (abbbrexiated o-$phen\cdot H_2O$, with a mass fraction higher than 0.9950) were commercially obtained from the Shanghai Reagent Factory (China). 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 (China). Potassium chloride (mass fraction 0.9999) was purchased from the Shanghai Reagent Factory (China) and dried in a vacuum oven at 500 K for 8 h prior to use. The γ-aluminum oxide is of spectroscopic pure grade from the Shanghai Reagent Factory (China). It was transformed to α-aluminum oxide in a muffle oven at 1473.15 K prior to use and maintained in a desiccator with P_4O_{10}.

Equipments and Analytical Methods. Elemental analyses were carried out using a Vario EL III CHNOS instrument (Germany). IR spectra were recorded on a EQUINOX-55 series FT-IR spectrophotometer (KBr pellets) in the range (4000 to 400) cm^{-1}. X-ray diffractions were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker CCD diffractometer for $Eu(Me_2dtc)_3(phen)$ at 298(2) K. TG−

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* Corresponding author. E-mail: gaoshli@nwu.edu.cn.

10.1021/je8000969 CCC: $40.75

DTG−DSC tests were performed on a NETZSCH STA 449C instrument under a dynamic atmosphere of high purity N_2 with a heating rate of 5 °C·min^{-1}. The XRD patterns were recorded using a Rigaku D/Max-III type X-ray power diffractometer with a scanning rate of 4 deg·min^{-1}.

The calorimetric experiment was performed using an improved RD496-III type microcalorimeter.[13] ICP-OES spectroscopy was carried out to check the progress of the reaction occurring in the calorimetric experiments using a Perkin-Elmer ICP Liberty 150 instrument. The purity of the compound was verified by an HP-1100-type high-performance liquid chromatography analyzer: the solvent was CH_2Cl_2, the rinsing reagent was CH_2Cl_2, and the column was contra-phase carbon-18.

Experimental Conditions of the Calorimetric Method. All the enthalpies of solution and those of reaction were measured by an improved RD496-III microcalorimeter.[13] The calorimetric constants at (295.15, 298.15, 301.15, and 304.15) K were determined by the Joule effect before the experiments, which were [(63.780 ± 0.018), (63.966 ± 0. 013), (64.172 ± 0. 052), and (64. 490 ± 0. 023)] μV·mW^{-1}, respectively.

The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in double-distilled water at 298.15 K. According to the molar ratio of KCl to water, $n_{\mathrm{KCl}}:n_{\mathrm{H2O}} \approx 1{:}500$, and a known amount of KCl is dissolved in double distilled water at (298.15 ± 0.001) K. The average enthalpy of dissolution of KCl, $\Delta_s H^{\theta}_{\mathrm{m,KCl}}$, determined from the six tests, was (17.581 ± 0.039) kJ·mol^{-1}, which is in agreement with the literature value of (17.584 ± 0.007) kJ·mol^{-1}.[14] The accuracy and the precision of the calorimeter were 0.02 % and 0.2 %, respectively.

Syntheses of the Complexes. $LnCl_3 \cdot nH_2O$ (Ln = Eu, Gd, Tb, Dy; n = 3.94, 3.63, 3.75, 3.74), NaMe$_2$dtc, and phen·H$_2$O (molar relation = 1/3/1) were dissolved independently in a minimal amount of anhydrous ethanol. To the mixed ethanolic solutions of phen·H$_2$O and NaMe$_2$dtc, the ethanolic solution of the salt was slowly added dropwise under electromagnetic stirring. The reaction mixture was allowed to stand for 1 h and filtered. The crude product was washed with three small portions of absolute ethanol and purified with dichloromethane. The resulting crystals were dried in a vacuum and stored in a desiccator over P_4O_{10} ready to be used.

3. Results and Discussion

IR Spectra of the Complexes. The IR spectra of the title complexes are similar to each other. For example, the IR spectrum of complex Eu(Me$_2$dtc)$_3$(phen) was identified as follows. The characteristic absorption of the hydroxyl group is not present in the complex, showing that the complex does not contain water. The peaks at (1622, 1588, 1567, and 1510) cm^{-1} are assigned to the skeleton vibration of the benzene ring, and the peaks at (841 and 721) cm^{-1} are assigned to the bend vibration of C−H in the complex, which displays certain shifts in contrast with those of (1617, 1587, 1561, and 1504) cm^{-1} and (854 and 739) cm^{-1} in the ligand. Two nitrogen atoms in the ligand of phen·H$_2$O coordinate to Eu^{3+}. The changes of ν_{CN} and ν_{CS} indicate that the two sulfur atoms of the ligand coordinate to Eu^{3+} in a bidentate manner. The molecular structure of the complex is illustrated in Figure 1.

Description of the Crystal Structure. The single-crystal structure of Eu(Me$_2$dtc)$_3$(phen) was obtained. Crystal data and structure refinement details are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

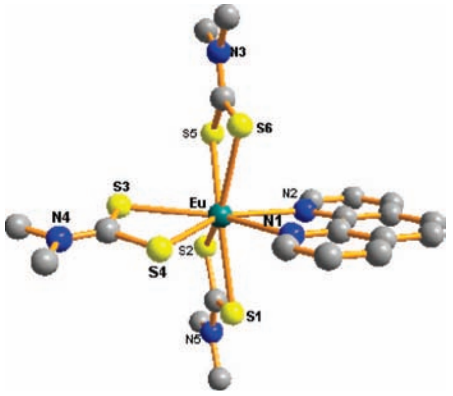

Figure 1. Molecular structure of Eu(Me$_2$dtc)$_3$(phen).

Table 1. Crystal Data and Structure Refinement Summary for Eu(Me$_2$dtc)$_3$(phen)

empirical formula	$C_{21}H_{26}EuN_5S_6$
formula weight	692.79
temperature (K)	273(2)
crystal system	monoclinic
space group	triclinic
a (Å)	9.6386(10)
b (Å)	10.1249(10)
c (Å)	16.3820(17)
α (°)	93.0620(10)
β (°)	103.8200(10)
γ (°)	114.2580(10)
V (Å^3)	1394.5(2)
Z	2
D_{calc} (g·cm^{-3})	1.650
μ (mm^{-1})	2.718
F(000)	692
θ range for data collection (°)	1.30 to 27.80
limiting indices	$-12 \le h \le 12$
	$-12 \le h \le 12$
	$-11 \le h \le 21$
crystal size (mm^3)	0.20 × 0.11 × 0.08
numbers of reflections	total: 8464
	unique: 6108 (R_{int} = 0.0261)
goodness-of-fit on F^2	1.026
final R indices[$I > 2\sigma(I)$]	R_1 = 0.0484, wR_2 = 0.0872
R indices (all data)	R_1 = 0.0745, wR_2 = 0.0991 wR_2 = 0.1192
largest peak and hole (e /Å^{-3})	1.058 and −1.041

Table 2. Select Bond Lengths (Å) and Bond Angles (°) for Eu(Me$_2$dtc)$_3$(phen)

Eu(1)−N(1)	2.621(5)	Eu(1)−N(2)	2.591(5)
Eu(1)−S(1)	2.8483(17)	Eu(1)−S(2)	2.8653(16)
Eu(1)−S(3)	2.8362(16)	Eu(1)−S(4)	2.8722(18)
Eu(1)−S(5)	2.8380(16)	Eu(1)−S(6)	2.8230(17)
S(1)−C(13)	1.719(7)	C(19)−N(3)	1.326(7)
S(1)−Eu(1)−S(2)	62.33(5)	S(3)−Eu(1)−S(4)	61.77(5)
S(5)−Eu(1)−S(6)	62.73(5)	N(2)−Eu(1)−S(5)	81.31(11)
N(2)−Eu(1)−S(6)	86.14(11)	S(6)−Eu(1)−S(3)	97.58(6)
N(1)−Eu(1)−S(5)	125.11(11)	N(1)−Eu(1)−S(2)	131.24(12)
N(1)−Eu(1)−S(3)	140.72(11)	N(2)−Eu(1)−S(3)	155.84(11)

Figure 1 illuminates the molecular structure of Eu(Me$_2$dtc)$_3$(phen), in which the Eu(III) ion has a coordination number of 8, the dithiocarbamates are bidentate, and the neutral phenanthroline fills the coordination sphere. The Eu−S bond distances range from 2.8230(17) to 2.8722(18), which are close to the reported values for trivalent europium Eu−S[15] and also close to similar dithiocarbamate complexes (2.783(1) to 2.914(2)).[16] These data are accordant to values predicted by the summation of ionic radii for eight coordinate Eu^{3+} and S^{2-} (2.90 Å).[17] In this dithiocarbamate complex, the largest C−S bond distance is only 1.728(6), significantly shorter than the idealized C−S single bond (1.81 Å).[18] The C−N bond lengths range from 1.326(7) to 1.336(7), which are between a single bond (1.47 Å) and a double bond (1.30

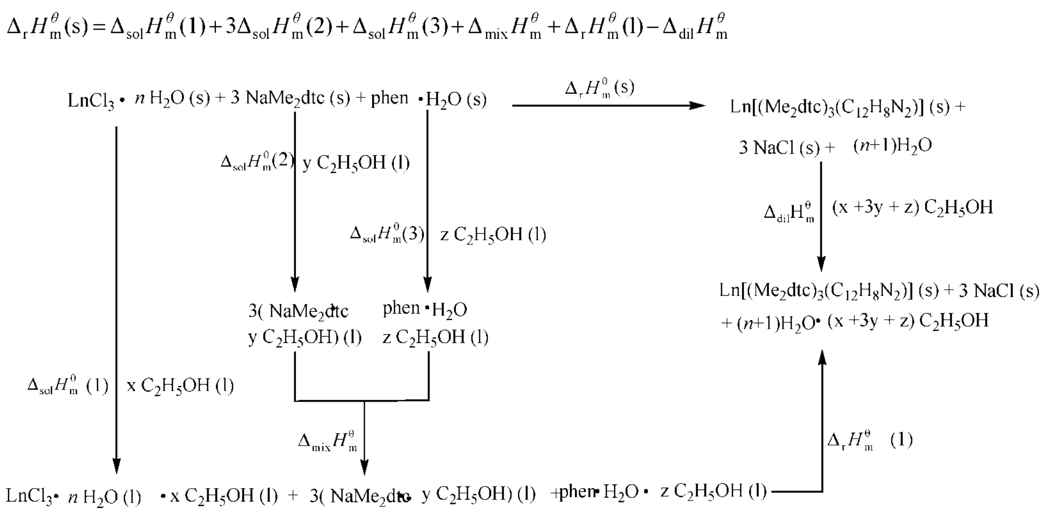

Figure 2. Thermochemical cycle for calculating the enthalpy change of the reaction of the formation of the complex $Ln(Me_2dtc)_3(phen)$ in the solid state.

Table 3. Enthalpy Changes of Reactions in Ethanol and Those in the Solid State for the Complexes

complex	no.	Q mJ	$\Delta_r H_m^\theta(l)$ $kJ \cdot mol^{-1}$	$\Delta_r H_m^\theta(s)$ $kJ \cdot mol^{-1}$
Eu $(Me_2dtc)_3(phen)$	1	−159.324	−9.958	117.107 ± 0.123
	2	−158.156	−9.885	
	3	−155.978	−9.749	
	4	−158.713	−9.920	
	5	−158.208	−9.888	
	6	−157.303	−9.831	
	$(\bar{x} \pm \sigma_a)^a$	−157.947 ± 0.479	−9.872 ± 0.030	
$Gd(Me_2dtc)_3(phen)$	1	−312.981	−19.561	97.053 ± 0.121
	2	−315.346	−19.709	
	3	−313.831	−19.614	
	4	−316.931	−19.808	
	5	−317.120	−19.820	
	6	−312.075	−19.505	
	$(\bar{x} \pm \sigma_a)^{a,a}$	−314.714 ± 0.853	−19.670 ± 0.053	
$Tb(Me_2dtc)_3(phen)$	1	−476.922	−29.808	80.392 ± 0.092
	2	−475.314	−29.707	
	3	−472.125	−29.508	
	4	−473.550	−29.597	
	5	−474.709	−29.669	
	6	−475.028	−29.689	
	$(\bar{x} \pm \sigma_a)^a$	−474.608 ± 0.666	−29.663 ± 0.042	
$Dy(Me_2dtc)_3(phen)$	1	−162.914	−10.182	108.279 ± 0.363
	2	−164.995	−10.312	
	3	−162.006	−10.125	
	4	−163.562	−10.223	
	5	−163.605	−10.225	
	6	−162.736	−10.171	
	$(\bar{x} \pm \sigma_a)^a$	−163.303 ± 0.415	−10.206 ± 0.026	

[a] $\sigma_a \sqrt{\sum_{i=1}^{6}(x_1 - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i is a simple value in a set of measurements; and $\bar{x}$ is the mean value of a set of measurement results.

Å).[19] The Eu−N bond distance is approximately 2.606(5), which is close to previously reported trivalent, eight coordinate europium complexes (2.52(1) Å[20] and 2.54 to 2.67 Å[21]).

Thermostability of $Ln(Me_2dtc)_3(phen)$. The TG−DTG−DSC curves indicate that the four complexes experience a similar step of weight loss, and thermal decomposition occurs in one step. The decomposition pathway was further investigated under a vacuum at 900 °C. On the basis of the X-ray powder diffraction pattern, the resulting decomposition residuals were identified as lanthanide sulfides, which reveals that the title complexes could be favorable precursors to prepare lanthanide sulfides.

Calculation of the Standard Molar Enthalpy Changes for the Reactions in the Solid State. The molar enthalpies of $\Delta_{sol}H_m^\theta(2)$, $\Delta_{sol}H_m^\theta(3)$, and $\Delta_{mix}H_m^\theta$ in anhydrous ethanol at 298.15 K are given in Table S1 of the Supporting Information, respectively. The molar enthalpies of solution $\Delta_{sol}H_m^\theta(1)$ for $LnCl_3 \cdot nH_2O$ in anhydrous ethanol at 298.15 K are listed in Table S2 of the Supporting Information. The enthalpy of dilution of water in ethanol is so small that it can be regarded as zero. Figure 2 gives an experimental thermochemical cycle, from which the enthalpy changes of the reactions of the formation in the solid state at 298.15 K can be derived. The enthalpy changes of reactions in ethanol and those in the solid state for the complexes are listed in Table 3.

The crude products of liquid-phase reactions from the calorimetric experiments were collected and separated by centrifugal effect, and they were purified and identified as the general formula of $Ln(Me_2dtc)_3(C_{12}H_8N_2)$ as that obtained in

Table 4. Thermodynamic and Kinetic Parameters of the Reactions in Ethanol

$LnCl_3 \cdot nH_2O + NaMe_2dtc + o$-phen	T K	$k \cdot 10^{-3}$ S^{-1}	n	E $kJ \cdot mol^{-1}$	ln A	$\Delta G^{\theta}_{\neq}$ $kJ \cdot mol^{-1}$	$\Delta H^{\theta}_{\neq}$ $kJ \cdot mol^{-1}$	$\Delta S^{\theta}_{\neq}$ $J \cdot mol^{-1} \cdot K^{-1}$
Eu^{3+}	295.15	4.4387	0.6853	28.31	6.1173	85.2721	25.0675	−202.4020
	298.15	4.9806	0.6874			85.9529		
	301.15	5.5653	0.6820			86.6330		
Gd^{3+}	304.15	6.2505	0.6847			87.2895		
	295.15	4.0905	0.7778	39.76	10.7050	85.7545	37.2642	−164.2582
	298.15	4.8479	0.7750			86.2301		
	301.15	5.6846	0.7736			86.7242		
	304.15	6.6072	0.7793			87.232		
Tb^{3+}	295.15	3.7775	0.8503	30.27	6.7535	85.9498	27.7754	−197.1126
	298.15	4.2548	0.8559			86.5518		
	301.15	4.8161	0.8532			87.1393		
	304.15	5.4388	0.8564			87.7250		
Dy^{3+}	295.15	4.0737	0.7533	27.73	5.7956	85.7646	25.2380	−205.0766
	298.15	4.5542	0.7515			86.3850		
	301.15	5.0838	0.7540			87.0039		
	304.15	5.6942	0.7555			87.6089		

Table 5. Data of the Heat and Heat Capacities of the Empty Cell and the Standard Substances

experimental data	empty cell	α-Al_2O_3	benzoic acid
q (1) (mJ)	7940.761	8347.927	8620.310
q (2) (mJ)	7953.287	8349.710	8633.710
q (3) (mJ)	7958.855	8372.466	8603.060
q (4) (mJ)	7933.804	8361.101	8633.198
q (5) (mJ)	7930.113	8350.931	8629.164
q (6) (mJ)	7936.176	8369.453	8614.664
$(\bar{x} \pm \sigma_a)$ (mJ)	7942.166 ± 4.674	8358.598 ± 4.351	8622.351 ± 4.928
precision $(\sigma_a/\bar{x})$	$5.884 \cdot 10^{-4}$	$5.206 \cdot 10^{-4}$	$5.715 \cdot 10^{-4}$
m/g		3.26468	2.90230
c $(J \cdot mol^{-1} \cdot K^{-1})$		79.098 ± 2.364	145.202 ± 1.627
c_0 from lit. $(J \cdot mol^{-1} \cdot K^{-1})$		79.03[24]	145.327[25]
accuracy $(c_0 - c)/c_0$		$8.604 \cdot 10^{-4}$	$1.080 \cdot 10^{-3}$

Table 6. Data of the Specific Heat Capacities of the Complexes at 298.15 K

Ln	m/g	q/mJ	$C/(J \cdot mol^{-1} \cdot K^{-1})$
Eu	3.51197	8408.126 ± 2.780	82.194 ± 0.774
Gd	2.63882	8347.454 ± 5.332	95.147 ± 1.344
Tb	2.61408	8326.433 ± 5.649	91.066 ± 1.402
Dy	2.49082	8276.680 ± 7.089	83.198 ± 1.705

the direct synthesis. The concentration of Ln^{3+} left in the centrifugal liquid was determined as the numerical value of $6 \cdot 10^{-3}$ $\mu g \cdot mL^{-1}$ by the ICP-AES experiment, indicating the starting reactants were transformed fully to the title products. All of these indicate that the final thermodynamic states of title solid reaction and that of liquid-phase reaction are the same, and the designed thermochemical cycle is reasonable.

Calculation of the Thermodynamic Parameters for the Reactions in the Liquid State. The calorimetric experiment showed that these reactions are exothermic. On the basis of the thermodynamic equations[22] and thermokinetic data of the reactions in solution at different temperatures as shown in Table S3 of the Supprting Information, the thermodynamic parameters and kinetic parameters of the reactions in solution are obtained and shown in Table 4.

Molar Heat Capacities of the Title Complexes. The molar specific heat capacities of the complexes were measured according to ref 23 (measuring six times for each sample), and their molar specific heat capacities were calculated from the data in Table 5 and presented in Table 6.

4. Conclusions

The result of the experiment showed that the title solid complexes can be easily synthesized in absolute ethanol by reacting with the mixed ligands of $NaMe_2dtc$ and o-phen.

By an improved RD496-III microcalorimeter through a designed thermochemical cycle, the standard molar enthalpies of the reactions for the solid-phase reaction, $LnCl_3 \cdot nH_2O(s) + 3(NaMe_2dtc)(s) + (phen \cdot H_2O)(s) = Ln(Me_2dtc)_3(phen)(s) + (n + 1)H_2O(l) + 3NaCl(s)$, were derived as [(117.107 ± 0.123), (97.053 ± 0.121), (80.392 ± 0.092), and (108.279 ± 0.363)] $kJ \cdot mol^{-1}$ at 298.15 K, when Ln represents Eu, Gd, Tb, and Dy, respectively.

On the basis of thermokinetic data of the liquid-phase reactions at four different temperatures, the thermodynamic parameters and kinetic parameters of the reactions in the liquid state were obtained.

The molar heat capacities of the title complexes were determined at 298.15 K using an improved RD496-III type microcalorimeter, which were [(82.194 ± 0.774), (95.147 ± 1.344), (91.066 ± 1.402), and (83.198 ± 1.705)] $J \cdot mol^{-1} \cdot K^{-1}$.

Supporting Information Available:

Tables S1 to S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review February 8, 2008. Accepted May 16, 2008. This work was supported by the NNSF of China (Grant No. 20771089), the National Natural Science Fundation of Shaanxi Province (Grant No. 2007B02), Shaanxi Physico-chemical Key Laboratory, and Shaanxi Key Laboratory of Chemical Reaction Engineering.

JE8000969