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Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$

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Low-temperature heat capacities of the solid coordination compound $Cr(C_6H_4NO_2)_3(s)$ have been measured by a precision automated adiabatic calorimeter over the temperature range $T = 78$ K to $T = 391$ K. The experimental values of the molar heat capacities in the temperature region were fitted to a polynomial equation of heat capacities ($C_{p,m}$) with the reduced temperatures (X), [$X = f(T)$], by a least-squares method. The smoothed molar heat capacities and thermodynamic functions of the complex $Cr(C_6H_4NO_2)_3(s)$ were calculated based on the fitted polynomial. The smoothed values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K are tabulated with an interval of 5 K. Enthalpies of dissolution of $\{3C_6H_5NO_2(s)\}$ [$\Delta_d H_m^{\ominus}(1)$] and $Cr(C_6H_4NO_2)_3(s)$ [$\Delta_d H_m^{\ominus}(3)$] in 100.00 mL of 0.1 $mol \cdot dm^{-3}$ HCl and $\{Cr(OH)_3(s)\}$ [$\Delta_d H_m^{\ominus}(2)$] in 100.00 mL of 0.1 $mol \cdot dm^{-3}$ HCl solution containing certain amounts of nicotinic acid (named as solution A_1) at $T = 298.15$ K were, respectively, determined to be [(14.44 ± 0.14), −(34.47 ± 0.26), and −(25.74 ± 0.13)] $kJ \cdot mol^{-1}$ by means of an isoperibol solution reaction calorimeter. The enthalpy change $\Delta_r H_m(5)$ of the designed solid-state coordination reaction of $Cr(OH)_3(s)$ with nicotinic acid can be calculated as $\Delta_r H_m(5) = (52.04 \pm 0.52)$ $kJ \cdot mol^{-1}$ in accordance with a thermochemical cycle and the experimental results. The standard molar enthalpy of formation of the compound was determined as $\Delta_f H_m^{\ominus}[Cr(C_6H_4NO_2)_3, s, 298.15 K] = -(1189.6 \pm 2.8)$ $kJ \cdot mol^{-1}$, from the enthalpies of dissolution and other auxiliary thermodynamic data.

Introduction

Chromium is an essential element. It exists in the form of Cr^{3+} in the human body. Great attention has been paid to the role of chromium in curing sugar diabetes and cardiovascular diseases. It was found from a lot of surveys, experimental, and clinical research that the reduction of chromium in the human body would deleteriously effect the metabolism of sugar and fat, increasing the risk of sugar diabetes and cardiovascular diseases. In the 1960s, Schroeder[1] suggested that the content of chromium in organisms would tend to decrease with age, which therefore requires regular supplement of chromium for growth and subsistence. Many reports have indicated that the absorption percentage of inorganic chromium by organisms is only (0.3 to 3) % but is (10 to 25) % for organic chromium. Nicotinic acid is an important alkaloid and crude material in the fields of medicine, domestic, and nutrition, is used to treat many diseases in the human body, and can promote absorption of chromium in humans and animals. The coordination compound (chromium nicotinate) of nicotinic acid with chromium as an organic chromium can facilitate the absorption of chromium in organisms and greatly enhance the utilization ratio of chromium in the biological body.[2]

The literature[1–3] has reported two kinds of chelate compounds of nicotinic acid with chromium, and the composition and structure of these complexes were characterized by elemental analysis, thermogravimetric analysis, UV and FTIR spectra, and X-ray crystallography. When nicotinic acid bonds to chromium(III), it is coordinated with the chromium(III) by two donor atoms (carboxylate oxygen and pyridine nitrogen). The chelate compound $Cr(C_6H_4NO_2)_3$ formed contains three chelate rings (six-membered rings) with the chromium(III) ion.[1] It was also shown that chromium nicotinate of bidentate coordination has been used as a new type of feed additive for pigs and has higher biological activity than other additives without toxicity, so it has broad prospects.[2] However, up to now, low-temperature heat capacities, thermodynamic functions, and standard molar enthalpy of formation of the chelate compound $Cr(C_6H_4NO_2)_3$ have not been reported in the literature. 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 designed solid-state coordination reaction of chromium(III) with nicotinic acid by isoperibol solution calorimetry. In addition, the thermodynamic functions and standard molar enthalpy of formation of the product $Cr(C_6H_4NO_2)_3$ were derived from these experimental results.

Experimental Section

Synthesis and Characterization of the Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$. The compound was synthesized according to the reported method in the literature.[1,3] An amount of 12.4 g of nicotinic acid was weighed and put into a beaker with a volume of 250 mL, and 20 mL of the water was added for wetness. The pH was adjusted to 8.0. The solid−liquid mixture was heated and kept at 80 °C until the solution was transparent. An amount of 8.8 g (0.033 mol) of $CrC1_3 \cdot 6H_2O$ was weighed, dissolved in 50 mL of water at a temperature of 80 °C, then added to the above sodium nicotinate solution under sufficient

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

compound	$\nu_{C=O}$	ν_{-OH}	$\nu_{C=N}$	$\nu_{C=C}$	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
$Cr(C_6H_4NO_2)_3$	1613.5	/	1525.5 1429.6	1619.2	858.5, 752.0	1147.2 1091.6 1041.5	708.7

stirring, and the pH was adjusted to 6.8 to 7.2. Then water was added to give a total volume of 120 mL. The final solution was cooled to room temperature and filtered. The filter cake was washed three times using deionized water, three times using ethyl alcohol (A. R.) with a concentration of 95 %, filtered, and dried to a constant weight at 110 °C.

Finally, the sample was placed in a vacuum desiccator at ambient temperature to vacuum dry for 6 h. The final product was gray with a weight of 14 g. Theoretical contents of Cr, C, H, and N in the compound have been calculated to be (12.43, 51.68, 2.89, and 10.05) %, respectively. The content of Cr^{3+} in the coordination compound was determined with five duplicate EDTA chemical titrations, and the contents of C, N, and H were determined by elemental analysis (model - 2400, Perkin-Elmer, USA). The contents of Cr, C, H, and N in the compound have been measured to be (12.47, 51.60, 2.84, and 10.01) %, respectively. This showed the purity of the sample prepared was higher than 99.90 mol %. FTIR was used to determine the bond mode of the chromium ion with nicotinic acid.

Vibration characteristic absorptions of the main functional groups of the compound and nicotinic acid obtained from FTIR spectral analysis are listed in Table 1.

It can be seen from Table 1 that, as for the 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 acids. 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 at (3200 to 2500) cm^{-1}. However, the organic component of the coordination compound possessed distinctly different characteristic absorption peaks relative to those of nicotinic acid, especially the absorption peak of the O−H stretching vibration γ_{O-H} which has disappeared in the title compound. It is shown that the oxygen atom of the organic component in the complex is directly linked with the chromium ion, and the hydrogen atom of COOH in nicotinic acid has been replaced by the chromium ion so that 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 chromium ion.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities 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 were described in detail elsewhere.[4,5] 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 $78 \leq (T/K) \leq 390$. 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·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 over the whole temperature range.[6]

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·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·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 3.5165 g, which was equivalent to 0.0084 mol in terms of its molar mass, $M = 418.304$ g·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.[5,7] The precisions of controlling and measuring the temperatures of the calorimeter were ± 0.001 K and ± 0.0001 K, respectively.

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetric primary standard) in double distilled water at $T = 298.15$ K.[7] The mean dissolution enthalpy was (17 597 ± 13) J·mol^{-1} for KCl, which compared with corresponding published data, (17 536 ± 3.4) J·mol^{-1}.[8]

In all dissolution experiments of the sample, 100.00 mL of 0.1 mol·dm^{-3} HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of $\{3C_6H_5NO_2(s)\}$, $\{Cr(OH)_3(s)\}$, and $Cr(C_6H_4NO_2)_3(s)$ at $T = 298.15$ K.

Table 2. Experimental Molar Heat Capacities of Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$ ($M = 418.304\ g\cdot mol^{-1}$)

T	$C_{p,\mathrm{m}}$	T	$C_{p,\mathrm{m}}$	T	$C_{p,\mathrm{m}}$
K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$	K	$J\cdot K^{-1}\cdot mol^{-1}$
78.295	123.81	163.846	240.81	268.501	397.46
79.579	125.36	165.847	243.11	271.485	402.07
80.785	127.92	167.870	246.05	274.548	406.39
83.268	130.33	169.894	248.77	277.774	410.55
85.751	132.64	171.909	251.87	280.837	415.32
87.667	134.61	173.844	254.46	283.982	420.08
88.873	136.08	175.860	257.44	287.046	425.14
90.151	137.63	177.795	260.13	290.110	429.31
91.995	139.67	179.730	262.72	293.254	432.73
93.272	141.41	181.665	265.17	296.237	436.89
94.621	142.98	183.601	268.44	299.140	441.06
95.898	144.85	185.616	271.07	302.204	445.38
97.317	146.89	187.712	274.19	305.268	449.99
98.807	148.83	189.728	277.14	308.251	453.86
100.392	151.39	191.824	280.35	311.395	458.92
102.327	154.15	193.921	283.85	314.621	464.13
104.424	157.04	196.017	286.68	317.684	468.44
106.520	159.91	198.113	289.66	320.909	472.31
108.564	162.72	200.290	293.01	324.135	476.78
110.573	165.32	202.306	295.75	327.118	480.35
112.553	168.16	204.322	298.67	329.779	484.81
114.510	171.37	206.418	301.71	332.439	488.54
116.442	174.23	208.434	304.98	335.099	492.26
118.506	177.09	210.449	308.04	337.841	495.98
120.699	180.42	212.465	310.72	340.502	499.71
122.863	183.21	214.401	313.38	343.243	503.86
125.002	186.13	216.416	316.97	346.065	507.44
127.116	189.86	218.351	320.03	348.968	511.45
129.204	192.42	220.286	324.12	351.790	514.88
131.273	194.83	222.302	325.43	354.531	518.75
133.289	197.19	224.237	328.85	357.434	523.81
135.344	199.39	226.091	332.72	360.336	528.42
137.350	202.21	228.833	337.34	362.997	532.73
139.335	205.13	231.735	341.35	365.901	536.45
141.271	208.55	234.718	345.07	368.641	539.88
143.286	211.67	237.782	349.99	371.365	543.64
145.181	214.31	241.007	354.61	374.084	547.89
147.237	217.25	244.071	360.78	376.978	552.51
149.262	220.52	247.135	364.57	379.691	556.21
151.276	222.96	250.280	369.63	382.380	559.42
153.407	226.31	253.263	373.95	385.119	562.83
155.542	229.13	256.327	378.71	387.846	566.51
157.615	231.64	259.390	383.32	390.524	569.91
159.696	235.03	262.454	388.08		
161.750	238.11	265.518	392.41		

The solid $C_6H_5NO_2(s)$ and $Cr(OH)_3(s)$ were, respectively, ground within an agate mortar into a fine powder. About 1.2 mmol of $C_6H_5NO_2(s)$ was dissolved in 100 mL of 0.1 $mol\cdot dm^{-3}$ HCl at $T = (298.150 \pm 0.001)$ K. The final solution obtained from five tests was designated as solution A_1. Then, 0.4 mmol of $Cr(OH)_3(s)$ was dissolved in the solution A_1 (0.1 $mol\cdot L^{-1}$of HCl containing certain amounts of nicotinic acid). The final solution obtained from five tests was named solution A.

The solid complex $Cr(C_6H_4NO_2)_3(s)$ 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 0.4 mmol (about 0.25 g) of $Cr(C_6H_4NO_2)_3(s)$ in 100 mL of 0.1 M HCl was determined under the same conditions as above. The final solution was represented as A′.

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

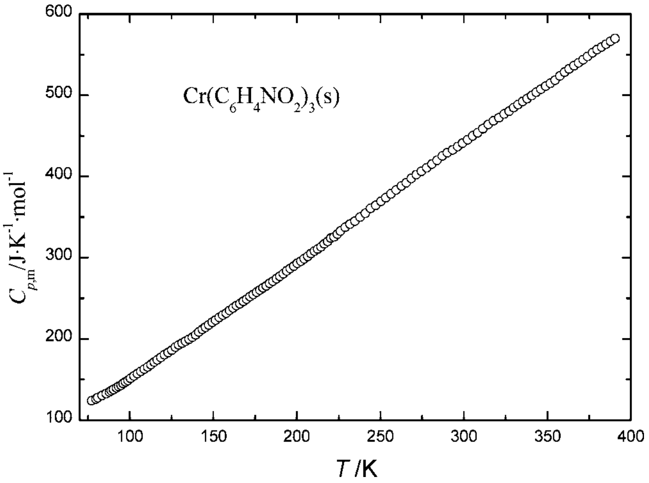

Figure 1. Curve of the experimental molar heat capacities of the complex $Cr(C_6H_4NO_2)_3(s)$ vs the temperature (T).

Results and discussion

Low-Temperature Heat Capacities. All experimental results, listed in Table 2 and plotted in Figure 1, show that the structure of the coordination compound was stable over the temperature range between $T = 78$ K and $T = 391$ K; that is, no phase change, association, or thermal decomposition occurred. The 133 experimental points in the temperature region between $T = 78$ K and $T = 391$ K were fitted by means of the least-squares method and a polynomial equation of the experimental molar heat capacities ($C_{p,\mathrm{m}}$) vs reduced temperature (X), $X = f(T) = [T/\mathrm{K} - (1/2)(T_1 + T_2)]/[(1/2)(T_1 - T_2)]$ (where $T_1 = 391$ K and $T_2 = 78$ K), has been obtained

$$C_{p,\mathrm{m}}/(J\cdot K^{-1}\cdot mol^{-1}) = 345.042 + 234.263X - 0.164X^2 - 10.666X^3 + 1.813X^4 \quad (1)$$

in which $X = (T/\mathrm{K} - 234.5)/156.5$. 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.

Thermodynamic Functions of Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$. The smoothed molar heat capacities and thermodynamic functions of chromium nicotinate $Cr(C_6H_4NO_2)_3(s)$ 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

$$H_T - H_{298.15\,\mathrm{K}} = \int_{298.15\mathrm{K}}^{T} C_{p,\mathrm{m}}\mathrm{d}T \quad (2)$$

$$S_T - S_{298.15\,\mathrm{K}} = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}T^{-1}\mathrm{d}T \quad (3)$$

$$G_T - G_{298.15\,\mathrm{K}} = \int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}\mathrm{d}T - T\cdot\int_{298.15\,\mathrm{K}}^{T} C_{p,\mathrm{m}}T^{-1}\mathrm{d}T \quad (4)$$

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 with an interval of 5 K.

Table 3. Smoothed Molar Heat Capacities and Thermodynamic Functions of Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$

T	$C_{p,\mathrm{m}}$	$(H_T - H_{298.15\mathrm{K}})$	$(S_T - S_{298.15\mathrm{K}})$	$(G_T - G_{298.15\mathrm{K}})$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
80	125.60	−60.868	−322.90	−35.036
85	131.91	−60.224	−315.12	−33.438
90	138.31	−59.548	−307.41	−31.881
95	144.79	−58.840	−299.75	−30.364
100	151.35	−58.100	−292.14	−28.886
105	157.98	−57.327	−284.58	−27.446
110	164.67	−56.520	−277.05	−26.044
115	171.43	−55.680	−269.57	−24.680
120	178.26	−54.806	−262.11	−23.353
125	185.14	−53.897	−254.68	−22.063
130	192.08	−52.954	−247.27	−20.809
135	199.07	−51.977	−239.88	−19.592
140	206.12	−50.964	−232.51	−18.412
145	213.21	−49.915	−225.16	−17.267
150	220.34	−48.831	−217.81	−16.159
155	227.52	−47.712	−210.48	−15.088
160	234.73	−46.556	−203.15	−14.052
165	241.98	−45.364	−195.83	−13.053
170	249.26	−44.136	−188.51	−12.090
175	256.58	−42.872	−181.19	−11.164
180	263.92	−41.571	−173.87	−10.274
185	271.28	−40.233	−166.55	−9.420
190	278.67	−38.858	−159.23	−8.604
195	286.08	−37.446	−151.91	−7.824
200	293.51	−35.997	−144.58	−7.080
205	300.95	−34.511	−137.25	−6.374
210	308.41	−32.987	−129.92	−5.705
215	315.87	−31.427	−122.58	−5.073
220	323.34	−29.829	−115.23	−4.478
225	330.82	−28.193	−107.88	−3.919
230	338.31	−26.520	−100.53	−3.398
235	345.79	−24.810	−93.169	−2.915
240	353.27	−23.062	−85.806	−2.469
245	360.75	−21.277	−78.438	−2.059
250	368.23	−19.455	−71.067	−1.688
255	375.70	−17.595	−63.693	−1.353
260	383.16	−15.698	−56.316	−1.056
265	390.61	−13.763	−48.937	−0.795
270	398.05	−11.792	−41.556	−0.571
275	405.48	−9.782	−34.174	−0.385
280	412.89	−7.737	−26.792	−0.235
285	420.28	−5.654	−19.410	−0.122
290	427.65	−3.534	−12.028	−0.046
295	435.00	−1.378	−4.6485	−0.006
298.15	439.62	0	0	0
300	442.33	0.816	2.7295	−0.003
305	449.64	3.046	10.105	−0.036
310	456.92	5.312	17.477	−0.106
315	464.17	7.615	24.846	−0.212
320	471.40	9.954	32.211	−0.354
325	478.60	12.329	39.571	−0.532
330	485.76	14.740	46.927	−0.746
335	492.89	17.186	54.278	−0.997
340	500.00	19.669	61.624	−1.284
345	507.06	22.186	68.965	−1.607
350	514.09	24.739	76.301	−1.967
355	521.09	27.327	83.632	−2.362
360	528.04	29.950	90.958	−2.795
365	534.96	32.608	98.281	−3.265
370	539.10	34.219	102.67	−3.566
375	547.32	37.478	111.45	−4.206
380	548.68	38.026	112.92	−4.318
385	555.48	40.786	120.23	−4.901
390	562.24	43.581	127.54	−5.524

Determination of Enthalpy Change for the Designed Solid-State Coordination Reaction of $Cr(OH)_3(s)$ with Nicotinic Acid. The solid-state coordination reaction of $Cr(OH)_3(s)$ with nicotinic acid is shown as follows

$$3C_6H_5NO_2(s) + Cr(OH)_3(s) \rightarrow Cr(C_6H_4NO_2)_3(s) + 3H_2O(l) \quad (5)$$

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

	$W_{C_6H_5NO_2}$	t	ΔE_s	ΔE_e	Q	$\Delta_d H_m^\ominus(1)$
no.	g	s	mV	mV	J	$kJ \cdot mol^{-1}$
1	0.14779	32.202	5.417	4.859	17.420	14.511
2	0.14740	35.062	5.340	5.238	17.346	14.488
3	0.14773	36.312	5.438	5.467	17.527	14.606
4	0.14764	24.344	5.324	3.665	17.158	14.307
5	0.14775	35.484	5.286	5.312	17.136	14.278

avg. $\Delta_d H_m^\ominus(1) = (14.44 \pm 0.14)\ kJ \cdot mol^{-1}$

[a] In which m/g is mass of sample; $\Delta\ E_e$/mV is the voltage change during the electrical calibration; ΔE_s/mV is the voltage change during the sample dissolution; Q/J is the heat effect of the dissolution; $\Delta_d H_m^\ominus = (\Delta E_s / \Delta E_e) \cdot I^2 R t (M/m)$, where R is the electro-resistance (T = 298.15 K, R = 1213.09 Ω); I is the electrical current (I = 20.015 mA); M is the molar mass; and t is the heating period of electrical calibration.

Table 5. Dissolution Enthalpy of Chromium Hydroxide $Cr(OH)_3(s)$ in 0.1 $mol \cdot L^{-1}$ HCl Containing Certain Amounts of Nicotinic Acid [T = 298.15 K, $M(Cr(OH)_3)$ = 103.02 $g \cdot mol^{-1}$]

	$W_{Cr(OH_3)}$	t	ΔE_s	ΔE_e	Q	$\Delta_d H_m^\ominus(2)$
no.	g	s	mV	mV	J	$kJ \cdot mol^{-1}$
1	0.04124	34.616	−3.875	4.222	−15.439	−25.719
2	0.04122	31.986	−3.782	3.879	−15.155	−25.255
3	0.04124	30.423	−3.914	3.703	−15.629	−26.037
4	0.04123	29.775	−3.876	3.608	−15.548	−25.897
5	0.04121	30.213	−3.866	3.666	−15.484	−25.801

avg. $\Delta_d Hm^\ominus(2) = -(25.74 \pm 0.13)\ kJ \cdot mol^{-1}$

Table 6. Dissolution Enthalpy of Chromium Nicotinate $Cr(C_6H_4NO_2)_3(s)$ in 0.1 $mol \cdot L^{-1}$ HCl [T = 298.15 K, $M(Cr(C_6H_4NO_2)_3)$ = 418.30 $g \cdot mol^{-1}$]

	$W_{Cr(C_6H_4NO_2)_3}$	t	ΔE_s	ΔE_e	Q	$\Delta_d H_m^\ominus(3)$
no.	g	s	mV	mV	J	$kJ \cdot mol^{-1}$
1	0.25099	37.462	−6.187	5.576	−20.202	−33.668
2	0.25095	38.164	−6.301	5.655	−20.665	−34.447
3	0.25098	40.826	−6.261	5.985	−20.752	−34.587
4	0.25091	40.744	−6.298	5.892	−21.163	−35.281
5	0.25096	39.901	−6.254	5.885	−20.604	−34.343

avg. $\Delta_d H_m^\ominus(3) = -(34.47 \pm 0.26)\ kJ \cdot mol^{-1}$

The enthalpy change of reaction 5 was determined by measuring enthalpies of dissolution of $C_6H_5NO_2(s)$, $Cr(C_6H_4NO_2)_3(s)$, and $Cr(OH)_3(s)$ in 0.1 $mol \cdot dm^{-3}$ HCl and solution A_1 at 298.15 K, respectively.

About 0.377 g of a sample of $\{3C_6H_5NO_2(s)\}$ 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, the measurements of the dissolution enthalpy of nicotinic acid $\Delta_d H_m^\ominus(1)$ were represented as follows

$$\{3C_6H_5NO_2(s)\} + \text{'s'} = \text{solution } A_1$$

The results have been listed in Table 4.

The dissolution enthalpies of $Cr(OH)_3(s)$ $\Delta_d H_m^\ominus(2)$ in 100 mL of the solution A_1 were measured under the same conditions

$$\{Cr(OH)_3(s)\} + \text{solution } A_1 = \text{solution } A$$

The results have been listed in Table 5.

The dissolution enthalpies of $Cr(C_6H_4NO_2)_3(s)$ $\Delta_d H_m^\ominus(3)$ in 100 mL of 0.1 $mol \cdot dm^{-3}$ HCl at 298.15 K were measured under the same conditions as above.

$$\{Cr(C_6H_4NO_2)_3(s)\} + \text{'s'} = \text{solution } A'$$

The results have been listed in Table 6.

Table 7. Reaction Scheme Used to Determine the Standard Molar Enthalpy of Formation of the Complex $Cr(C_6H_4NO_2)_3(s)$ at 298.15 K[a]

no.	reactions	solution	$\Delta_f H_m^\ominus$ or $(\Delta_d H_m^\ominus \pm \sigma_a)^b$ kj·mol^{-1}
1	$\{3C_6H_5NO_2(s)\} + \text{'s'} =$	A_1	(14.44 ± 0.14), ΔH_1
2	$\{Cr(OH)_3(s)\} + \text{solution } A_1 =$	A	$-(25.74 \pm 0.13)$, ΔH_2
3	$\{Cr(C_6H_4NO_2)_3(s)\} + \text{'s'} =$	A′	$-(34.47 \pm 0.26)$, ΔH_3
4	$\{3H_2O(l)\} + \text{solution } A' =$	A	0, ΔH_4
5	$6C(s) + 5/2\ H_2(g) + O_2(g) + 1/2\ N_2(g) = C_6H_5NO_2(s)$		$-(344.81 \pm 0.92)$, ΔH_5
6	$Cr(s) + 3/2\ H_2(g) + 3/2\ O_2(g) = Cr(OH)_3(s)$		-1064.70, ΔH_6
7	$H_2(g) + 1/2O_2\ (g) = H_2O(l)$		$-(285.83 \pm 0.04)$, ΔH_7
8	$Cr(s) + 18C(s) + 6H_2(g) + 3/2\ N_2(g) + 3O_2(g) = Cr(C_6H_4NO_2)_3(s)$		$-(1189.6 \pm 2.8)$, ΔH_8

[a] The solvent 's' is 0.1 mol·L^{-1} HCl. [b] $\sigma_a = \sqrt{\sum_{i=1}^{5} (x_i - \bar{x})^2 / n(n-1)}$, in which n is the experimental number; x_i is a single value in a set of dissolution measurements; and x^- is the mean value of a set of measurement results.

The dilution enthalpy of $\{3H_2O(l)\}$ $\Delta_d H_m^\ominus(4)$ in solution A′ at 298.15 K was represented as follows

$$\{3H_2O(l)\} + \text{solution } A' = \text{solution } A$$

The enthalpy produced from the dilution of stoichiometrically $3H_2O$ in reaction 5 in solution A′ is within the scope of the experimental error and cannot be detected by the existing isoperibol solution calorimetry. So, the enthalpy $\Delta_d H_m^\ominus(4)$ may be approximated to be equal to zero.

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

$$\Delta_r H_m(5) = 3\Delta_d H_m^\ominus(1) + \Delta_d H_m^\ominus(2) - \Delta_d H_m^\ominus(3) - 3\Delta_d H_m^\ominus(4) = (52.05 \pm 0.51)\ \text{kJ}\cdot\text{mol}^{-1}$$

Standard Molar Enthalpy of Formation of $Cr(C_6H_4NO_2)_3(s)$. The reaction scheme used to derive the standard molar enthalpy of formation of $Cr(C_6H_4NO_2)_3(s)$ 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 some auxiliary thermodynamic data $\Delta_f H_m^\ominus[C_6H_5NO_2, s] = -(344.81 \pm 0.92)$ kJ·mol^{-1} ,[9] $\Delta_f H_m^\ominus[Cr(OH)_3, s] = -1064.70$ kJ·mol^{-1} ,[10] and $\Delta_f H_m^\ominus(H_2O, l) = -(285.83 \pm 0.04)$kJ·mol^{-1} ,[11] to derive the standard molar enthalpy of formation of $Cr(C_6H_4NO_2)_3(s)$.

$\Delta_f H_m^\ominus[Cr(C_6H_4NO_2)_3, s] = \Delta_r H_m(5) + 3\Delta_f H_m^\ominus[C_6H_5NO_2, s] + \Delta_f H_m^\ominus[Cr(OH)_3, s] - 3\Delta_f H_m^\ominus(H_2O, l) = \Delta H_8 = 3\Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 + 3\Delta H_5 + \Delta H_6 - 3\Delta H_7 = -(1189.6 \pm 2.8)$ kJ·mol^{-1}, in which $\Delta H_1 \sim \Delta H_8$ are the enthalpy changes of the reactions corresponding to the no. of the reaction listed 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 measured values of the refractive indexes of solution A and solution A′ were (1.3817 ± 0.0015) and (1.3821 ± 0.0011), respectively. The results of UV–vis spectra were shown in Figure 2. UV/vis spectra and the data of the refractive indexes of solution A obtained agreed with those of solution A′, and no difference in the structure and chemical composition existed between the two solutions. Solution A is in thermodynamic equivalent states to solution A′.

Conclusions

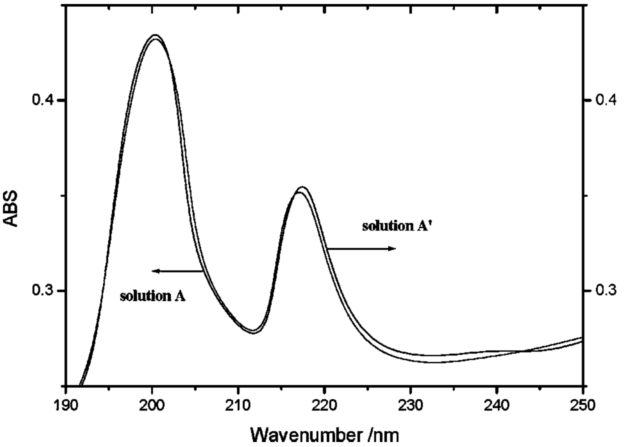

Figure 2. UV/vis spectra of solution A and solution A′ obtained from the dissolutions of $C_6H_5NO_2(s)$, $Cr(OH)_3(s)$, and $Cr(C_6H_4NO_2)_3(s)$ in the supposed reaction 5 in the chosen solvents (diluted into 1:20).

This paper reports low-temperature heat capacities measured by adiabatic calorimetry and the dissolution enthalpies of the reactants and the products of the designed solid-state coordination reaction of chromium(III) hydroxide with nicotinic acid by isoperibol solution calorimetry. Additionally, the thermodynamic functions and standard molar enthalpy of formation of the product $Cr(C_6H_4NO_2)_3(s)$ were derived from these experimental results.

The reliability of the designed thermochemical cycle has been verified by UV spectroscopy and the data of the refractive indices. It is shown that the cycle is reasonable and can be used to determine the standard molar enthalpy of formation of the product $Cr(C_6H_4NO_2)_3(s)$. 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.

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