Synthesis, Characterization, and Thermodynamic Study of the Coordination Compound $Cd(HNic)_2Cl_2(s)$

You-Ying Di,*,[†] Wei-Jie Gao,[†] Wei-Wei Yang,[†] Yu-Xia Kong,[†] and Zhi-Cheng Tan[‡]

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong, PRC, and
Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PRC

Nicotinic acid and cadmium chloride were used as the reactants, absolute ethanol as solvent, and a novel coordination compound $Cd(HNic)_2Cl_2$ was synthesized by the method of liquid phase reaction. Chemical and elemental analyses, FTIR, and X-ray powder diffraction techniques were applied to characterize its composition and structure. Low-temperature heat capacities of the solid coordination compound have been measured by a precision automated adiabatic calorimeter over the temperature range from $T = 78$ K to $T = 400$ K. The experimental values of the molar heat capacities in the temperature region were fitted to a polynomial. Smoothed heat capacities and thermodynamic functions of the complex relative to 298.15 K were calculated based on the fitted polynomial and tabulated at 5 K intervals. In accordance with Hess's law, a reasonable thermochemical cycle was designed based on the preparation reaction of the new substance, and 100 mL of 0.1 M HCl solution was chosen as the calorimetric solvent. The standard molar enthalpies of dissolution for the reactants and products of the reaction in the selected solvent were measured by an isoperibol solution-reaction calorimeter. The enthalpy change of the liquid phase reaction was determined as $\Delta_r H_m^o = (23.46 \pm 0.30)\ kJ\cdot mol^{-1}$, and the standard molar enthalpy of formation of the complex was determined to be $-(1088.8 \pm 1.9)\ kJ\cdot mol^{-1}$ by means of the enthalpy change of the reaction and other auxiliary thermodynamic quantities.

Introduction

Nicotinic acid is also called Vitamin PP or Vitamin B_3. It is one of 13 kinds of vitamins required in the body. It has various remarkable uses in medicine or as a nutrient for growth. Cadmium exists broadly in the environment. It is severely dangerous to the health of animals and humans. Cadmium is mainly distributed in the liver and kidneys in animals. It impairs liver, kidney, spleen, and intestine function and induces immune suppression and cancer. Cadmium has a strong coordination tendency to some active molecules, such as nicotinic acid. The coordination of cadmium with some biologically active small molecules can facilitate the removal of cadmium from the body and can decrease the accumulation of the element in the human body.[1] In recent years, great attention has been paid to the application of nicotinic acid and its compounds with metals in many fields such as animal feed, pharmaceutical, and nutrient. Research work concerning the synthesis and crystal structure of the compounds of nicotinic acid with many metals has been reported in large quantities. However, the synthesis, characterization, and thermochemical study of the coordination compound of nicotinic acid with cadmium chloride have not been discovered in the literature. As an important part of the research plan about the thermochemical study of the coordination behavior of biological metal elements with nicotinic acid, in this paper, the synthesis, characterization, and thermodynamic properties of a novel coordination compound, $Cd(HNic)_2Cl_2(s)$, are reported.

Experimental Section

Synthesis and Characterization of the Coordination Compound $Cd(HNic)_2Cl_2(s)$. Nicotinic acid and $CdCl_2\cdot 2.5H_2O(s)$ used as the reactants were of analytical grade with a labeled purity of more than 99.5 %, which was precisely weighed at the molar ratio of $n(HNic):n(CdCl_2\cdot 2.5H_2O(s)) = 2:1$. Absolute ethyl alcohol (A. R. grade) was chosen as solvent. The mixture of nicotinic acid and $CdCl_2\cdot 2.5H_2O(s)$ was added to a 3-neck flask with the absolute ethanol, heated at (70 ~ 75) °C and refluxed for 6 h. The final solution was cooled to room temperature and filtered. The filter cake was washed three times using absolute ethyl alcohol, filtered, and dried to a constant weight at l00 °C. Finally, the sample was placed in a vacuum desiccator at 50 °C to vacuum-dry for 6 h. The final product was white with a weight of 8 g. The theoretical content of Cd, Cl, C, H, and N in the compound has been calculated to be 26.17 %, 16.51 %, 33.55 %, 2.35 %, and 6.52 %, respectively. Chemical and element analyses have indicated that the content of Cd, Cl, C, H, and N in the compound is 26.15 %, 16.50 %, 33.49 %, 2.33 %, and 6.50 %, respectively. This shows the purity of the sample prepared was higher than 99.50 mol %. The content of cadmium of the sample was measured by five duplicate EDTA complex titrations, and that of chloride by precipitation titration with an acidic solution of $AgNO_3$. The contents of C, N, and H were determined by elemental analysis (model - 2400, Perkin-Elmer, USA).

FTIR (Nicolet 5700 FT-IR, USA, KBr) was used to determine the bond mode of the cadmium ion with nicotinic acid, and the range of the wavelength is (400 ~ 4000) cm^{-1}. Vibration characteristic absorptions of main groups obtained from the FTIR spectra of the title compound and nicotinic acid are listed in Table 1.

---

* To whom correspondence may be addressed. Fax: +86-635-8239121. E-mail: yydi@lcu.edu.cn; diyouying@126.com.
[†] Liaocheng University.
[‡] Chinese Academy of Sciences.

10.1021/je800141t CCC: $40.75

Table 1. Characteristic Vibration Absorptions of Main Groups Obtained from FTIR Spectra of the Title Compound and Nicotinic Acid (cm^{-1})

compound	$\nu_{C=O}$	$\nu_{-OH(-COOH)}$	$\nu_{C=N}$	$\nu_{C=C}$	ν_{C-N}	ν_{C-H}	δ_{ring}
$C_6H_5NO_2$	1708.2	2827, 2441	1491.3, 1417.2	1595.7	810.7, 748.5	1136.7, 1088.1, 1037.1	694.7
$Cd(HNic)_2Cl_2$	1701.6	2818, 2435	1540.7, 1433.0	1603.5	867.5, 766.0	1159.3, 1099.7, 1056.4	701.5

Table 2. Experimental Molar Heat Capacities of Anhydrous Cadmium Nicotinate $Cd(HNic)_2Cl_2(s)$ (M = 429.54 $g \cdot mol^{-1}$)

T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
78.67	48.53	185.34	123.6	298.01	230.3
80.83	50.38	188.54	126.0	301.17	234.0
83.17	52.52	191.88	128.6	304.17	237.6
86.17	54.68	195.00	131.7	307.33	241.2
89.00	56.71	198.17	135.0	310.50	244.1
91.83	58.78	201.51	137.6	313.67	247.4
94.83	60.78	205.33	140.7	317.00	251.1
97.83	62.92	209.33	144.0	320.17	256.0
100.67	65.21	212.50	147.5	323.37	259.2
104.71	67.44	215.83	150.6	326.50	263.6
108.85	69.60	219.17	153.5	329.67	267.1
111.78	71.37	222.33	156.7	332.67	271.2
114.82	72.95	225.50	159.4	336.00	274.7
118.01	74.78	228.67	162.2	339.17	278.3
121.05	76.50	232.17	165.4	342.50	282.8
123.94	78.34	235.50	168.6	345.83	286.7
127.00	80.49	238.83	171.7	349.17	291.4
130.17	82.33	242.67	174.8	352.67	295.3
133.21	84.29	246.55	178.3	356.00	299.2
136.40	86.33	249.61	180.8	359.33	303.3
139.29	88.41	252.83	183.5	362.67	307.0
142.48	90.76	255.90	187.1	366.07	310.7
145.50	93.19	258.97	190.4	369.26	314.5
148.72	95.02	262.01	193.8	372.46	318.4
152.67	98.31	265.33	197.4	375.80	322.2
156.69	100.4	268.67	200.3	379.14	326.3
159.83	103.6	271.83	203.8	382.34	330.4
163.00	106.3	275.17	207.3	385.53	334.1
166.17	108.3	278.44	209.6	388.87	338.4
169.33	111.6	281.81	213.4	391.76	341.6
172.50	114.3	285.03	216.3	394.95	345.5
175.67	116.5	288.41	220.1	398.14	349.2
178.83	118.6	291.47	222.6		
182.00	121.2	294.67	226.7		

It can be seen from Table 1 that, for nicotinic acid, the absorption peak of the O−H stretching vibration, γ_{O-H}, obviously shifted to a low wavenumber, and two strong absorption peaks appeared at (2827 and 2441) cm^{-1} owing to the strong intermolecular hydrogen bonds of nicotinic acid. The hydrogen bonds decrease the strength of the double bond of the carbonyl in the molecule, and as a result, the absorption peak of the C=O stretching vibration, $\gamma_{C=O}$, will shift to a low wavenumber, 1708.2 cm^{-1}. The absorption peak of the O−H stretching vibration, γ_{O-H}, of the free carbonyl was at 3500 cm^{-1}. As for the coordination compound, the absorption peak of the O−H stretching vibration γ_{O-H} of its carbonyl possessed almost the same characteristic absorption peaks relative to those of nicotinic acid. It was shown that the oxygen atom of the organic component in the complex was not coordinated and linked with the cadmium ion. The shifts of the γ_{O-H} absorption peaks were completely due to the change of the surroundings near the C−O bonds after the formation of the novel substance. In addition, the characteristic absorption $\nu_{C=N}$ of the C=N stretching symmetrical vibration on the pyridine ring in the complex has drifted to a high wavenumber, which indicates that the nitrogen atom on the pyridine ring is coordinated with the cadmium ion. In addition, a wide and strong absorption peak of the complex at 3434 cm^{-1} did not appear, which demonstrates that crystal water was not present in the title compound.

X-ray powder diffraction (XRD) was used to determine whether the new synthesized compound is novel or not. XRD spectra of nicotinic acid, $CdCl_2 \cdot 2.5H_2O(s)$, and $Cd(HNic)_2Cl_2(s)$ have been plotted in Figure 1. The step length of the powder diffraction angle was 0.01°; the wavelength was 0.154056 nm (Cu Kα1 radiation); the electric voltage was 36 kV; and the electric current was 20 mA. The scanning rate was $4° \cdot min^{-1}$, and a graphite monochromator was used for filtering. Figure 1 illustrates that four obvious absorption peaks are seen in the angle range of $2\theta = 25° \sim 30°$ in the diffraction chart of nicotinic acid; three distinct absorption peaks appeared near $2\theta = 12° \sim 17°$ in the chart of $CdCl_2 \cdot 2.5H_2O(s)$; and six characteristic absorption peaks are seen in the angle range of $2\theta = 13° \sim 20°$ in the chart of $Cd(HNic)_2Cl_2(s)$. Therefore, some novel characteristic peaks which are completely different from those of nicotinic acid and $CdCl_2 \cdot 2.5H_2O(s)$ appeared in the diffraction spectrum of $Cd(HNic)_2Cl_2(s)$. Therefore, a new substance was produced by the liquid-phase reaction of nicotinic acid with $CdCl_2 \cdot 2.5H_2O(s)$.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities over the temperature range $78 \le (T/K) \le 400$. The calorimeter was established in the Thermochemistry Laboratory of the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere.[2,3] Briefly, the calorimeter is mainly comprised of a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junction chromel−constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No.2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter, and a nominal resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The temperature difference between the sample cell and the inner adiabatic shield was kept at about 0.5 mK or smaller during the entire experimental process. The vacuum can was evacuated to 10^{-3}

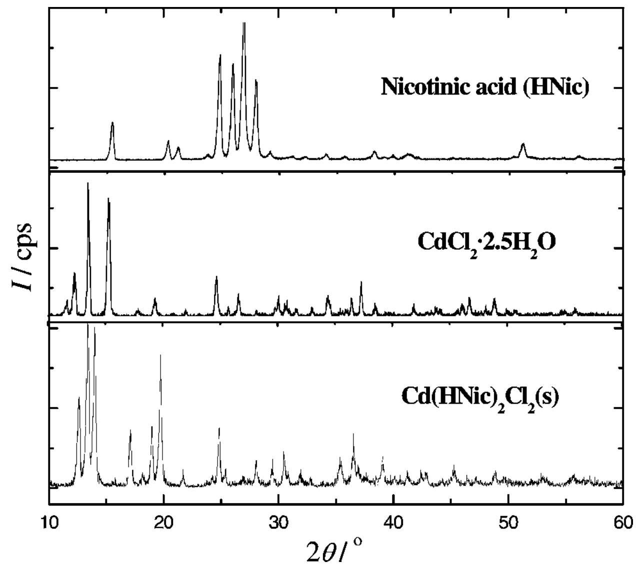

Figure 1. XRD spectra of nicotinic acid, $CdCl_2 \cdot 2.5H_2O(s)$, and $Cd(HNic)_2Cl_2(s)$.

Table 3. Smoothed Heat Capacities and Thermodynamic Functions of Anhydrous Cadmium Nicotinate $Cd(HNic)_2Cl_2(s)$

T / K	$C_{p,\mathrm{m}}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$H_T - H_{298.15\ K}$ / $kJ\cdot mol^{-1}$	$S_T - S_{298.15\ K}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$G_T - G_{298.15\ K}$ / $kJ\cdot mol^{-1}$
80	50.88	−28.74	−148.8	−16.84
85	53.91	−28.48	−145.7	−16.10
90	56.98	−28.20	−142.5	−15.38
95	60.07	−27.91	−139.3	−14.68
100	63.20	−27.60	−136.2	−13.99
105	66.36	−27.28	−133.0	−13.31
110	69.57	−26.94	−129.8	−12.66
115	72.81	−26.58	−126.7	−12.02
120	76.10	−26.21	−123.5	−11.39
125	79.44	−25.82	−120.3	−10.78
130	82.82	−25.42	−117.2	−10.19
135	86.25	−25.00	−114.0	−9.611
140	89.73	−24.56	−110.8	−9.049
145	93.27	−24.10	−107.6	−8.503
150	96.86	−23.62	−104.3	−7.973
155	100.5	−23.13	−101.1	−7.460
160	104.2	−22.62	−97.85	−6.962
165	108.0	−22.09	−94.59	−6.481
170	111.8	−21.54	−91.31	−6.016
175	115.7	−20.97	−88.02	−5.567
180	119.6	−20.38	−84.70	−5.135
185	123.6	−19.77	−81.37	−4.720
190	127.7	−19.15	−78.03	−4.321
195	131.8	−18.50	−74.66	−3.939
200	136.0	−17.83	−71.27	−3.574
205	140.2	−17.14	−67.86	−3.226
210	144.6	−16.43	−64.43	−2.895
215	148.9	−15.69	−60.98	−2.581
220	153.4	−14.94	−57.51	−2.285
225	157.9	−14.16	−54.01	−2.006
230	162.5	−13.36	−50.49	−1.745
235	167.2	−12.53	−46.94	−1.501
240	171.9	−11.69	−43.37	−1.275
245	176.7	−10.81	−39.78	−1.068
250	181.5	−9.918	−36.16	−0.8780
255	186.4	−8.999	−32.52	−0.7064
260	191.4	−8.054	−28.85	−0.5532
265	196.4	−7.085	−25.16	−0.4185
270	201.6	−6.090	−21.44	−0.3022
275	206.7	−5.069	−17.69	−0.2047
280	212.0	−4.022	−13.92	−0.1260
285	217.2	−2.950	−10.12	−0.06613
290	222.6	−1.850	−6.292	−0.02534
295	228.0	−0.7236	−2.440	−0.003725
298.15	231.4	0	0	0
300	233.5	0.4300	1.438	−0.001392
305	239.0	1.611	5.343	−0.01847
310	244.6	2.820	9.274	−0.05508
315	250.2	4.057	13.23	−0.1113
320	255.9	5.322	17.22	−0.1874
325	261.6	6.616	21.23	−0.2834
330	267.4	7.938	25.27	−0.3994
335	273.3	9.290	29.33	−0.5355
340	279.1	10.67	33.42	−0.6920
345	285.0	12.08	37.54	−0.8689
350	291.0	13.52	41.68	−1.066
355	297.0	14.99	45.85	−1.285
360	303.0	16.49	50.04	−1.524
365	309.1	18.02	54.26	−1.784
368	312.8	18.95	56.80	−1.950
374	320.1	20.85	61.92	−2.305
375	321.3	21.17	62.78	−2.367
380	327.5	22.80	67.07	−2.691
385	333.7	24.45	71.39	−3.037
390	339.9	26.13	75.73	−3.404
395	346.1	27.85	80.10	−3.794
400	352.3	29.59	84.50	−4.206

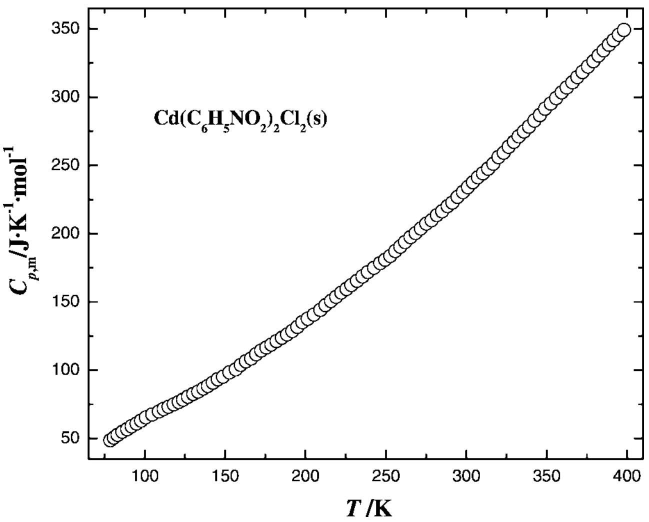

Figure 2. Relation curve of experimental molar heat capacities against the temperature ($C_{p,\mathrm{m}} \sim T$) of cadmium nicotinate bichloride $Cd(HNic)_2Cl_2(s)$.

Pa during the heat capacity measurements so as to eliminate heat transfer by convection. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a Data Acquisition/Switch Unit (model 34970A, Agilent, USA) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard material (α-Al_2O_3) were measured over the temperature range $78 \leq (T/K) \leq 400$. The sample mass used was 1.7324 g, which was equivalent to 0.01699 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ g\cdot mol^{-1}$. Deviations of the experimental results from those of the smoothed curve lie within ± 0.2 %, while the uncertainty is ± 0.3 %, as compared with the values given by the former National Bureau of Standards[4] over the whole temperature range.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $K\cdot min^{-1}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $K\cdot min^{-1}$ during the acquisition of all heat capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.[2] The sample mass of the novel compound used for the calorimetric measurements was 3.7166 g, which was equivalent to 0.00865 mol in terms of its molar mass, $M = 429.54\ g\cdot mol^{-1}$.

Isoperibol Solution-Reaction Calorimetry. The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere.[5]

The reliability of the calorimeter was verified previously[5] by measuring the dissolution enthalpy of KCl (calorimetrical primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was (17 547 ± 13) $J\cdot mol^{-1}$ for KCl, which compared with corresponding published data, (17 536 ± 3.4) $J\cdot mol^{-1}$.[6]

In all dissolution experiments of the sample, 100.00 mL of 0.1 $mol\cdot dm^{-3}$ HCl was chosen as the calorimetric solvent for respective measuring enthalpies of dissolution of HNic(s) and $Cd(HNic)_2Cl_2(s)$ in 0.1 $mol\cdot dm^{-3}$ HCl and $CdCl_2\cdot 2.5H_2O(s)$

Table 4. Dissolution Enthalpy of Nicotinic Acid in 0.1 M HCl at T = 298.15 K [$M(C_6H_5NO_2)$ = 123.11 g·mol^{-1}]^a

	W_{HNic}	ΔE_s	ΔE_e	t_e	Q_s	$\Delta_s H^o_{m,1}$
no.	g	mV	mV	s	J	kJ·mol^{-1}
1	0.12340	−3.4157	4.9177	47.141	15.912	15.874
2	0.12251	−3.2811	4.6302	46.422	15.986	16.064
3	0.12501	−3.4016	4.3596	44.516	16.879	16.623
4	0.12260	−3.3282	4.5717	46.172	16.335	16.403
5	0.12299	−3.2686	4.3977	45.484	16.428	16.444

Avg. $\Delta_s H^o_{m,1}$ = (16.28 ± 0.14) kJ·mol^{-1}

[a] W, Mass of sample; t_e, Heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)\cdot I^2Rt$, Heat effect during the sample dissolution; ΔE_s, The voltage change during the sample dissolution; ΔE_e, The voltage change during the electrical calibration; $\Delta_s H^o_{\text{HNic}} = Q_s/n = -(\Delta E_s/\Delta E_e)\cdot I^2Rt(M/W)$, where R is the electro-resistance (R = 1213.09 Ω at T = 298.15 K), I is the current (I = 20.015 mA), and M is the molar mass of the sample.

Table 5. Dissolution Enthalpy of Hydrated Cadmium Chloride in 0.1 M HCl Solution Containing Nicotinic Acid at T = 298.15 K [$M(CdCl_2\cdot 2.5H_2O)$ = 228.35 g·mol^{-1}]

	$W_{CdCl_2}\cdot 2.5H_2O$	ΔE_s	ΔE_e	t_e	Q_s	$\Delta_s H^o_{m,2}$
no.	g	mV	mV	s	J	kJ·mol^{-1}
1	0.11416	−1.2633	1.8066	36.734	4.545	12.483
2	0.11486	−1.2846	1.9540	38.751	4.743	12.380
3	0.11455	−1.2799	1.7038	33.687	3.733	12.298
4	0.11406	−1.2493	1.7440	34.750	3.889	12.097
5	0.11439	−1.2502	1.8054	36.752	3.905	12.367

Avg. $\Delta_s H^o_{m,2}$ = (12.33 ± 0.06) kJ·mol^{-1}.

Table 6. Dissolution Enthalpy of Cadmium Nicotinate Chloride in 0.1 M HCl Solution at T = 298.15 K [$M_{Cd(HNic)_2Cl_2}$ = 429.54 g·mol^{-1}]

	$W_{Cd(HNic)_2}Cl_2$	ΔE_s	ΔE_e	t_e	Q_s	$\Delta_s H^o_{m,3}$
no.	g	mV	mV	s	J	kJ·mol^{-1}
1	0.21419	−3.3338	4.1544	27.187	10.602	21.262
2	0.21470	−3.4776	4.4688	28.218	10.671	21.349
3	0.21478	−3.2863	4.2781	28.951	10.807	21.614
4	0.21428	−3.2122	4.2517	29.485	10.825	21.700
5	0.21506	−3.3074	4.6111	30.469	10.620	21.212

Avg. $\Delta_s H^o_{m,3}$ = (21.43 ± 0.10) kJ·mol^{-1}.

in 0.1 mol·dm^{-3} HCl solution containing certain amounts of the nicotinic acid at T = 298.15 K.

The solid HNic(s) and $CdCl_2\cdot 2.5H_2O$(s) were, respectively, ground within an agate mortar into a fine powder. About 1 mmol of HNic(s) when weighing at a mole ratio of $n(CdCl_2\cdot 2.5H_2O)$: n(HNic) = 1:2 was dissolved in 100 mL of 0.1 mol·dm^{-3} HCl at T = 298.15 K. The final solution obtained was named as solution A′. Then, about 0.5 mmol of $CdCl_2\cdot 2.5H_2O$(s) was dissolved in 100 mL of 0.1 mol·dm^{-3} HCl containing certain amounts of HNic(s). The final solution obtained was named as solution A.

The solid complex $Cd(HNic)_2Cl_2$(s) was dried in a vacuum desiccator to take off some additional adsorbing water. Then, it was ground into a fine powder. The dissolution enthalpy of about 0.5 mmol of $Cd(HNic)_2Cl_2$(s) in 100 mL of 0.1 mol·dm^{-3} HCl was determined under the same conditions as the above. The final solution obtained was named as solution B.

Finally, UV/vis spectroscopy and the data of the refractive indexes were used to confirm whether solution A was in the same thermodynamic state as that of solution B. These results have indicated that the chemical components and physicochemical properties of solution A were consistent with those of solution B.

Results and Discussion

Low-Temperature Heat Capacities. All experimental results, listed in Table 2 and plotted in Figure 2, showed that the structure of the coordination compound was stable over the temperature range between T = 78 K and T = 400 K; that is, no phase change, association, or thermal decomposition occurred. The 100 experimental points in the temperature region of (78 to 400) K were fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,m}$) vs reduced temperature (X), $X = f(T) = [T/\text{K} - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$ (where T_1 = 400 K and T_2 = 78 K) has been obtained

Table 7. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of $Cd(HNic)_2Cl_2$(s)

no.	reactions	formed solution	$\Delta_f H^o_m$ ($\Delta_s H^o_m \pm \sigma_a$)^a kJ·mol^{-1}
1	{HNic(s)} +"s" =	A′	(16.28 ± 0.14), ΔH_1
2	{$CdCl_2\cdot 2.5H_2O$} + solution A′ =	A	(12.33 ± 0.06), ΔH_2
3	{$Cd(HNic)_2Cl_2$(s)} + "s" =	B	(21.43 ± 0.10), ΔH_3
4	$6C(s) + 5/2H_2(g) + O_2(g) + 1/2N_2(g) = C_6H_5NO_2(s)$		−(344.81 ± 0.92), ΔH_4
5	$4C(s) + 5H_2(g) + 3O_2(g) + Cd(s) = CdCl_2\cdot 2.5H_2O(s)$		−1132.7, ΔH_5
6	$H_2(g) + 1/2O_2(g) = H_2O(l)$		−(285.83 ± 0.04), ΔH_6
7	$12C(s) + 5H_2(g) + N_2(g) + 2O_2(g) + Cl_2(g) + Cd(s) = Cd(HNic)_2Cl_2(s)$		−(1088.8 ± 1.9), ΔH_7

[a] $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \Big/ n(n-1)}$, in which n is experimental number; x_i is the experimental value of each series of repeated measurement; $\bar{x}$ is the mean value.

$$C_{p,m}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 170.923 + 152.540X + 34.135X^2 - 1.207X^3 - 4.050X^4 \quad (1)$$

in which $X = (T - 239)/161$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.3 % except for several points around the lower and upper temperature limits. The coefficient of determination for the fitting R^2 equals 0.9998. The uncertainties of the coefficients of the equation have been determined to be 0.08 %, 0.52 %, 0.49 %, 0.76 %, and 1.5 %, respectively.

Thermodynamic Functions of the Compound. The smoothed molar heat capacities and thermodynamic functions were calculated based on the fitted polynomial of the heat capacities as a function of the reduced temperature (X) according to the following thermodynamic equations

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T \quad (2)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p\cdot T^{-1}\mathrm{d}T \quad (3)$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \mathrm{d}T - T\cdot\int_{298.15}^{T} C_p\cdot T^{-1}\mathrm{d}T \quad (4)$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated in Table 3 at 5 K intervals. The uncertainties of $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ were evaluated to be ± 0.45 %, ± 0.48 %, and ± 0.53 %, respectively, mainly accounting for uncertainties in the temperature, experimental heat capacities, and relative deviations of the experimental heat capacities from the smoothed values.

Determination of Enthalpy Change of the Liquid Phase Coordination Reaction of $CdCl_2\cdot 2.5H_2O(s)$ with HNic(s). The liquid-phase coordination reaction of $CdCl_2\cdot 2.5H_2O(s)$ with nicotinic acid is shown as follows

$$2\text{HNic(s)} + \text{CdCl}_2\cdot 2.5\text{H}_2\text{O(s)} = \text{Cd(HNic)}_2\text{Cl}_2\text{(s)} + 2.5\text{H}_2\text{O(l)} \quad (5)$$

The enthalpy change of reaction 5 can be determined by respective measuring enthalpies of dissolution of the HNic(s) and $Cd(HNic)_2Cl_2(s)$ in 0.1 $mol\cdot dm^{-3}$ HCl solution and $CdCl_2\cdot 2.5H_2O(s)$ in 0.1 $mol\cdot dm^{-3}$ HCl solution containing certain amounts of nicotinic acid at 298.15 K.

The solid $CdCl_2\cdot 2.5H_2O(s)$ and HNic(s) were, respectively, ground within an agate mortar into a fine powder.

About 0.123 g of HNic(s) was dissolved in 100 mL of 0.1 $mol\cdot dm^{-3}$ HCl at 298.15 K. If "s" = calorimetric solvent, 0.1 $mol\cdot dm^{-3}$ HCl, then

$$\{\text{HNic(s)}\} + \text{"s"} = \text{solution A}'$$

The results obtained from five dissolution experiments are listed in Table 4.

The stoichiometric number of $CdCl_2\cdot 2.5H_2O(s)$ in reaction 5 or $[n(CdCl_2\cdot 2.5H_2O)/n(HNic)] = 1:2$ was regarded as a norm for sample weighing, about 0.5 mmol or 0.114 g of $(CdCl_2\cdot 2.5H_2O(s))$ was dissolved in the solution A', i.e.

$$\{\text{CdCl}_2\cdot 2.5\text{H}_2\text{O(s)}\} + \text{solution A}' = \text{solution A}$$

The results obtained from five dissolution experiments are listed in Table 5.

The dissolution enthalpy of $Cd(HNic)_2Cl_2(s)$ in 100 mL of 0.1 $mol\cdot dm^{-3}$ HCl at 298.15 K was measured under the same conditions as above

$$\text{Cd(HNic)}_2\text{Cl}_2\text{(s)} + \text{"s"} = \text{solution B}$$

The results obtained from five dissolution experiments are listed in Table 6.

In addition, the dilution enthalpy of the product $\{2.5H_2O(l)\}$ in reaction 5 is within the scope of the experimental error, cannot be measured, and may be omitted.

The enthalpy change of the liquid-phase coordination reaction 5 can be calculated in accordance with a thermochemical cycle and the experimental results as follows

$$\Delta_r H_m^o = \Sigma\Delta_s H^o_{m(\text{Reactants})} - \Sigma\Delta_s H^o_{m(\text{Products})} = 2\Delta_s H^o_{m,1} + \Delta_s H^o_{m,2} - \Delta_s H^o_{m,3} = 2\Delta H_1 + \Delta H_2 - \Delta H_3 = 2\cdot 16.282 + (12.325) - (21.427) = (23.46 \pm 0.30)\ \text{kJ}\cdot\text{mol}^{-1}$$

Standard Molar Formation Enthalpies of the Complex $Cd(HNic)_2Cl_2(s)$. A reaction scheme used to derive the standard molar formation enthalpy of $Cd(HNic)_2Cl_2(s)$ is given in Table 7. The experimental values of the dissolution enthalpies of the reactants and products in the solid-state coordination reaction 5 were combined with auxiliary thermodynamic data of $\Delta_f H_m^o(\text{HNic,s}) = -(344.81 \pm 0.92)$ $kJ\cdot mol^{-1}$,[7] $\Delta_f H_m^o(CdCl_2\cdot 2.5H_2O,s) = -1132.7$ $kJ\cdot mol^{-1}$,[8]and $\Delta_f H_m^o(H_2O,l) = -(285.83 \pm 0.04)$ $kJ\cdot mol^{-1}$ [9]to derive the standard molar enthalpy of formation of $Cd(HNic)_2Cl_2(s)$

$$\Delta_f H_m^o[\text{Cd(HNic)}_2\text{Cl}_2,\text{s}] = \Delta H_7 = \Delta_r H_m^o + 2\Delta_f H_m^o(\text{HNic, s}) + \Delta_f H_m^o(\text{CdCl}_2\cdot 2.5\text{H}_2\text{O, s}) - 2.5\Delta_f H_m^o(\text{H}_2\text{O, l}) = 2\Delta H_1 + \Delta H_2 - \Delta H_3 + 2\Delta H_4 + \Delta H_5 - 2.5\Delta H_6 = 23.462 + 2\cdot(-344.81) + (-1132.70) - 2.5\cdot(-285.83) = -(1088.8 \pm 1.9)\ \text{kJ}\cdot\text{mol}^{-1}$$

in which $\Delta H_1 \sim \Delta H_7$ are the enthalpy changes of the reactions corresponding to the number of reaction in Table 7.

In this paper, all of the reactants and products of the solid-state coordination reaction can be easily dissolved in the corresponding solvent. Solution A is in a thermodynamic equivalent state to solution B, as verified by UV spectroscopy and data of the refractive indexes.

Conclusions

1. The enthalpy change of the liquid phase reaction (5) obtained by solution calorimetry was determined to be (23.46 ± 0.30) $kJ\cdot mol^{-1}$ and is an endothermic reaction. On the basis of the thermodynamic theory, the liquid-phase synthesis reaction was not an enthalpy-driven process. However, all of the reactants were solid, and the products included a solid and a liquid. It is concluded from an increase of degree of chaos or disorder in the reaction that entropy change of the liquid-phase reaction is more than zero according to statistical explanation of the entropy of the system in statistical thermodynamics. Therefore, this synthesis reaction should be an entropy-driven process.

2. The standard molar enthalpy of formation of anhydrous $Cd(HNic)_2Cl_2(s)$ is negative with a larger absolute value, which showed that it has lower energy and a more stable structure than those of the stable elementary substances which it was made up from. The uncertainty of the standard molar enthalpy of formation obtained by isoperibol solution calorimetry was estimated to be between 0.3 % and 0.5 %, chiefly considering the measurements of voltage changes ΔE_s and ΔE_e, the duration time of electric calibration t, final data processing, and so on.

Literature Cited

(1) Gan, X. F.; Zheng, J. H.; Xie, J. S. Application of nicotinic acid and development of its downstream products. *J. Anhui Chem. Eng.* **2005**, *136* (4), 2–4.

(2) Tan, Z. C.; Sun, G. Y.; Sun, Y. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. *J. Therm. Anal.* **1995**, *45*, 59–67.

(3) Di, Y. Y.; Cui, Y. C.; Tan, Z. C. Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of the Solid-State Coordination Compound *trans*-$Cu(Gly)_2\cdot H_2O(s)$ (Gly = L-α-Glycine). *J. Chem. Eng. Data* **2006**, *51*, 1551–1555.

(4) Ditmars, D. A.; Ishihara, S.; Chang, S. S.; Bernstein, G. ; West, E. D. Enthalpy and heat-capacity standard reference material: synthetic sapphire (α-Al_2O_3) from 10 to 2250K. *J. Res. Natl. Bur. Stand.* **1982**, *87*, 159–163.

(5) Di, Y. Y.; Tan, Z. C.; Gao, S. L.; Wang, S. X. Determination of Standard Molar Enthalpy of Formation for the Coordination Compound Zn-(His)$Cl_2\cdot 1/2H_2O(s)$ by an Isoperibol Solution-Reaction Calorimeter. *J. Chem. Eng. Data* **2004**, *49*, 965–956.

(6) Rychly, R.; Pekarek, V. The Use of Potassium Chloride and Tris-(hydroxymethyl) Aminomethane as Standard Substances for Solution Calorimetry. *J. Chem. Thermodyn.* **1977**, *9*, 391–396.

(7) Sato-Toshima, T.; Kamagughi, A.; Nishiyama, K.; Sakiyama, M.; Seki, S. Enthalpies of combustion of organic compounds. IV. Acetaneilide and nicotinic acid. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 51–54.

(8) Yao, Y. B.; Xie, T.; Gao Y. M. *Handbook of Physical Chemistry*; Press of Science and Technology of Shanghai: Shanghai, 1984; p 848

(9) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: New York, 1984; pp 1.

Received for review February 26, 2008. Accepted April 20, 2008. This work was financially supported by the National Science Foundation of China under the contract NSFC No. 20673050.

JE800141T