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THERMODYNAMIC PROPERTIES AND THERMAL STABILITY OF THE SYNTHETIC ZINC FORMATE DIHYDRATE

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Zinc formate dihydrate has been synthesized and characterized by powder X-ray diffraction, elemental analysis, FTIR spectra and thermal analysis. The molar heat capacity of the coordination compound was measured by a temperature modulated differential scanning calorimetry (TMDSC) over the temperature range from 200 to 330 K for the first time. The thermodynamic parameters such as entropy and enthalpy *vs.* 298.15 K based on the above molar heat capacity were calculated. The thermal decomposition characteristics of this compound were investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). TG curve showed that the thermal decomposition occurred in two stages. The first step was the dehydration process of the coordination compound, and the second step corresponded to the decomposition of the anhydrous zinc formate. The apparent activation energy of the dehydration step of the compound was calculated by the Kissinger method using experimental data of TG analysis. There are three sharply endothermic peaks in the temperature range from 300 to 650 K in DSC curve.

Keywords: *DSC, heat capacity, TG, TMDSC, zinc formate dihydrate*

Introduction

The formate anion, $HCOO^-$ is the simplest and smallest carboxylate and is of benefit for the formation of metal organic frameworks (MOFs) [1] due to its small stereo effect. It has been reported that the formates of large numbers of divalent metals (Me=Mg, Mn, Fe, Cd, Co, Ni, Cu, Zn) form isostructural monoclinic crystals with general formula $Me(HCOO)_2{\cdot}2H_2O$ (space group $P2_1/c$, No. 14) [2, 3]. In recent years, many metal organic frameworks using the formate with a variety of divalent metal ions have been synthesized, analyzed in crystal structure. Gas sorption studies indicate they are porous and promising candidates as sorbents for hydrogen storage [4, 5].

It is well known that hydrated zinc formate is one of the most important divalent metal formate. And the crystal structure and the thermal dehydration properties have been studies by some researchers [3, 6–9]. However, no report about heat capacity and thermodynamic properties of the coordination compound is found in the literature. Molar heat capacities of the materials at different temperatures are basic data in chemistry and engineering, from which many other thermodynamic properties such as enthalpy and entropy can be calculated. These parameters are important for both theoretical and practical purposes. Heat capacities determinations of various compounds have attracted many researchers' attention [10–13].

Temperature modulated differential scanning calorimetry (TMDSC) was initially published by Reading and co-workers in 1992, and has been greatly developed for directly determining heat capacities of various materials [14, 15]. TMDSC which applies a small sinusoidal modulation of temperature superimposed onto a linear underlying heating rate is a recently developed extension to conventional DSC. The structure and principle of the calorimeter have been described in detail in the literatures [16–18].

In the present paper, molar heat capacity of zinc formate dihydrate was measured by TMDSC and reported for the first time. The accuracy of TMDSC is established by comparing the measured heat capacities of standard sapphire (Al_2O_3) and benzoic acid with previously reported values (NIST and NBS) [19, 20]. The thermal decomposition characteristics of this compound were investigated by TG and DSC.

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Experimental

Sample preparation

All reagents not specifically listed below were obtained from commercial sources of analytical grade and were used as received. Zinc nitrate (10.0 g, 33.6 mmol) was dissolved in DMF/1, 4-Dioxane (2:1 by volume, 200 mL). The mixture was stirred at room temperature until zinc nitrate entirely dissolved. Then, excessive formic acid (3.9 g, 84.8 mmol) was slowly added to the above transparent mixed solution. The solution was distributed to twenty vials of 20 mL. The vials were open, and the solvent was slowly volatilized. After several weeks, white polyhedral crystals were produced, collected and washed three times with DMF (50 mL).

Elemental analyses for $C_2H_6O_6Zn$ found (%): C, 12.10; H, 2.59; calc. (%): C, 12.55; H, 3.16; FTIR (KBr pellet, 4000–400 cm^{-1}): 3354, 1580 (OCO, str., asym.), 1398 and 1379 (OCO, deform., asym.), 1354 (OCO, str., sym.), 767 (OCO, deform., sym.), 567. A broad absorption band for *v* (hydroxyl) appearing at 3354 cm^{-1} shows the presence of water molecules in the complex.

The crystal structure of zinc formate dihydrate was determined by the powder X-ray diffraction. The resolved diffraction peaks match the standard zinc formate hydrate sample perfectly, and no characteristic peaks of impurities were observed [21].

Methods

Instrument

Elemental analysis was carried on PE-2400 II Series CHNS/O analyzer. A FTIR spectrum was recorded on Bruker Equinox 55 infrared spectrometer using KBr pellet in the range of 4000–400 cm^{-1}. Powder X-ray diffraction measurement was recorded on a X'Pert PRO X-ray diffractometer using CuK_α radiation (40 kV, 40 mA).

Heat capacity measurement

The modulated temperature and standard DSC measurements were performed on DSC Q1000 (T-zero DSC-technology, TA Instruments Inc., USA). A liquid nitrogen cooling system was used for the experiment at the low temperature range. And dry nitrogen gas was used as a purge gas (50 cm^3 min^{-1}) through the DSC cell. The temperature scale of the instrument was initially calibrated in the standard DSC mode, using the extrapolated onset temperatures of the melting of indium (429.75 K) at a heating rate of 10 K min^{-1}. The energy scale was calibrated with the heat of fusion of indium (28.45 J g^{-1}). The heat capacity calibration was made by running a standard sapphire (Al_2O_3) at each temperature. The calibration method and the experiment were performed at the same conditions as follows: 1) sampling interval: 1.00 s/pt, 2) zero heat flow at –253.15 K, 3) equilibrate at 133.15 K, 4) Modulate temperature amplitude of ±0.5°C with period of 100 s, 5) isothermal for 5.00 min, 6) temperature ramp at 5 K min^{-1} to 373.15 K.

Heat capacity ratios at T=200 to 330 K: K_1=0.9931; K_2=1.008.

The masses of the reference and sample pans with lids were measured to within 30±0.05 mg. Samples were crimped in non-hermetic aluminum pans with lids. Sample mass was weighed on a Mettler Toledo electrobalance (AB135-S, Classic) with an accuracy of (±0.01 mg).

Thermal analysis

The standard DSC of zinc formate dihydrate was performed by heating at 5 K min^{-1} under dry nitrogen flow (50 cm^3 min^{-1}) from 300 to 650 K, and samples mass was about 10 mg.

A thermogravimetric analyzer (Model: Setsys 16/18, SETARAM Co., France) was used for TG measurement of this sample under nitrogen atmosphere (99.999%). Several experiments were carried out at heating rates of β=5, 10, 15, 20, 25 K min^{-1} and the flow rate of nitrogen was 45 cm^3 min^{-1}. The mass of the sample was about 10 mg. Two Al_2O_3 crucibles were used (capacity: 100 μL). The reference crucible was filled with α-Al_2O_3. The TG equipment was calibrated by the $CaC_2O_4\cdot H_2O$ (99.9%).

Results and discussion

Heat capacity of standard sapphire (α-Al_2O_3) and benzoic acid

Heat capacity measurements of each compound are repeated three times unless stated elsewhere. The emphasis of this work is to assess the reproducibility and ensure accuracy of the measured data using TMDSC (Q1000). For sapphire measurement, the data of three reduplicate experiments and the experimental standard deviation for standard sapphire is given in Table 1. The experimental standard deviation is below ±0.20, and the result shows that the testing system of TMDSC is steady. Relative deviations have been calculated by the following equation:

$$RD(\%) = 10^2\{C_{p,m}(\exp) - C_{p,m}(\mathrm{ref})\}/C_{p,m}(\mathrm{ref}) \qquad (1)$$

where $C_{p,m}(\exp)$ is the experimental heat capacities and $C_{p,m}(\mathrm{ref})$ is the referenced heat capacities.

In Table 1, the results show that the relative deviation of our calibration data from the recommended value [19] over the whole temperature range was within ±1.3%.

To further attest to the reliability of the measurements using TMDSC, the benzoic acid is measured at the same experimental conditions and the results are listed in Table 2. The experimental standard deviations fluctuate below ±3.09 and also show good reproducibility of our TMDSC data. In the temperature range of 200 to 330 K, the RD (%) values below ±3.1% are obtained as compared with the recommended value [20].

Heat capacity of zinc formate dihydrate

The molar heat capacities of zinc formate dihydrate are listed in Table 3. The experimental standard deviations below ±2.80 are obtained and show reasonably good reproducibility in the temperature range from 200 to 330 K.

Table 1 The experimental molar heat capacities of standard sapphire (molecular formula: Al_2O_3, molar mass: 101.96 g mol^{-1})

T/K	$C_{p,m\,(exp)}$/J mol^{-1} K^{-1}				Standard deviation	$C_{p,m\,(ref)}$/ J mol^{-1} K^{-1}	Relative deviation
	Test 1	Test 2	Test 3	Average			
200	51.35	51.38	51.25	51.33	0.07	51.12	0.41
210	54.25	54.32	54.14	54.24	0.09	54.61	–0.68
220	57.39	57.44	57.25	57.36	0.10	57.95	–1.02
230	60.51	60.47	60.34	60.44	0.09	61.14	–1.14
240	63.55	63.50	63.35	63.47	0.10	64.17	–1.09
250	66.46	66.42	66.24	66.37	0.12	67.06	–1.03
260	69.31	69.32	69.08	69.24	0.14	69.80	–0.80
270	72.12	72.08	71.89	72.03	0.12	72.41	–0.52
280	74.95	75.04	74.77	74.92	0.14	74.88	0.05
290	77.71	77.63	77.55	77.63	0.08	77.23	0.52
300	80.06	79.94	79.74	79.91	0.16	79.45	0.58
310	82.40	82.28	82.08	82.25	0.16	81.56	0.85
320	84.62	84.42	84.22	84.42	0.20	83.55	1.04
330	86.66	86.49	86.30	86.48	0.18	85.44	1.22

Table 2 The experimental molar heat capacities of benzoic acid (molecular formula: $C_7H_6O_2$, molar mass: 122.12 g mol^{-1})

T/K	$C_{p,m\,(exp)}$/J mol^{-1} K^{-1}				Standard deviation	$C_{p,m\,(ref)}$/ J mol^{-1} K^{-1}	Relative deviation
	Test 1	Test 2	Test 3	Average			
200	103.44	100.16	101.86	101.82	1.64	102.89	–1.04
210	107.01	103.53	105.41	105.32	1.74	107.11	–1.67
220	111.34	107.72	109.87	109.64	1.82	111.40	–1.58
230	115.98	112.18	114.60	114.25	1.92	115.78	–1.32
240	120.89	116.86	119.52	119.09	2.05	120.22	–0.94
250	125.42	121.66	124.56	123.88	1.97	124.71	–0.67
260	130.30	126.64	129.94	128.96	2.02	129.24	–0.22
270	135.80	132.01	135.43	134.41	2.09	133.81	0.45
280	141.78	137.39	141.17	140.11	2.38	138.40	1.24
290	147.52	143.00	147.03	145.85	2.48	143.03	1.97
300	153.26	147.89	152.28	151.14	2.86	147.66	2.36
310	157.53	153.14	157.78	156.15	2.61	152.30	2.53
320	162.18	158.02	163.52	161.24	2.86	156.96	2.73
330	167.43	163.15	169.14	166.57	3.09	161.60	3.08

Table 3 The experimental molar heat capacities of zinc formate dihydrate (molecular formula: $Zn(O_2CH)_2{\cdot}2H_2O$, molar mass: 191.45 g mol^{-1})

T/K	$C_{p,m}$/J mol^{-1} K^{-1}				Standard deviation
	Dataset 1	Dataset 2	Dataset 3	Average	
200	170.51	170.43	166.50	169.15	2.29
205	172.23	172.04	168.15	170.81	2.30
210	174.64	174.30	170.51	173.15	2.29
215	177.05	176.78	172.84	175.56	2.36
220	179.48	179.22	175.16	177.95	2.42
225	181.99	181.72	177.59	180.43	2.47
230	184.56	184.33	180.17	183.02	2.47
235	187.26	186.93	182.78	185.66	2.51
240	189.96	189.48	185.40	188.28	2.50
245	192.79	192.02	188.14	190.98	2.49
250	195.47	194.70	190.97	193.71	2.41
255	198.15	197.58	193.75	196.49	2.39
260	200.83	200.26	196.43	199.17	2.39
265	203.89	203.13	199.49	202.17	2.35
270	206.96	206.00	202.17	205.04	2.53
275	209.83	208.68	205.23	207.91	2.39
280	212.70	211.55	208.11	210.79	2.39
285	215.76	214.62	211.17	213.85	2.39
290	218.83	217.68	214.23	216.91	2.39
295	222.27	220.93	217.30	220.17	2.57
300	224.95	223.61	220.36	222.97	2.36
305	228.21	226.87	223.23	226.10	2.58
310	231.85	230.70	226.68	229.74	2.71
315	235.29	234.14	230.12	233.18	2.71
320	238.74	237.59	233.57	236.63	2.71
325	242.38	241.23	237.40	240.33	2.61
330	246.59	245.44	242.18	244.74	2.29

The molar heat capacities of the sample are fitted to the Shomate equation [22] of heat capacities ($C_{p,m}$) with reduced temperature (t) by means of the nonlinear least squares fitter using the OriginPro 7.5 software:

From 200 to 330 K

$$C_{p,m}\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = -1157.93568 + 10095.48024t - 28371.33053t^2 + 30241.08189t^3 + 8.03318/t^2 \quad (2)$$

where t=T/1000, and T/K is the experimental temperature. The correlation coefficient of the fitting, R^2=0.99997, and Chi^2/DoF=0.0186 (DoF is the abbreviation of the degree of freedom). The relative deviations of all the experimental points from the fitting heat-capacity values are within ±0.15%.

Based on Eq. (2), the heat capacity of the sample was calculated at 298.15 K to be 221.87 J mol^{-1} K^{-1}.

From Table 3, it can be seen that the heat capacity of the sample increases with increasing temperature, and no phase transition or thermal anomaly was observed. This indicates that the sample is stable in this temperature region.

Thermodynamic functions of zinc formate dihydrate

Enthalpy and entropy of substances are basic thermodynamic functions. The thermodynamic functions relative to the reference temperature of 298.15 K were calculated in the temperature ranges from 200 to 330 K with an interval of 5 K. The thermodynamic relationships are as follows:

$$S_{\mathrm{T}} - S_{298.15} = \int_{298.15}^{\mathrm{T}} (C_{\mathrm{p,m}}/T)\mathrm{d}T \qquad (3)$$

The values of thermodynamic function H_{T}–$H_{298.15}$, S_{T}–$S_{298.15}$ are tabulated in Table 4.

Table 4 Calculated thermodynamic function data of zinc formate dihydrate

T/K	$C_{\mathrm{p,m}}$/ J mol^{-1} K^{-1}	H_{T}–$H_{298.15}$/ kJ mol^{-1}	S_{T}–$S_{298.15}$/ J mol^{-1} K^{-1}
200	169.07	–19.03	–76.70
205	171.02	–18.18	–72.50
210	173.16	–17.32	–68.35
215	175.46	–16.45	–64.25
220	177.88	–15.56	–60.19
225	180.39	–14.67	–56.17
230	182.98	–13.76	–52.17
235	185.62	–12.84	–48.21
240	188.31	–11.90	–44.27
245	191.03	–10.95	–40.36
250	193.77	–9.99	–36.48
255	196.54	–9.02	–32.61
260	199.34	–8.03	–28.77
265	202.16	–7.02	–24.94
270	205.00	–6.00	–21.14
275	207.88	–4.97	–17.35
280	210.80	–3.93	–13.58
285	213.77	–2.86	–9.82
290	216.79	–1.79	–6.08
295	219.89	–0.70	–2.35
298.15	221.87	0.00	0.00
300	223.06	0.41	1.38
305	226.32	1.53	5.09
310	229.68	2.67	8.80
315	233.17	3.83	12.50
320	236.78	5.01	16.20
325	240.55	6.20	19.90
330	244.48	7.41	23.60

DSC and TG analysis

In the temperature range from 300 to 650 K, the DSC curve of zinc formate dihydrate in Fig. 1 exhibits three sharply endothermic peaks. The first significant sharply endothermic peak corresponding to the dehydration of zinc formate dihydrate is observed with the peak temperature at 392.45 K. The onset temperature and the molar enthalpy (ΔH_{m}) of the stage are determined to be 376.24 K and 114.33 kJ mol^{-1}, respectively. Next to the first peak, two peaks occur successively corresponding to the decomposition of zinc formate, and the second peak temperature is 552.82 K and the third peak temperature is 565.68 K. The molar enthalpies (ΔH_{m}) of the second and third endothermic peaks are determined to be 7.03 kJ mol^{-1} and 56.27 kJ mol^{-1}, respectively.

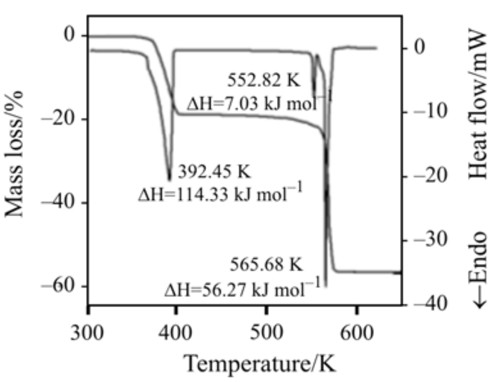

Fig. 1 TG and DSC curves of zinc formate dihydrate under high purity nitrogen atmosphere at 5 K min^{-1}

From the TG curve (Fig. 1), TG analysis of zinc formate dihydrate shows that the two-step mass loss occurs in the temperature range of 300 to 650 K at 5 K min^{-1}. The first mass loss is about 18.80% in the temperature range of 355–430 K, it is likely due to dehydrate from zinc formate dihydrate to zinc formate, which very coincides with the calculated theory value of 18.82%. Further decomposition of zinc formate occurs in the region of 430–650 K and the mass loss is 37.91% (calculated 38.66%), which is decomposed to zinc oxide in this step. The overall mass loss of the sample was ca. 56.71% in accord with the calculated percentage (57.48%).

Thermal kinetic study for TG analysis

Thermal kinetic parameter of zinc formate dihydrate was analyzed using Kissinger method [23], which has been widely applied to estimate the apparent

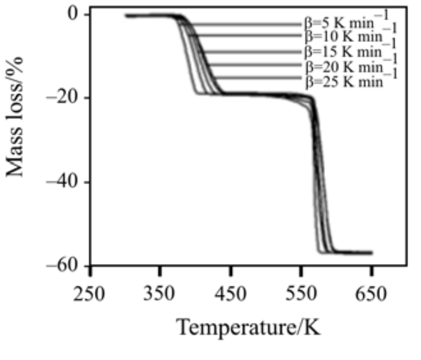

Fig. 2 TG curves of zinc formate dihydrate under high purity nitrogen atmosphere at 5, 10, 15, 20, 25 K min^{-1}

activation energy. Figure 2 shows the TG curves of zinc formate dihydrate measured in N_2 atmosphere from 300 to 650 K with the heating rate of 5, 10, 15, 20, 25 K min^{-1}, respectively. The basic data (β, T_p) taken from the TG curves are used in the following Kissinger equation:

$$\ln(\beta/T_p^2) = \ln(AR/E) - E/RT \qquad (4)$$

where β is heating rate, T_p peak temperature of the corresponding DTG curves, E apparent activation energy, A pre-exponential factor and R gas constant. Plot of $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ should fit to a straight line with a slope of $-E_\alpha/R$. Such plot for the dehydration step of the complex is exhibited in Fig. 3. The E value and A value of the sample was calculated to be 97.94 kJ mol^{-1} and $4.36\cdot10^{12}$.

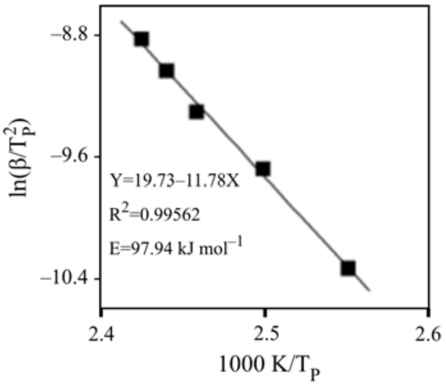

Fig. 3 Fitting using Kissinger method for the corresponding DTG curves

Conclusions

In this work, zinc formate dihydrate has been synthesized and characterized by powder X-ray diffraction, elemental analysis, FTIR spectra and thermal analysis. The molar heat capacity, $C_{p,m}$, of zinc formate dihydrate, was measured from 200 to 330 K using TMDSC for the first time. The thermodynamic functions $[H_T-H_{298.15}]$ and $[S_T-S_{298.15}]$ were derived from T=200 K to T=330 K with a temperature interval of 5 K. The thermal stability of the compound was investigated by the TG and DSC techniques. The apparent activation energy of the dehydration step of the complex was calculated to be 97.94 kJ mol^{-1}, by the Kissinger method using experimental data of TG analysis.

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