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Synthesis, Characterization, and Thermodynamic Study of the Solid State Coordination Compound $Ca(Nic)_2(s)$ (Nic = Nicotinate)

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A novel compound, anhydrous calcium nicotinate $Ca(Nic)_2(s)$ (Nic = nicotinate), was synthesized by the method of room-temperature solid phase synthesis. FTIR, chemical, and elemental analyses and an X-ray powder diffraction technique were applied to characterize the structure and composition of the complex. 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 regions of (78 ~ 400) K were fitted to one polynomial. 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 were calculated and tabulated at intervals of 5 K. In accordance with Hess' law, a thermochemical cycle was designed; the enthalpy change of the solid phase reaction of nicotinic acid with calcium hydroxide was determined to be $\Delta_r H_m^o = -(9.121 \pm 0.336)$ $kJ \cdot mol^{-1}$ by use of an isoperibol solution-reaction calorimeter; and the standard molar enthalpy of formation of the complex $Ca(Nic)_2(s)$ was calculated to be $\Delta_f H^o_{Ca(Nic)_2} = -(1113.17 \pm 1.87)$ $kJ \cdot mol^{-1}$ by use of the enthalpies of dissolution and other auxiliary thermodynamic quantities.

1. Introduction

It is well-known that calcium is one of the trace elements necessary for humans, animals, and plants. Calcium is the root of life, which has important physiological functions and nutritional values and participates in many metabolic processes of cells in the body. It is necessary for growth of the bones in the human body, growth and propagation of cells, development of the brain, regular pulsation of the heart, maintaining normal permeability of blood vessels, helping in the coagulation of blood and the concrescence of wounds, activation of many kinds of enzymes in the human body, and promoting growth and development of issues. The shortening of calcium may result in many kinds of diseases, including sugar diabetes and cardiovascular diseases and so on. Nicotinic acid (abbreviated as HNic) is an important alkaloid and crude material in the fields of medicine, cosmetics, and nutrition, is used in therapy of many diseases in the human body, and can promote the absorption of calcium and other biological metals in humans and animals. The coordination compound (calcium nicotinate) of nicotinic acid with calcium as an organic calcium compound can facilitate the absorption of calcium in humans and animals and greatly enhance the utilization ratio of calcium in the body.[1,2] However, up to now, synthesis, characterization, and thermodynamic properties of the chelate compound $Ca(Nic)_2(s)$ have not been reported in the literature.

The method of solid state chemical synthesis has been widely used to synthesize various solid state coordination compounds of many metal salts with biologically active ligands because it avoids complicated experimental operations and harsh reaction conditions.[3] The purpose of the present study is to measure the low temperature heat capacities by adiabatic calorimetry and determine the dissolution enthalpies of the reactants and the products of the solid state coordination reaction of calcium(II) with nicotinic acid by isoperibol solution-reaction calorimetry. In addition, some thermodynamic parameters such as the enthalpy change of the synthesis reaction and the standard molar enthalpy of formation of the product $Ca(Nic)_2(s)$ were derived from these experimental results.

2. Experimental Section

2.1. Synthesis and Characterization of the Calcium Nicotinate $Ca(Nic)_2(s)$. Nicotinic acid and calcium hydroxide used as the reactants were of analytical grade with a labeled purity of more than 99.6 % and were accurately weighed at the molar ratio of $n(HNic):n(Ca(OH)_2) = 2:1$, mixed, and ground by a ball grinder. After grinding for 6 h at the rate of 400 rpm ($r \cdot min^{-1}$), the agate cup in the ball grinder was opened. The obtained solid product was scraped from the wall of the agate cup, and more small balls useful for grinding were put into the agate cup, and grinding continued for 5 h. Finally, the sample was placed in a vacuum desiccator at 130 °C to vacuum-dry for 6 h. If subsequent XRD measurement showed that the refraction peaks of the two reactants in the system of the solid-state coordination reaction had disappeared, the reaction was complete. The product was washed three times with absolute ethyl alcohol and once with ethyl ether of analytical grade. The final product was white with a weight of 10 g. Theoretical contents of Ca, C, O, H, and N in the compound have been calculated to be 14.10 %, 50.70 %, 22.51 %, 2.84 %, and 9.85 %, respectively. Chemical and elemental analyses (model: PE-2400, Perkin-Elmer, USA) have shown that practical contents of Ca, C, H, and N in the compound have been measured to be

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

compound	$\nu_{C=O}$	$\nu\text{-}_{OH(-COOH)}$	$\nu_{C=N}$	$\nu_{C=C}$	ν_{C-N}	ν_{C-H}	δ_{C-H}
HNic(s)	1708.2	2827.0	1491.3	1595.7	810.7	3071, 1137	694.7
		2441.4	1417.2		748.5	1088, 1037	
$Ca(Nic)_2(s)$	1666.5	/	1526.7	1599.8	811.8	3067, 1199	700.2
			1431.8		757.6	1091, 1032	

14.06 %, 50.67 %, 2.88 %, and 9.89 %, respectively. This showed that the purity of the sample prepared was higher than 99.50 mol %. The content of calcium in the sample was measured by EDTA complex titration. It was demonstrated from results of chemical analysis that no crystal H_2O exists in the coordination compound.

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

It can be seen from Table 1 that, as for nicotinic acid, the absorption peak of 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}. The absorption peak based on the association of its two molecules will shift to a low wavenumber due to formation of a hydrogen bond between the hydroxyl and carbonyl, and a wide peak appeared in (3200 to 2500) cm^{-1}. However, the organic component of the coordination compound possesses distinctly different characteristic absorption peaks relative to those of nicotinic acid, and especially the absorption peak of the O−H stretching vibration γ_{O-H} has disappeared in the title compound. It is shown that the oxygen atom of the organic component in the compound is directly linked with the calcium ion, and the hydrogen atom of −COOH in nicotinic acid has been replaced by the calcium ion so the carboxyl (−COOH) behaves as a carboxylate ($-COO^-$). The shifts in the absorption peaks result from 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 has been coordinated with the calcium ion. In addition, a wide and strong absorption peak at 3434 cm^{-1} does not appear in the FTIR of the complex, which showed that no crystal water exists in the compound.

The X-ray powder diffraction (XRD) technique was used to determine whether the new synthesized compound is novel or not. XRD spectra of nicotinic acid, calcium hydroxide, and calcium nicotinate have been plotted in Figure 1. The step length of the powder diffraction angle is 0.01°; wavelength is 0.154056 nm (Cu Kα 1 radiation); electric voltage is 36 kV; and electric current is 20 mA. The scanning rate is $4° \cdot min^{-1}$, and a graphite monochromator is used for the filtering. It was found from Figure 1 by comparison of three charts that four obvious diffraction peaks were seen in the angle range of $2\theta = 25° \sim 30°$ in the diffractogram of nicotinic acid, seven distinct diffraction peaks appeared near 2θ = 18°, 29°, 30°, 35°, 47°, 52°, and 55° in the chart of calcium hydroxide, and two characteristic diffraction peaks were seen near $2\theta = 22°$ in the chart of calcium nicotinate. Three other characteristic diffraction peaks were seen in the angle range of 2θ = 12°, 24°, and 33° in the chart of calcium nicotinate. Therefore, novel characteristic peaks different from those of nicotinic acid and calcium hydroxide appeared in the diffraction spectrum of calcium nicotinate. It was shown that a new substance was produced by the solid phase reaction of nicotinic acid with calcium hydroxide.

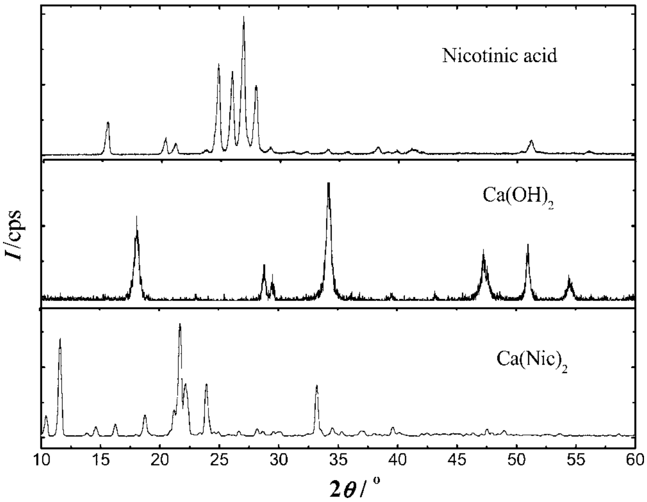

Figure 1. XRD spectra of nicotinic acid, calcium hydroxide, and anhydrous calcium nicotinate.

2.2. Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities of the compound over the temperature range $78 \leq (T/K) \leq 400$. 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 have been described in detail elsewhere.[3,4] Briefly, the calorimeter mainly comprised 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 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 1.7143 g, which was equivalent to 0.0168 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[5] 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.[4] The sample mass used for calorimetric measurements was 2.8961 g, which was equivalent to 0.0102 mol in terms of its molar mass, $M = 284.28\ g \cdot mol^{-1}$.

2.3. 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 are described in detail elsewhere.[3,6]

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. However, the input signal of the modified high-precision temperature controller (model: DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which worked in the PID (proportional-integral-derivative) mode, was not directly from the thermistor sensor but from the signal of the self-made Wheatstone electric bridge used for temperature controlling. The water was used as the thermostatic medium. During the whole experiment, the water thermostat was automatically maintained at $T = (298.150 \pm 0.001)$ K by regulating an adjustable precision resistor in the Wheatstone bridge. Experiments have demonstrated that the precision of temperature controlling of this kind of system can reach $\pm 1 \cdot 10^{-3}$ K.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the temperature measurement system, and the sampling system. The measuring temperature system consisted of a Wheatstone electric bridge similar to that of the controlling temperature system and another thermistor with large negative temperature coefficient of resistance. The thermistor used as a thermometer was calibrated on the basis of ITS-90 by the station of Low-Temperature Metrology and Measurements, Academia Sinica. A Data Acquisition/Switch Unit (model: 34970A, Agilent, USA) was used to determine the temperature of the solution in the chamber with an accuracy of 0.1 mK. The unbalanced voltage signal was a linear response to the change of temperature over the temperature range from (295 to 310) K. Measurements[6] indicate that the precision of the temperature measurement system can reach $\pm 1 \cdot 10^{-4}$ K at least, and the time constant of the calorimeter was about 3 s. The system of electric energy calibration consisted of the electric heater and the precision power supply with stepwise constant currents. During each electrical energy calibration, the electrical current through the heater was set at $I = 20.015$ mA, and the resistance of the electrical heater was $R = 1213.09\ \Omega$ at $T = 298.15$ K.

The reliability of the calorimeter was verified previously[3,6] by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17547 \pm 13)\ J \cdot mol^{-1}$ for KCl, which compared with corresponding published data, $(17536 \pm 3.4)\ J \cdot mol^{-1}$.[7]

Table 2. Experimental Molar Heat Capacities of Anhydrous Calcium Nicotinate $Ca(Nic)_2(s)$

T / K	$C_{p,m}$ / $(J \cdot K^{-1} \cdot mol^{-1})$	T / K	$C_{p,m}$ / $(J \cdot K^{-1} \cdot mol^{-1})$	T / K	$C_{p,m}$ / $(J \cdot K^{-1} \cdot mol^{-1})$
78.179	125.57	186.227	216.29	296.443	330.57
80.514	128.06	189.395	219.24	299.944	333.73
84.015	130.89	192.397	222.77	303.446	337.34
87.517	133.38	195.398	225.52	307.114	341.38
90.714	135.80	198.399	228.47	310.783	344.65
93.928	138.42	201.401	231.81	314.284	349.24
97.021	141.42	204.402	234.86	317.952	352.84
100.022	143.97	207.403	237.61	321.621	356.77
104.191	147.41	210.571	240.26	325.122	361.03
108.526	150.66	213.406	243.01	328.791	365.61
111.861	153.41	216.407	245.96	332.292	370.20
115.362	156.26	219.409	248.42	335.794	374.78
118.697	159.10	222.578	251.36	338.962	378.82
122.199	162.15	225.578	254.12	341.796	382.53
125.534	164.71	228.413	257.46	345.465	386.57
129.035	167.46	231.080	260.21	348.799	390.83
132.537	170.40	234.749	263.45	352.301	395.85
135.872	173.25	238.250	266.79	355.636	400.01
139.373	176.01	242.419	270.72	358.971	403.82
142.875	178.76	246.754	274.95	362.305	407.97
146.376	181.99	250.256	278.97	365.807	412.55
149.878	184.55	253.591	283.30	369.142	417.03
152.879	186.81	257.259	287.91	372.810	421.41
156.047	189.56	260.927	291.94	376.478	425.66
159.204	192.28	264.429	295.38	380.147	429.91
161.716	194.76	268.097	299.90	383.648	434.50
164.718	197.60	271.765	304.37	387.317	438.76
167.886	200.08	275.267	307.97	390.318	442.58
170.887	202.34	278.768	311.79	393.486	446.07
174.055	205.19	282.271	315.72	396.487	449.86
177.056	208.72	285.938	319.54	399.655	454.12
180.225	210.98	289.441	323.14		
183.226	213.64	292.941	326.75		

In all dissolution experiments of the sample, 100 mL of 0.5 $mol \cdot dm^{-3}$ HCl was chosen as the calorimetric solvent.

Finally, UV/vis spectra and the data of the refractive indexes were used to confirm whether initial solution was in the same thermodynamic state as that of the reacted solutions.

3. Results and Discussion

3.1. 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

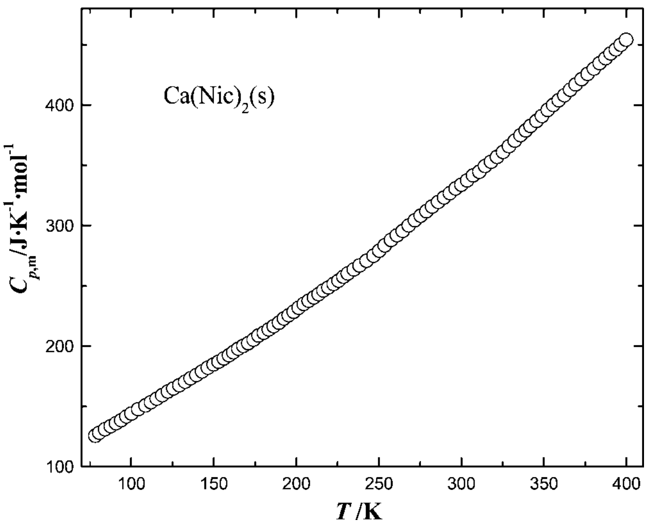

Figure 2. Relation curve of experimental molar heat capacities against the temperature ($C_{p,m} \sim T$) of calcium nicotinate $Ca(Nic)_2(s)$.

temperature range between $T = 78$ K and $T = 400$ K; that is, no phase change, association, or thermal decomposition occurred. The 97 experimental points in the temperature region between $T = 78$ K and $T = 400$ K were fitted by means of a least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,\mathrm{m}}$) versus reduced temperature (X), $X = f(T)$, has been obtained

$$C_{p,\mathrm{m}}/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 268.24766 + 163.94137X + 24.23705X^2 + 0.33261X^3 - 1.87481X^4 \quad (1)$$

in which $X = (T - 239)/161$. This equation is valid between $T = 78$ K and $T = 400$ K.

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 0.99995. The uncertainties of the coefficients of the equation have been determined to be 0.09 %, 0.6 %, 0.75 %, 0.96 %, 1.5 %, and 3.7 %, respectively.

3.2. 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

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

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

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

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 of the temperature, experimental heat capacities, and relative deviations of the experimental heat capacities from the smoothed values.

3.3. Determination of Enthalpy Change for the Solid State Coordination Reaction of Ca(OH)$_2$(s) with HNic(s). The solid-state coordination reaction of $\mathrm{Ca(OH)_2(s)}$ with nicotinic acid is shown as follows

$$2\mathrm{HNic(s)} + \mathrm{Ca(OH)_2(s)} = \mathrm{Ca(Nic)_2(s)} + 2\mathrm{H_2O(l)} \quad (5)$$

The enthalpy change of reaction (5) can be determined by measuring enthalpies of dissolution of the HNic(s) and $\mathrm{Ca(OH)_2(s)}$ in 0.5 $\mathrm{mol \cdot dm^{-3}}$ HCl and $\mathrm{Ca(OH)_2(s)}$ in 0.5 $\mathrm{mol \cdot dm^{-3}}$ HCl solution containing certain amounts of the nicotinic acid at 298.15 K.

The solid $\mathrm{Ca(OH)_2(s)}$ and HNic(s) were, respectively, ground within an agate mortar into a fine powder.

About 2 mmol or 0.246 g of HNic(s) was dissolved in 100 mL of 0.5 $\mathrm{mol \cdot dm^{-3}}$ HCl at 298.15 K. If "s" = calorimetric solvent, 0.5 $\mathrm{mol \cdot dm^{-3}}$ HCl, then,

$$\{\mathrm{HNic(s)}\} + \text{“s”} = \text{solution A}'$$

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

The stoichiometric number of $\mathrm{Ca(OH)_2(s)}$ in reaction (5) or $[n(\mathrm{Ca(OH)_2})/n(\mathrm{HNic})] = 1{:}\ 2]$ was regarded as a norm for sample weighing. About 1 mmol or 0.074 g of $\{\mathrm{Ca(OH)_2(s)}\}$ was dissolved in solution A′, i.e.,

$$\{\mathrm{Ca(OH)_2(s)}\} + \text{solution A}' = \text{solution A}$$

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

Table 3. Smoothed Heat Capacities and Thermodynamic Functions of Anhydrous Calcium Nicotinate

T / K	$C_{p,\mathrm{m}}$ / ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$H_T - H_{298.15\ \mathrm{K}}$ / ($\mathrm{kJ \cdot mol^{-1}}$)	$S_T - S_{298.15\ \mathrm{K}}$ / ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$G_T - G_{298.15\ \mathrm{K}}$ / ($\mathrm{kJ \cdot mol^{-1}}$)
80	127.88	−48.67	−265.6	27.42
85	131.75	−48.03	−257.8	26.11
90	135.65	−47.36	−250.2	24.84
95	139.57	−46.67	−242.7	23.61
100	143.52	−45.96	−235.5	22.42
105	147.49	−45.23	−228.3	21.26
110	151.51	−44.49	−221.3	20.14
115	155.55	−43.72	−214.5	19.06
120	159.62	−42.93	−207.7	18.01
125	163.73	−42.12	−201.1	16.98
130	167.87	−41.29	−194.6	15.99
135	172.04	−40.44	−188.2	15.04
140	176.26	−39.57	−181.8	14.12
145	180.51	−38.68	−175.5	13.23
150	184.79	−37.77	−169.4	12.36
155	189.12	−36.83	−163.2	11.53
160	193.49	−35.88	−157.2	10.73
165	197.90	−34.89	−151.2	9.954
170	202.35	−33.89	−145.2	9.209
175	206.84	−32.88	−139.3	8.494
180	211.37	−31.83	−133.5	7.808
185	215.95	−30.76	−127.6	7.151
190	220.57	−29.67	−121.8	6.523
195	225.24	−28.56	−116.1	5.924
200	229.95	−27.42	−110.3	5.354
205	234.70	−26.26	−104.6	4.813
210	239.50	−25.07	−98.90	4.301
215	244.35	−23.86	−93.22	3.819
220	249.24	−22.63	−87.56	3.365
225	254.17	−21.37	−81.91	2.940
230	259.16	−20.09	−76.27	2.544
235	264.19	−18.78	−70.64	2.178
240	269.27	−17.44	−65.02	1.839
245	274.39	−16.08	−59.40	1.531
250	279.56	−14.69	−53.79	1.250
255	284.78	−13.29	−48.19	0.999
260	290.04	−11.85	−42.60	0.776
265	295.35	−10.39	−37.01	0.581
270	300.71	−8.898	−31.42	0.415
275	306.12	−7.381	−25.83	0.277
280	311.57	−5.837	−20.25	0.167
285	317.06	−4.265	−14.67	0.084
290	322.60	−2.666	−9.091	0.031
295	328.19	−1.039	−3.513	0.003
298.15	331.73	0	0	0
300	333.82	0.6156	2.063	0.003
305	339.49	2.299	7.639	0.031
310	345.22	4.011	13.21	0.086
315	350.98	5.751	18.79	0.167
320	356.78	7.521	24.36	0.276
325	362.63	9.319	29.94	0.411
330	368.52	11.15	35.51	0.573
335	374.45	13.01	41.09	0.761
340	380.42	14.89	46.67	0.977
345	386.43	16.81	52.26	1.219
350	392.48	18.76	57.84	1.489
355	398.57	20.73	63.43	1.785
360	404.69	22.74	69.03	2.109
365	410.85	24.78	74.63	2.461
368	414.56	26.02	78.01	2.686
374	422.02	28.53	84.75	3.167
375	423.27	28.95	85.87	3.252
380	429.53	31.08	91.51	3.691
385	435.83	33.25	97.16	4.161
390	442.15	35.44	102.8	4.663
395	448.50	37.671	108.5	5.198
400	454.88	39.93	114.2	5.767

Table 4. Dissolution Enthalpy of Nicotinic Acid in 0.5 mol·dm^{-3} HCl [T = 298.15 K, M_{HNic}= 123.11 g·mol^{-1}]^a

no.	$W_{\mathrm{HNic(s)}}$ / g	$\Delta E_s/\Delta E_e$	t_e / s	Q_s / J	$\Delta_s H^o_{m,1}$ / kJ·mol^{-1}
1	0.24620	−1.0671	46.422	24.072	12.037
2	0.24629	−1.0872	46.359	24.493	12.243
3	0.24610	−1.0273	46.609	23.268	11.640
4	0.24602	−0.9980	46.828	23.197	11.608
5	0.24608	−1.0745	46.875	24.478	12.247
Avg. $\Delta_s H^o_{m,1}$ = (11.955 ± 0.140) kJ·mol^{-1}					

[a] W, Mass of sample; t_e, Heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)\cdot I^2 R t_e$, Heat effect during the sample dissolution; ΔE_s, The voltage change during the sample dissolution; ΔE_e, the voltage change during the electrical calibration; $\Delta_s H^o_{m,1} = Q_s/n = -(\Delta E_s/\Delta E_e)\cdot I^2 R t_e (M/W)$, where R is the electroresistance (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 Calcium Hydroxide in Solution A′ [T = 298.15 K, $M_{\mathrm{Ca(OH)_2}}$ = 74.09 g·mol^{-1}]

no.	$W_{\mathrm{Ca(OH)_2}}$(s) / g	$\Delta E_s/\Delta E_e$	t_e / s	Q_s / J	$\Delta_s H^o_{m,2}$ / kJ·mol^{-1}
1	0.07412	1.1638	175.375	−99.190	−99.150
2	0.07412	1.1655	175.329	−99.305	−99.265
3	0.07418	1.1604	175.359	−98.884	−98.765
4	0.07403	1.1585	175.859	−99.005	−99.095
5	0.07417	1.1558	175.375	−98.505	−98.534
Avg. $\Delta_s H^o_{m,2}$ = −(98.962 ± 0.135) J·mol^{-1}					

Table 6. Dissolution Enthalpy of Anhydrous Calcium Nicotinate Ca(Nic)$_2$(s) in 0.5 mol·dm^{-3} HCl [T = 298.15 K, $M_{\mathrm{Ca(Nic)_2}}$ = 284.28 g·mol^{-1}]

no.	$W_{\mathrm{Ca(Nic)_2}}$(s) / g	$\Delta E_s/\Delta E_e$	t_e / s	Q_s / J	$\Delta_s H^o_{m,3}$ / kJ·mol^{-1}
1	0.28487	1.1738	116.391	−66.392	−66.259
2	0.28482	1.1673	116.032	−65.824	−65.703
3	0.28432	1.1735	116.127	−66.227	−66.222
4	0.28439	1.1632	116.385	−65.788	−65.767
5	0.28427	1.1640	116.390	−65.824	−65.703
Avg. $\Delta_s H^o_{m,3}$ = −(65.931 ± 0.127) kJ·mol^{-1}					

The dissolution enthalpy of Ca(Nic)$_2$(s) in 0.5 mol·dm^{-3} HCl was measured under the same condition as the above

$$\{\mathrm{Ca(Nic)_2(s)}\} + \text{“s”} = \text{solution B}$$

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

In addition, the dilution enthalpy of product H$_2$O(l) in reaction (5) is within the scope of the experimental error, cannot be measured, and may be omitted. The enthalpy change of the solid state coordination reaction (5) can be calculated in accordance with a thermochemical cycle and the experimental results as follows

$$\Delta_r H^o_m = \sum \Delta_s H^o_{m(\mathrm{Reactants})} - \sum \Delta_s H^o_{m(\mathrm{Products})} = 2\Delta_s H^o_{\mathrm{HNic}} + \Delta_s H^o_{\mathrm{Ca(OH)_2}} - \Delta_s H^o_{\mathrm{Ca(Nic)_2}}$$
$$= 2\Delta H_1 + \Delta H_2 - \Delta H_3 = 2\cdot 11.955 + (-98.962) - (-65.931) = -(9.121 \pm 0.336)\ \mathrm{kJ\cdot mol^{-1}}$$

Table 7. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of Anhydrous Calcium Nicotinate Ca(Nic)$_2$(s)

no.	reactions	formed solution	$\Delta_f H^o_m$ or $(\Delta_s H^o_m \pm \sigma_a)^a$ (kJ·mol^{-1})
1	{HNic(s)} + “s” =	A′	(11.955 ± 0.140), ΔH_1
2	{Ca(OH)$_2$(s)} + solution A′ =	A	−(98.962 ± 0.135), ΔH_2
3	{Ca(Nic)$_2$(s)}+ “s” =	B	−(65.931 ± 0.127), ΔH_3
4	6C(s) + (5)/(2)H$_2$(g) + O$_2$(g) + (1)/(2)N$_2$(g) = HNic(s)		−(344.81 ± 0.92), ΔH_4
5	H$_2$(g) + O$_2$(g) + Ca(s) = Ca(OH)$_2$(s)		−986.09, ΔH_5
6	H$_2$(g) + (1)/(2)O$_2$(g) = H$_2$O(l)		−(285.83 ± 0.04), ΔH_6
7	12C(s) + 4H$_2$(g) + N$_2$(g) + 2O$_2$(g) + Ca(s) = Ca(Nic)$_2$(s)		−(1113.17 ± 1.87), ΔH_7

[a] $\sigma_a = \sqrt{(\sum_{i=1}^{5} (x_i - \bar{x})^2)/(n(n-1))}$, in which n is the experimental number; x_i is a single value in a set of dissolution measurements; and $\bar{x}$ is the mean value of a set of measurement results.

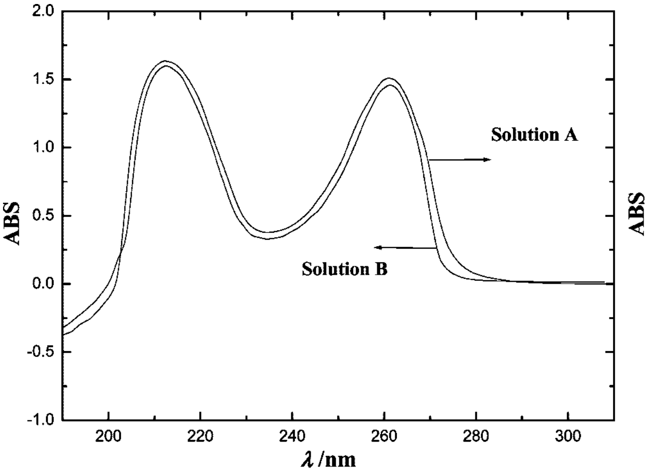

Figure 3. UV/vis spectra of solution A obtained from dissolution of the reactants in the solid phase reaction and solution B from dissolution of the products (diluted to 1:20).

3.4. Standard Molar Enthalpy of Formation of the Complex Ca(Nic)$_2$(s). A reaction scheme used to derive the standard molar enthalpy of formation of Ca(Nic)$_2$(s) is given in Table 7. The experimental values of the dissolution enthalpies of the reactants and products in the solid state coordination reactions (5) were combined with auxiliary thermodynamic data of $\Delta_f H^o_{\mathrm{Ca(OH)_2}} = -986.09$ kJ·mol^{-1},[8] $\Delta_f H^o_{\mathrm{HNic}} = -(344.81 \pm 0.92)$ kJ·mol^{-1},[9] and $\Delta_f H^o_{\mathrm{H_2O}} = -(285.83 \pm 0.04)$ kJ·mol^{-1},[10] to derive the standard molar enthalpy of formation of Ca(Nic)$_2$(s)

$$\Delta_f H^o_{\mathrm{Ca(Nic)_2}} = \Delta H_7$$
$$= \Delta_r H^o_m + 2\Delta_f H^o_{\mathrm{HNic}} + \Delta_f H^o_{\mathrm{Ca(OH)_2}} - 2\Delta_f H^o_{\mathrm{H_2O}}$$
$$= 2\Delta H_1 + \Delta H_2 - \Delta H_3 + 2\Delta H_4 + \Delta H_5 - 2\Delta H_6$$
$$= 11.955\cdot 2 + (-98.962) - (-65.931) + 2\cdot(-344.81) + (-986.09) - 2\cdot(-285.83)$$
$$= -(1113.17 \pm 1.87)\ \mathrm{kJ\cdot mol^{-1}}$$

in which $\Delta H_1 \sim \Delta H_7$ are the enthalpy changes of the reactions corresponding to number of reactions 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 solvents. The UV/vis spectra of solution A obtained from dissolution of the reactants in the solid phase reaction and solution B from dissolution of the product (diluted to 1:20) are shown in Figure 3. The experimental values of the refractive indexes of solution A and solution B were measured to be (1.340 ± 0.003) and (1.342 ± 0.004), respectively. These results indicate that solution A is in a thermodynamic equivalent state to solution B. There is no difference in the structure, chemical components, and physicochemical characteristic between the two solutions.

4. Conclusions

The enthalpy change of the solid phase reaction (5) obtained by solution calorimetry was determined to be $\Delta_r H_m^o = -(9.121 \pm 0.336)\ \text{kJ}\cdot\text{mol}^{-1}$, which is an exothermic reaction. On the basis of thermodynamic theory, the solid phase synthesis reaction was an enthalpy-driven process. Moreover, all of the reactants were solid, and the products included a solid and a stable liquid. From an increase of degree of disorder or chaos in the reaction, it is clear that the entropy change of the solid state reaction is more than zero. Therefore, this solid phase synthesis reaction was also an entropy-driven process. This is also propitious for the direction of the products under the mechanical force of the ball mill.

The standard molar enthalpy of formation of anhydrous calcium nicotinate $\Delta_f H^o_{\text{Ca(Nic)}_2} = -(1113.17 \pm 1.87)\ \text{kJ}\cdot\text{mol}^{-1}$, which is negative with a larger absolute value, showed that it has lower energy and more stable structure in comparison with 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_e, final data processing, and so on.

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