Thermodynamics of Sodium 5-Nitroisophthalic Acid Monohydrate

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Low-temperature heat capacities of sodium 5-nitroisophthalic acid monohydrate ($C_8O_6NH_3Na_2 \cdot H_2O$, s) were measured by a precision automated adiabatic calorimeter over the temperature range from (78 to 398) K. The experimental values of the molar heat capacities 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 compound ($C_8O_6NH_3Na_2 \cdot H_2O$, s) were calculated on the basis of the fitted polynomial. The constant volume energy of combustion of the compound at $T = 298.15$ K was measured by a precise rotating-bomb combustion calorimeter to be $\Delta_c U = -(3969.41 \pm 1.74)$ kJ·mol^{-1}. The standard molar enthalpy of combustion of the compound was determined to be $\Delta_c H^\theta_m = -(3965.07 \pm 1.74)$ kJ·mol^{-1}. The standard molar enthalpy of formation of the compound was calculated to be $\Delta_f H^\theta_m$ ($C_8O_6NH_3Na_2 \cdot H_2O$, s) $= -(408.45 \pm 2.03)$ kJ·mol^{-1} in accordance with Hess's law. The standard molar enthalpy of solution of the compound, $\Delta_{sol} H^\theta_m$ ($C_8O_6NH_3Na_2 \cdot H_2O$, s), has been determined as (22.133 ± 0.111) kJ·mol^{-1}. The standard molar enthalpy of the hydrated anion of the compound was determined as $\Delta_f H^\theta_m$ ($C_8O_6NH_3^{2-}$, aq) $= (380.11 \pm 2.04)$ kJ·mol^{-1}, from the standard molar enthalpy of solution and other auxiliary thermodynamic data through a thermochemical cycle. The thermostability of the compound was investigated by thermogravimetric/differential thermogravimetric/differential scanning calorimetry (TG-DTG-DSC).

Introduction

As one of derivatives of isophthalic acid, 5-nitroisophthalic acid ($5\text{-}NO_2-H_2bdc$) is an important intermediate of disperse dyes (X-ray contrast agent) for clinical diagnosis. It is also a precursor for the preparation of polyesters, medicine, and plasticizers during commercial manufacturing processes. With the growth of the study of metal−organic frameworks (MOFs), it has been extensively employed in the preparations of metal−organic coordination polymers.[1–9] Since it does not dissolve in water, sodium 5-nitroisophthalic acid is inevitably used to synthesize related compounds. To further investigate the relevant complexes, there is an urgent need for relevant thermodynamic data of sodium 5-nitroisophthalic acid.

In this paper, we synthesized sodium 5-nitroisophthalic acid monohydrate ($C_8O_6NH_3Na_2 \cdot H_2O$, s). The low-temperature heat capacities of the title compound over the temperature range [(78 to 398) K] were measured by an automated adiabatic calorimeter. The standard molar enthalpies of combustion at 298.15 K were determined by an RBC-type II type precise rotating-bomb calorimeter. In addition, some thermodynamic parameters such as the standard molar enthalpy of formation of the title compound were derived.

Experimental Section

Chemicals and Equipment. $5\text{-}NO_2-H_2bdc$ was purchased from the Tokyo Kasti Kogyo Co., Ltd., was of GC grade with a purity of 99 %. The γ-aluminum oxide was of spectroscopic pure grade from the Shanghai No. 1 Reagent Factory. It was transformed to α-aluminum oxide in a muffle oven at 1473.15 K prior to use and maintained in a desiccator with P_4O_{10}. Potassium chloride (mass fraction 0.9999) was purchased from the Shanghai No. 1 Reagent Factory, Shanghai, China, and dried in a vacuum oven at 500 K for 8 h prior to use. The relative atomic masses used were those recommended by the IUPAC Commission in 1999.[10] Elemental analyses were performed on an Elemental Vario EL III CHNOS analyzer. Thermogravimetric/differential thermogravimetric/differential scanning calorimetry (TG-DTG-DSC) analyses were performed on a Netzsch STA 449C instrument under a dynamic atmosphere of high purity N_2 with a heating rate of 5 °C·min^{-1}.

Adiabatic Calorimeter. A precision automatic adiabatic calorimeter was used to measure the heat capacities of the compound over the temperature range $78 \leq (T/\text{K}) \leq 398$. 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.[11–13]

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 $78 \leq (T/\text{K}) \leq 398$. The sample mass used was 1.7143 g, which is 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[14] 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·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

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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.[15,16] The sample mass used for the calorimetric measurements was 2.8961 g, which is equivalent to 0.0102 mol in terms of its molar mass, $M = 273.107$ g·mol^{-1}.

Rotating-Bomb Combustion Calorimeter. The constant-volume combustion energy of the compound was determined by an RBC-type II type precise rotating-bomb combustion calorimeter. The main experimental procedures were described previously.[17,18] The initial temperature was regulated to (25.0000 ± 0.0005) °C, and the initial oxygen pressure was 2.5 MPa. The digital indicator for the temperature measurement was used to ensure a better precision and accuracy of the experiment. The correct value of the heat exchange was calculated according to the Linio−Pyfengdelel−Wsava formula.

The calorimeter was calibrated with benzoic acid. The calibrated experimental results with an uncertainty of $4.38 \cdot 10^{-4}$ are summarized in Table 1. The energy equivalent of the rotating-bomb calorimeter was calculated according to eq 1

$$W = \frac{Qa - Gb - 5.97c}{\Delta T} \qquad (1)$$

where W is the energy equivalent ($\varepsilon_{\text{calor}}$) of the rotating-bomb calorimeter (J·K^{-1}), Q is the combustion enthalpy of benzoic acid (J·g^{-1}), a is the mass of determined benzoic acid (g), G is the combustion enthalpy of Ni−Cr wire for ignition (0.9 J·cm^{-1}), b is the length of the actual Ni−Cr wire consumed (cm), 5.97 is the formation enthalpy and solution enthalpy of the acid corresponding to 1 mL of 0.1000 mol·L^{-1} solution of NaOH (J·mL^{-1}), c the volume (mL) for NaOH (0.1000 mol·L^{-1} solution) consumption, and ΔT is the correct value of the temperature rise.

The analytical methods for the final products (gas, liquid, and solid) were the same as those in ref 17. The results of the IR spectrum and powder X-ray diffraction (PXRD) showed that the final solid product was identified as hexagonal sodium peroxide. The analyses of the combustion products indicated that the compound was transformed to CO_2(g), H_2O(l), N_2(g), and Na_2O_2(s) under excess oxygen. The amounts of NO_x and CO in the final gas phase may be neglected. The analytical results of the final products showed that the combustion reactions were complete. The energy equivalent of the RBC-type II calorimeter was determined from seven combustion experiments in using approximately (0.8 to 0.9) g of NIST 39i benzoic acid under experimental conditions to be $\varepsilon_{\text{calor}} = (18604.99 \pm 8.14)$ J·K^{-1}, as indicated in Table S1 of the Supporting Information (SI). The corrections for nitric acid formation[19] were based on the value of −59.7 kJ·mol^{-1} for the standard molar energy of formation of 0.1 mol·dm^{-3} HNO_3 (aq) from N_2(g), O_2(g), and H_2O(l). Conversion of the energy of the actual bomb process to that of the isothermal process and the correction to standard states were made according to Hubbard et al.[20]

Microcalorimeter. The enthalpy of solution of the complex was measured by an RD496-2000 type microcalorimeter. The main experimental procedures were described previously.[18] The design, assemblage, and test of the microcalorimeter were published in ref 21. The calorimetric constant at 298.15 K was determined by the Joule effect before the experiment, which was (63.901 ± 0.030) μV·mW^{-1}. The enthalpy of solution of KCl in deionized water was measured to be (17.581 ± 0.039) kJ·mol^{-1}, which is in good agreement with the value of (17.584 ± 0.007) kJ·mol^{-1} in ref 22. The relative error of the experiment result is 0.02 %, and the RSD of the calorimeter is 0.3 %, which indicates that the calorimetric system is accurate and reliable.

Table 1. Smoothed Molar Heat Capacities and Thermodynamic Functions of the Compound

T	$C_{p,\text{m}}$	$H_T - H_{298.15\text{K}}$	$S_T - S_{298.15\text{K}}$	$G_T - G_{298.15\text{ K}}$
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
80.00	116.295	−49.52	−270.21	−27.90
85.00	122.826	−48.92	−262.92	−26.57
90.00	129.189	−48.29	−255.70	−25.28
95.00	135.392	−47.63	−248.53	−24.01
100.00	141.443	−46.93	−241.51	−22.79
105.00	147.348	−46.21	−234.44	−21.60
110.00	153.115	−45.46	−227.52	−20.44
115.00	158.751	−44.68	−220.63	−19.32
120.00	164.263	−43.87	−213.70	−18.23
125.00	169.657	−43.04	−206.91	−17.18
130.00	174.940	−42.18	−200.22	−16.16
135.00	180.118	−41.29	−193.51	−15.17
140.00	185.198	−40.38	−186.90	−14.22
145.00	190.184	−39.44	−180.31	−13.30
150.00	195.083	−38.47	−173.81	−12.41
155.00	199.901	−37.49	−167.33	−11.56
160.00	204.642	−36.48	−160.91	−10.74
165.00	209.311	−35.44	−154.51	−9.95
170.00	213.914	−34.38	−148.20	−9.20
175.00	218.456	−33.30	−141.92	−8.47
180.00	222.940	−32.20	−135.71	−7.78
185.00	227.371	−31.07	−129.50	−7.12
190.00	231.754	−29.92	−123.31	−6.49
195.00	236.092	−28.76	−117.32	−5.89
200.00	240.388	−27.56	−111.22	−5.32
205.00	244.648	−26.35	−105.21	−4.79
210.00	248.873	−25.12	−99.23	−4.28
215.00	253.068	−23.86	−93.31	−3.80
220.00	257.235	−22.59	−87.43	−3.35
225.00	261.377	−21.29	−81.58	−2.93
230.00	265.496	−19.97	−75.78	−2.54
235.00	269.596	−18.64	−70.01	−2.18
240.00	273.678	−17.28	−64.28	−1.85
245.00	277.744	−15.90	−58.58	−1.55
250.00	281.797	−14.50	−52.92	−1.27
255.00	285.838	−13.08	−47.29	−1.02
260.00	289.868	−11.64	−41.70	−0.80
265.00	293.888	−10.18	−36.13	−0.61
270.00	297.901	−8.70	−30.60	−0.44
275.00	301.906	−7.20	−25.10	−0.30
280.00	305.905	−5.68	−19.63	−0.19
285.00	309.898	−4.14	−14.19	−0.10
290.00	313.885	−2.58	−8.77	−0.04
295.00	317.866	−1.00	−3.38	−0.01
298.15	320.372	0.00	0.00	0.00
300.00	321.842	0.59	1.98	0.00
305.00	325.812	2.21	7.32	−0.02
310.00	329.776	3.85	12.63	−0.06
315.00	333.733	5.51	17.92	−0.14
320.00	337.683	7.19	23.19	−0.23
325.00	341.624	8.89	28.44	−0.36
330.00	345.555	10.61	33.67	−0.50
335.00	349.475	12.34	38.88	−0.68
340.00	353.382	14.10	44.06	−0.88
345.00	357.275	15.88	49.23	−1.11
350.00	361.151	17.67	54.39	−1.36
355.00	365.008	19.49	59.53	−1.64
360.00	368.845	21.32	64.65	−1.95
365.00	372.658	23.18	69.76	−2.28
370.00	376.445	25.05	74.85	−2.65
375.00	380.203	26.94	79.93	−3.03
380.00	383.929	28.85	85.00	−3.45
385.00	387.620	30.78	90.06	−3.89
390.00	391.271	32.73	95.11	−4.37
395.00	394.880	34.69	100.20	−4.87

Synthesis and Elemental Analysis. 5-NO_2−H_2bdc and sodium hydroxide at the molar ratio of n(5-NO_2−H_2bdc):n(NaOH) = 1:2 were mixed in water at a temperature of 80 °C, followed by evaporation and filtration, leading to white crystals. The

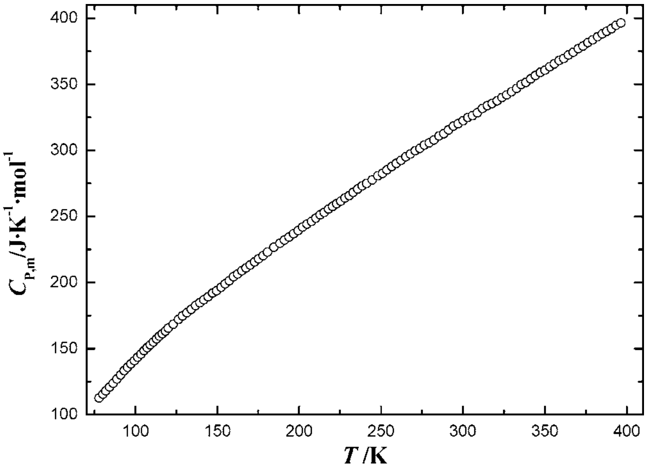

Figure 1. Curve of the experimental molar heat capacities of the sample vs the temperature (T).

compound was identified by elemental analysis as the formula $C_8O_7NH_5Na_2$. Calculated: C, 35.18 %; H, 1.85 %; N, 5.13 %. Found: C, 35.12 %; H, 1.79 %; N, 5.08 %.

Results and Discussion

TG-DTG-DSC Test. TG-DTG and DSC tests of the sample were under a dynamic atmosphere of oxygen with a flow rate of 30 $\mathrm{cm^3 \cdot min^{-1}}$ and a heating rate of 5 $\mathrm{K \cdot min^{-1}}$. As shown in Figure S1 of the SI, there are two stages of weight loss in the measured temperature range. The first step displays an endothermic effect at (384 to 451) K with the mass loss of 6.07 % (the calculated mass loss is 6.60 %), and the enthalpy of dehydration is 94.67 $\mathrm{J \cdot g^{-1}}$ from Figure S2 of the SI, which is due to dehydration. The second step shows a tremendous exothermic effect of -484.3 $\mathrm{J \cdot g^{-1}}$ and a sharp mass loss of 64.49 % (the calculated mass loss 64.84 %) from (666 to 746) K, in which the compound is decomposed to Na_2O_2 confirmed by PXRD.

Low-Temperature Heat Capacity. All experimental results, listed in Table S2 and plotted in Figure 1, show that the compound is stable over the temperature range of (78 to 398) K, that is, no phase change, association, or thermal decomposition occurred. The 120 experimental points in the temperature region of (78 to 398) K are fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,\mathrm{m}}$) versus reduced temperature (X), $X = f(T) = [T/\mathrm{K} - 1/2(T_1 + T_2)]/[1/2(T_1 - T_2)]$ (where $T_1 = 398$ K and $T_2 = 78$ K), has been obtained.

$$C_{p,\mathrm{m}}/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = 272.047 + 130.568X - 8.390X^2 + 11.127X^3 - 8.328X^4 \qquad (2)$$

in which $X = (T - 238)/160$. This equation is valid between $T_2 = 78$ K and $T_1 = 398$ K. The standard deviations of the 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 0.99997.

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

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \, \mathrm{d}T \qquad (3)$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p{\cdot}T^{-1} \, \mathrm{d}T \qquad (4)$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_p \, \mathrm{d}T - T{\cdot}\int_{298.15}^{T} C_p T^{-1} \, \mathrm{d}T \qquad (5)$$

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 1 at 5 K intervals.

Constant-Volume Energy of Combustion and Standard Molar Enthalpy of Combustion. The method for determining the constant-volume energy of combustion of the sample was the same as that used in the calibration of the combustion calorimeter with benzoic acid. The measured results for the constant-volume energy, $\Delta_c U/(\mathrm{J \cdot g^{-1}})$, of combustion of the sample are given in Table 2.

The standard molar enthalpy of combustion of the sample ($\Delta_c H^{\theta}_{\mathrm{m}}$) refers to the enthalpy change of reaction 6 at 298.15 K and 100 kPa.

$$C_8O_6NH_3Na_2{\cdot}H_2O(s) \rightarrow 27/4\ O_2(g) \rightarrow 8CO_2(g) + 5/2\ H_2O(l) + 1/2N_2(g) + Na_2O_2(s) \qquad (6)$$

The standard molar enthalpy of combustion of the sample can be derived from the constant-volume energy of combustion by eq 7.

$$\Delta_c H^{\theta}_{\mathrm{m}} = \Delta_c U + \Delta nRT \qquad (7)$$

where Δn is the total amount (in moles) of the gases present as products or as reactants, $R = 8.314$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $T =$

Table 2. Experimental Results for the Combustion Energy of the Compound[a]

no.	1	2	3	4	5	6
m/g	0.89565	0.96430	1.02383	0.98726	0.99866	0.96132
ΔT_{test}/K	0.6862	0.7361	0.7812	0.7545	0.7615	0.7338
ζ/K	0.0173	0.0198	0.0211	0.0202	0.0205	0.0196
ΔT/K[23]	0.7035	0.7559	0.8023	0.7747	0.7820	0.7534
W/J·K^{-1}	273.107	273.107	273.107	273.107	273.107	273.107
G/J·cm^{-1}	0.9	0.9	0.9	0.9	0.9	0.9
b/cm	12.6	12.6	12.6	12.6	12.6	12.6
$\Delta U(HNO_3)$/J	195.88	211.32	224.05	216.23	218.89	210.85
ΔU_Σ/J	36.20	38.97	41.38	39.90	40.36	38.85
Q_N/J	232.08	250.29	265.43	256.13	259.25	249.70
$-\Delta_c U$/J·g^{-1}	14559.05	14530.69	14526.63	14546.10	14515.59	14527.47
$-\Delta_c U_{\mathrm{mean}}$/J·g^{-1}			14534.26 ± 6.38			

[a] $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation, and ΔU_Σ is the standard state correction; Q_N is the total calibrated energy except for the combustion enthalpy of Ni−Cr wire for ignition. $\Delta_c U_{\mathrm{mean}}$ is the mean value of the combustion energy.

Table 3. Experimental Data of $\Delta_{sol}H^{\theta}_{m}$ at 298.15 K

	Q	$\Delta_{sol}H^{\theta}_{m}$	$W(H_2O)$	$W(C_8O_6NH_3Na_2\cdot H_2O)$
run	mJ	$kJ\cdot mol^{-1}$	g	g
1	1526.3	21.951	6.00222	0.01899
2	1542.9	22.189	5.99988	0.01899
3	1538.3	22.123	6.00268	0.01899
4	1535.8	22.087	6.00159	0.01899
5	1549.3	22.281	6.00213	0.01899
6	1541.3	22.166	6.00008	0.01899
mean ± SD	1539.0 ± 7.7	22.133 ± 0.111		

298.15 K. The standard molar enthalpy of combustion of the sample, $\Delta_c H^{\theta}_{m}$, is calculated to be $-(3965.070 \pm 1.742)$ $kJ\cdot mol^{-1}$.

Standard Molar Enthalpy of Formation. The standard molar enthalpy of formation of the compound, $\Delta_f H^{\theta}_{m}$, is calculated by Hess's law according to eq 8:

$$\Delta_f H^{\theta}_{m}(C_8O_6NH_3Na_2\cdot H_2O(s)) = 8\Delta_f H^{\theta}_{m}(CO_2(g)) + 5/2\Delta_f H^{\theta}_{m}(H_2O(l)) + \Delta_f H^{\theta}_{m}(Na_2O_2(s)) - \Delta_f H^{\theta}_{m} \quad (8)$$

In eq 8, the standard molar enthalpies of formation of $CO_2(g)$, $H_2O(l)$, and $Na_2O_2(s)$ recommended by refs 24 and 25. $\Delta_f H^{\theta}_{m}(CO_2(g)) = -(393.51 \pm 0.13)$ $kJ\cdot mol^{-1}$, $\Delta_f H^{\theta}_{m}(H_2O(l)) = -(285.830 \pm 0.042)$ $kJ\cdot mol^{-1}$, and $\Delta_f H^{\theta}_{m}(Na_2O_2(s)) = -(510.87 \pm 0.014)$ $kJ\cdot mol^{-1}$ are employed in the calculation of $\Delta_f H^{\theta}_{m}(C_8O_6NH_3Na_2\cdot H_2O(s))$. The standard molar enthalpy of formation of the compound can be derived to be $\Delta_f H^{\theta}_{m}(C_8O_6NH_3Na_2\cdot H_2O(s)) = -(408.45 \pm 2.03)$ $kJ\cdot mol^{-1}$.

Standard Molar Enthalpy of Solution and Standard Enthalpy of the Hydrated Anion. The molar enthalpies of solution, $\Delta_{sol}H^{\theta}_{m}(C_8O_6NH_3Na_2\cdot H_2O(s))$, in H_2O at 298.15 K are given in Table 3. The standard enthalpy of hydrated anion of the title complex can be calculated by Hess's law according to eq 9.

$$C_8O_6NH_3Na_2\cdot H_2O(s) \rightarrow 2Na^{+}(aq) + C_8O_6NH_3^{\;2-}(aq) + H_2O(l) \quad (9)$$

The standard molar enthalpy of the hydrated anion of the complex is calculated by eq 10.

$$\Delta_f H^{\theta}_{m}(C_8O_6NH_3^{\;2-}(aq)) = \Delta_{sol}H^{\theta}_{m} + \Delta_f H^{\theta}_{m}(C_8O_6NH_3Na_2\cdot H_2O(s)) - 2\Delta_f H^{\theta}_{m}(Na^{+}(aq)) - \Delta_f H^{\theta}_{m}(H_2O(l)) \quad (10)$$

$\Delta_f H^{\theta}_{m}$ $(C_8O_6NH_3^{2-}(aq))$ is calculated to be [(380.11 ± 2.04) $kJ\cdot mol^{-1}$], where the value of $\Delta_f H^{\theta}_{m}$ $(Na^{+}(aq))$ is from ref 24.

Conclusions

The heat capacities of sodium 5-nitroisophthalic acid monohydrate were measured over the temperature range from (78 to 398) K by a high-precision automated adiabatic calorimeter. The standard molar constant-volume combustion energy of the compound, $\Delta_c U$, has been determined as $-(3969.41 \pm 1.74)$ $kJ\cdot mol^{-1}$ by an RBC-II precision rotating-bomb combustion calorimeter at 298.15 K. The standard molar enthalpy of solution of the compound, $\Delta_{sol}H^{\theta}_{m}$ $(C_8O_6NH_3Na_2\cdot H_2O(s))$, has been determined as being (22.133 ± 0.111) $kJ\cdot mol^{-1}$ by an RD496-2000 type microcalorimeter. The standard molar enthalpy of combustion, $\Delta_c H^{\theta}_{m}$ $(C_8O_6NH_3Na_2\cdot H_2O(s))$, the standard molar enthalpy of formation, $\Delta_f H^{\theta}_{m}$ $(C_8O_6NH_3Na_2\cdot H_2O(s))$, and the standard molar enthalpy of hydrated anion of the complex, $\Delta_f H^{\theta}_{m}$ $(C_8O_6NH_3^{2-}(aq))$, have been calculated to be $-(3965.07 \pm 1.74)$ $kJ\cdot mol^{-1}$, $-(408.45 \pm 2.03)$ $kJ\cdot mol^{-1}$, and (380.11 ± 2.04) $kJ\cdot mol^{-1}$, respectively.

Supporting Information Available:

Results for calibration of energy equivalent (ε_{calor}) of the rotating-bomb calorimeter at 298.15 K, the experimental molar heat capacities of the sample, TG-DTG curve of $C_8O_6NH_3Na_2\cdot H_2O(s)$, and DSC curve of $C_8O_6NH_3Na_2\cdot H_2O(s)$. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Liang, X.-Q.; Zhou, X.-H.; Chen, C.; Xiao, H.-P.; Li, Y.-Z.; Zuo, J.-L.; You, X.-Z. Self-assembly of metal-organic coordination polymers constructed from a versatile multipyridyl ligand: diversity of coordination modes and structures. *Cryst. Growth Des.* **2009**, *9*, 1041–1053.

(2) Kirillov, A. M.; Karabach, Y. Y.; Haukka, M.; Guedes da Silva, M. F. C.; Sanchiz, J.; Kopylovich, M. N.; Pombeiro, A. J. L. Self-assembled copper(II) coordination polymers derived from aminopolyalcohols and benzenepolycarboxylates: structural and magnetic properties. *Inorg. Chem.* **2008**, *47*, 162–175.

(3) Guo, J.-Y.; Zhang, T.-L.; Zhang, J.-G.; Liu, Y.-H.; Yu, K.-B. Synthesis, Crystal structure and thermal behavior of 5-nitroisophthalate complex with Mn(II). Chin. *Energy Mater.* **2006**, *14*, 257–261.

(4) Ren, Y.-X.; Chen, S.-P.; Xie, G.; Gao, S.-L.; Shi, Q.-Z. Two novel erbium (III) coordination polymers with 5-nitroisophthalic acid: synthesis and crystal structures and thermal stabilities. *Inorg. Chim. Acta* **2006**, *359*, 2047–2052.

(5) Fyles, T. M.; Knoy, R.; Mullen, K.; Sieffert, M. Membrane activity of isophthalic acid derivatives: ion channel formation by a low molecular weight compound. *Langmuir* **2001**, *17*, 6669–6674.

(6) Xie, Y.-M.; Zhang, Q.-S.; Zhao, Z.-G.; Wu, X.-Y.; Chen, S.-C.; Lu, C.-Z. New optical supramolecular compound constructed from a polyoxometalate cluster and an organic substrate. *Inorg. Chem.* **2008**, *47*, 8086–8090.

(7) Petoud, S.; Muller, G.; Moore, E. G.; Xu, J. D.; Sokolnicki, J.; Riehl, J. P.; Le, U. N.; Cohen, S. M.; Raymond, K. N. Brilliant Sm, Eu, Tb, and Dy Chiral lanthanide complexes with strong circularly polarized Luminescence. *J. Am. Chem. Soc.* **2007**, *129*, 77–83.

(8) Kozlov, V. A.; Aleksanyan, D. V.; Nelyubina, Y. V.; Lyssenko, K. A.; Gutsul, E. I.; Puntus, L. N.; Vasil'ev, A. A.; Petrovskii, P. V.; Odinets, I. L. Cyclopalladated complexes of 3-Thiophosphorylbenzoic acid thioamides: hybrid pincer ligands of a new type. synthesis, catalytic activity, and photophysical properties. *Organomet. Chem.* **2008**, *27*, 4062–4070.

(9) He, J.; Zhang, J. X.; Tan, G. P.; Yin, Y. G.; Zhang, D.; Hu, M. H. Second ligand-directed assembly of photoluminescent Zn(II) coordination frameworks. *Cryst. Growth Des.* **2007**, *7*, 1508–1513.

(10) Coplen, T. B. Atomic weights of the elements. *J. Phys. Chem. Ref. Data* **2001**, *30*, 701–712.

(11) 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-R-Glycine). *J. Chem. Eng. Data* **2006**, *51*, 1551–1555.

(12) Tan, Z. C.; Sun, G. Y.; Sun, Y.; Yin, A. X.; Wang, W.-B.; Ye, J. C.; Zhou, L. X. An adiabatic low-temperature calorimeter for heat capacity measurement of small samples. *J. Therm. Anal.* **1995**, *45*, 59–67.

(13) Lv, X. C.; Liu, B.-P.; Tan, Z. C.; Li, Y. S.; Zhang, Z.-H.; Shi, Q.; Sun, L. X.; Zhang, T. Molar heat capacities, thermodynamic properties, and thermal stability of the synthetic complex $[Er(Pro)_2(H_2O)_5]Cl_3$. *J. Chem. Eng. Data* **2006**, *51*, 1526–1529.

(14) Archer, G. A. Thermodynamic properties of synthetic sapphire (α-Al_2O_3), standard Reference material 720 and the effect of temperature-scale difference on thermodynamic properties. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1441–1453.

(15) 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.

(16) Tan, Z. C.; Liu, B. P.; Yan, J. B.; Sun, L. X. A fully automated precision adiabatic calorimeter in the temperature range from 80 to 400 K. *J. Comput. Appl. Chem.* **2003**, *20*, 265–268.

(17) Yang, X. W.; Chen, S. P.; Gao, S. L.; Li, H. Y.; Shi, Q. Z. Combustion of rotating-bomb combustion calorimeter and measurement of thermal effects. *Instrum. Sci. Technol.* **2002**, *30*, 311–315.

(18) Chen, S. P.; Meng, X. X.; Xie, G.; Gao, S. L. Thermochemistry of the Ternary Solid Complex $Er(C_5H_8NS_2)_3(C_{12}H_8N_2)$. *J. Chem. Eng. Data* **2005**, *50*, 1204–1211.

(19) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(20) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1967; Chapter 5.

(21) Ji, M.; Liu, M. Y.; Gao, S. L.; Shi, Q. Z. The enthalpy of solution in water of complexes of zinc with methionine. *Instrum. Sci. Technol.* **2001**, *29*, 53–57.

(22) Kilday, M. V. The enthalpy of solution of SRM 1655 (KCl). *J. Res. Natl. Bur. Stand.* **1980**, *85*, 467–481.

(23) Popov, M. W. *Thermometry and calorimetry*, (in Russ.); Moscow Univ. Publishing House: Moscow, 1954; p 331.

(24) Cox, J. D. Codata Recommended Key Values for Thermodynamics, 1977. *J. Chem. Thermodyn.* **1978**, *10*, 903–906.

(25) Donald, D. W.; William, H. E.; Vivian, B. P. Translated by Liu, T. H.; Zhao, M. Y. *The NBS Tables of Chemical Thermodynamic Properties*; Chinese Standards Press: Beijing, 1998.

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