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Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of the Solid-State Coordination Compound *trans*-$Cu(Gly)_2 \cdot H_2O(S)$ (Gly = L-α-Glycine)

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Low-temperature heat capacities of the solid coordination compound *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ were measured by a precision automated adiabatic calorimeter over the temperature range from $T = 78$ K to $T = 381$ K. The initial dehydration temperature of the coordination compound was determined to be $T_D = 329.50$ K, by analysis of the heat-capacity curve. The experimental values of the molar heat capacities in the temperature region of 78−328 K 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 *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ 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 were tabulated with an interval of 5 K. Enthalpies of dissolution of $\{Cu(Ac)_2 \cdot H_2O(s) + 2Gly(s)\}$ [$\Delta_s H_m^{\ominus}(1)$] and HAc(l) [$\Delta_s H_m^{\ominus}(2)$] in 100.00 mL of 2 $mol \cdot dm^{-3}$ HCl and *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ [$\Delta_s H_m^{\ominus}(3)$] in the solvent [HAc(l) + 2 $mol \cdot dm^{-3}$ HCl] at $T = 298.15$ K were determined to be $\Delta_S H_m^{\ominus}(1) = (13.59 \pm 0.03)\ kJ \cdot mol^{-1}$, $\Delta_S H_m^{\ominus}(2) = -(0.93 \pm 0.03)\ kJ \cdot mol^{-1}$, and $\Delta_S H_m^{\ominus}(3) = -(14.64 \pm 0.02)\ kJ \cdot mol^{-1}$ by means of an isoperibol solution-reaction calorimeter. The standard molar enthalpy of formation of the compound was determined as: $\Delta_f H_m^0$(*trans*-$Cu(Gly)_2 \cdot H_2O$, s, 298.15 K) = $-(1251.6 \pm 1.0)\ kJ \cdot mol^{-1}$, from the enthalpies of dissolution and other auxiliary thermodynamic data through a Hess thermochemical cycle.

1. Introduction

Solid-state chemical synthesis is an important and promising method in the field of synthetic chemistry. The method[1] has been widely used to synthesize various solid-state coordination compounds of many metal salts with α-amino acids because it avoids complicated experimental operations and harsh reaction conditions. It is well-known that α-amino acids are basic structural units which constitute proteins and copper(II) is one of the trace elements necessary for the human body. It was established early that the complexes of α-amino acids with copper(II) form compounds with cis- and trans-geometric isomers, which have extensive application in food, cosmetics, and medicines as a nutrient.

In 1993, Zheng and Xin[2] synthesized a series of complexes (including *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ and others) by means of solid-state coordination reactions of copper(II) acetate with α-amino acids at ambient temperature. X-ray diffraction (XRD), IR, differential thermal analysis (DTA), and elemental analysis were employed to characterize their structures. However, up to now, the enthalpies of solid-state coordination reactions involved in the syntheses of these complexes and their respective low-temperature heat capacities, thermodynamic functions, and standard molar enthalpies of formation have not been reported in the literature. The purpose of the present study is to determine the dissolution enthalpies of the reactants and the products of the solid-state coordination reaction of copper(II) acetate with L-α-glycine by isoperibol solution calorimetry and measure the low-temperature heat capacities by adiabatic calorimetry. In addition, the initial dehydration temperature, thermodynamic functions, and standard molar enthalpy of formation of the product of the solid-state coordination reaction [*trans*-$Cu(Gly)_2 \cdot H_2O(s)$] were derived from these experimental results.

2. Experimental Section

Chemicals. Copper(II) acetate [$Cu(Ac)_2 \cdot H_2O(s)$], glycine(s), and other reagents used in these experiments were of analytical grade and obtained from the Shanghai Reagent Factory. KCl(s) and α-$Al_2O_3(s)$ used for calibration of the isoperibol solution calorimeter and adiabatic calorimeter were of a purity greater than 99.99 % and dried in a vacuum oven for 6 h at 210 to 240 °C prior to use. The water used in the measurements was twice distilled.

Sample Preparations and Characterization. The samples used in the present measurements were prepared according to the method given in the literature,[1,2] in which 10 mmol $Cu(Ac)_2 \cdot H_2O(s)$ of 80 to 100 mesh was mixed and ground with a certain amount of glycine, in a 1:2 molar ratio. These were retained for 4 h at ambient temperature. If subsequent XRD measurement showed that the refraction peaks of the two reactants in the system of the solid-state coordination reaction had disappeared, then the reaction was complete. The products were washed three times with absolute ethyl alcohol and once with ethyl ether of analytical grade. Finally, these were placed in a vacuum desiccator at ambient temperature to vacuum-dry for 4 h. Thermogravimetry/differential thermogravimetry (TG/DTG), chemical and element analyses (model, PE-2400,

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Perkin-Elmer, USA), have shown that the purities of the samples prepared were higher than 99.98 mol %.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter was used to measure heat capacities over the temperature range $78 \leq (T/\mathrm{K}) \leq 381$. 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.[3,4] Briefly, the calorimeter was mainly comprised of a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junction chromel−constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No.2, produced by the 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 $78 \leq (T/\mathrm{K}) \leq 380$. The sample mass used was 1.7143 g, which was equivalent to 0.0168 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ \mathrm{g{\cdot}mol^{-1}}$. 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) $\mathrm{K{\cdot}min^{-1}}$ 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}) $\mathrm{K{\cdot}min^{-1}}$ 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.[3,4] The sample mass used for calorimetric measurements was 3.5315 g, which was equivalent to 0.0152 mol in terms of its molar mass, $M = 231.60\ \mathrm{g{\cdot}mol^{-1}}$.

Isoperibol Solution-Reaction Calorimetry. The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere.[6]

The reliability of the calorimeter was verified previously[6] by measuring the dissolution enthalpy of KCl (calorimetrical primary standard) in double-distilled water at $T = 298.15$ K. The mean dissolution enthalpy was (17 597 ± 13) $\mathrm{J{\cdot}mol^{-1}}$ for KCl, which compared with corresponding published data,[7] (17 536 ± 3.4) $\mathrm{J{\cdot}mol^{-1}}$.

In all dissolution experiments of the sample, 100.00 mL of 2 $\mathrm{mol{\cdot}dm^{-3}}$ HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the $\{Cu(Ac)_2{\cdot}H_2O(s) + 2Gly(s)\}$ and the HAc(l), respectively. But *trans*-$Cu(Gly)_2{\cdot}H_2O(s)$ was dissolved in the solvent [HAc(l) + 2 $\mathrm{mol{\cdot}dm^{-3}}$ HCl] at $T = 298.15$ K.

The solid $Cu(Ac)_2{\cdot}H_2O(s)$ was ground within an agate mortar into a fine powder. The mixture of about 2 mmol Gly(s) and 1 mmol $Cu(Ac)_2{\cdot}H_2O(s)$ at a mole ratio of $n(Cu(Ac)_2{\cdot}H_2O(s))/n(Gly) = 1{:}2$ was dissolved in 100 mL of 2 $\mathrm{mol{\cdot}dm^{-3}}$ HCl at $T = (298.15 \pm 0.001)$ K. The final solution obtained from five tests was designated as solution A.

About 0.30 g of acetic acid, HAc(l), was dissolved in 100 mL of 2 $\mathrm{mol{\cdot}dm^{-3}}$ HCl at $T = (298.15 \pm 0.001)$ K. The final solution was named as solution A_1. The results obtained from five tests are listed in Table 3.

The solid complex *trans*-$Cu(Gly)_2{\cdot}H_2O(s)$ was dried in a vacuum desiccator to take off some additional adsorbing water. Then, it was ground into a fine powder. The dissolution enthalpy of about 0.23 g of *trans*-$Cu(Gly)_2{\cdot}H_2O(s)$ in 100 mL of solution A_1 was determined under the same condition as that above. The final solution obtained was named as solution A′.

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

3. Results and Discussion

Low-Temperature Heat Capacities. All experimental results, listed in Table 1 and plotted in Figure 1, showed that the structure of the coordination compound was stable over the temperature range between $T = 78$ K and $T = 328$ K, that is, no phase change, association, nor thermal decomposition occurred. However, at temperatures above 328 K, the heat-capacity curve began to rise steeply. This phenomenon was associated with the dehydration or thermal decomposition of the compound, as shown by TG analysis.[2] In addition, the initial dehydration temperature (T_D) has been obtained by means of the analysis of the heat-capacity curve. Two sections of the heat-capacity curves for (78 to 328) K and (329 to 381) K were extrapolated linearly. The intersection point of these two straight lines was the initial decomposition temperature, $T_D = 329.50$ K (see Figure 1). TG analysis had given the initial dehydration temperature (325.15 K), the final dehydration temperature (467.15 K), and the loss-mass percentage (7.80 %) of the compound. The loss-mass percentage was identical with the percentage of water molecules in the coordination compound (the theoretical loss-mass of the dehydration was 7.78 %). The initial dehydration temperature obtained from TG analysis was in agreement with that from the heat-capacity curve.

Because thermal decomposition or dehydration of the sample started at 329.50 K, the section of the heat-capacity curve in the temperature range $329 \leq (T/\mathrm{K}) \leq 381$ corresponded to the thermal anomaly of the compound on the basis of the above analysis. Therefore, the useful and real section of the heat-capacity curve of the compound itself was in the temperature region $78 \leq (T/\mathrm{K}) \leq 328$. The 94 experimental points in the temperature region between $T = 78$ K and $T = 328$ K were fitted by means of the least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,m}$) vs reduced temperature (X), $X = f(T)$, has been obtained

$$C_{p,m}/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 370.13 + 188.60X - 27.56X^2 - 38.18X^3 + 35.16X^4 + 116.76X^5 - 36.57X^6$$

Table 1. Experimental Molar Heat Capacities of the Complex *trans*-Cu(Gly)$_2$·H$_2$O(s) (M = 231.60 g·mol^{-1})

T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$
K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}	K	J·K^{-1}·mol^{-1}
78.097	73.87	173.854	322.8	289.858	499.1
80.150	86.96	176.427	327.3	292.779	506.8
81.930	98.72	178.792	331.8	295.769	512.3
84.258	110.8	181.434	336.3	298.621	517.4
86.586	123.2	183.869	340.8	301.472	522.9
88.982	136.3	186.233	344.3	304.393	528.3
91.378	144.0	188.876	348.5	307.384	534.7
93.706	152.8	191.379	352.6	310.235	545.0
95.965	160.8	193.814	356.8	313.156	554.3
98.224	169.2	196.317	361.6	316.147	564.9
100.415	176.3	198.821	365.8	318.928	571.7
102.537	185.0	201.812	370.3	321.849	585.2
104.728	193.1	204.872	375.1	324.770	596.1
107.192	201.5	207.932	379.6	327.691	608.0
109.523	209.1	210.992	383.8	330.612	623.4
112.305	214.5	213.913	388.3	333.464	634.0
115.087	223.5	217.112	392.2	336.176	650.7
116.617	227.4	220.102	395.7	338.888	666.1
119.329	232.5	222.954	400.2	340.915	683.6
121.902	236.7	226.153	403.1	343.379	704.1
124.476	241.5	229.143	407.9	345.433	722.9
127.049	245.4	232.204	412.1	347.693	744.7
129.553	249.6	235.055	415.9	349.472	763.9
131.152	253.7	238.046	418.5	351.047	780.0
133.795	261.8	241.036	422.0	352.622	799.1
136.438	265.9	244.096	426.5	354.402	822.3
138.875	269.1	247.156	431.3	355.771	844.1
141.376	273.3	250.077	434.9	357.574	859.2
143.045	276.9	252.998	439.0	359.149	874.4
145.827	282.0	255.849	444.2	360.263	896.4
148.330	286.2	258.841	449.0	362.301	915.0
151.043	290.0	262.039	453.5	364.311	935.3
153.616	293.2	265.029	457.0	366.348	952.2
156.398	298.0	268.159	462.2	368.821	967.6
158.901	301.9	271.219	467.0	372.189	986.2
161.266	304.8	274.279	472.1	374.879	1003
163.839	308.0	277.479	477.3	378.030	1018
166.343	312.2	280.539	481.8	380.719	1032
168.777	315.1	283.599	486.9		
171.350	318.6	286.728	493.0		

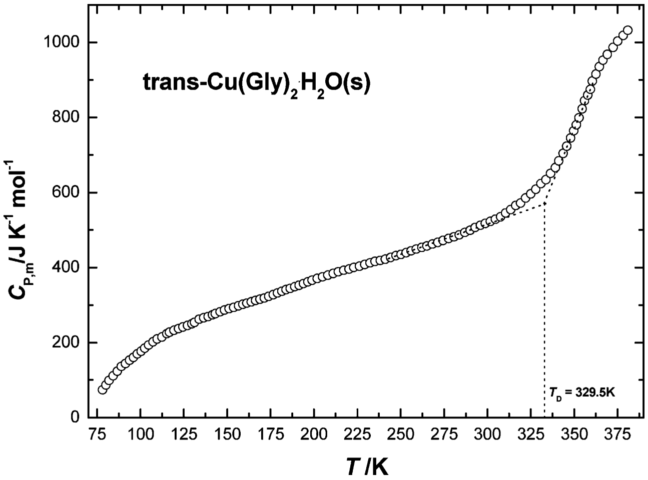

Figure 1. Curve of the experimental molar heat capacities of the complex *trans*-Cu (Gly)$_2$·H$_2$O(s) vs temperature (T).

in which $X = (T - 203)/125$. 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 correlation coefficient for the fitting R^2 equals 0.9998. 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.

Table 2. Thermodynamic Functions of the Complex *trans*-Cu(Gly)$_2$·H$_2$O(s)

T	$C_{p,m}$	$[H_{(T)} - H_{(298.15K)}]$	$[S_{(T)} - S_{(298.15K)}]$
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
80	86.29	−73.91	−103.14
85	114.2	−73.41	−102.38
90	138.4	−72.77	−102.03
95	159.4	−72.03	−101.16
100	177.8	−71.18	−100.82
105	193.9	−70.25	−100.08
110	208.2	−69.25	−99.97
115	221.0	−68.17	−98.55
120	232.6	−67.04	−96.87
125	243.1	−65.85	−94.96
130	252.9	−64.61	−92.86
135	262.1	−63.32	−90.61
140	270.8	−61.99	−88.23
145	279.3	−60.61	−85.75
150	287.4	−59.19	−83.19
155	295.5	−57.74	−80.57
160	303.4	−56.24	−77.91
165	311.3	−54.70	−75.22
170	319.1	−53.13	−72.52
175	327.0	−51.51	−69.80
180	334.8	−49.86	−67.09
185	342.5	−48.16	−64.37
190	350.3	−46.43	−61.66
195	358.0	−44.66	−58.94
200	365.6	−42.85	−56.24
205	373.1	−41.00	−53.53
210	380.6	−39.12	−50.82
215	388.0	−37.20	−48.10
220	395.2	−35.24	−45.37
225	402.3	−33.25	−42.63
230	409.3	−31.22	−39.87
235	416.2	−29.15	−37.08
240	423.1	−27.06	−34.28
245	429.8	−24.92	−31.44
250	436.6	−22.76	−28.57
255	443.4	−20.56	−25.67
260	450.3	−18.32	−22.75
265	457.3	−16.05	−19.79
270	464.6	−13.75	−16.81
275	472.3	−11.41	−13.82
280	480.4	−9.023	−10.81
285	489.0	−6.601	−7.813
290	498.3	−4.132	−4.812
295	508.5	−1.612	−1.851
298.15	515.4	0	0
300	519.8	0.963	1.084
305	532.0	3.591	3.942
310	545.6	6.282	6.723
315	560.7	9.054	9.391
320	577.6	11.90	12.94
325	596.2	14.83	16.32

Thermodynamic Functions of the Complex trans-Cu(Gly)$_2$·H$_2$O(s). The smoothed molar heat capacities and thermodynamic functions of the complex *trans*-Cu(Gly)$_2$·H$_2$O(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

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

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

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 tabulated in Table 2 with an interval of 5 K.

Determination of Enthalpy Change of the Solid-state Coordination Reaction of Cu(Ac)$_2$·H$_2$O(s) with Glycine. The

Table 3. Dissolution Enthalpies of [$Cu(Ac)_2 \cdot H_2O(s)$ + 2Gly(s)] and [HAc(l)] in 2 $mol \cdot L^{-1}$ HCl and [*trans*-$Cu(Gly)_2 \cdot H_2O(s)$] in [HAc(l) + 2 $mol \cdot L^{-1}$ HCl] at 298.15 K[a]

system	solvent	no.	m/g[b]	ΔE_e/mV[b]	ΔE_s/mV[b]	Q_e/J[b]	Q_s/J[b]	$\Delta_S H_m$/kJ·mol^{-1} [b]
			$\Delta_S H_m$ (1) = (13.59 ± 0.03) kJ·mol^{-1}					
$Cu(Ac)_2 \cdot H_2O(s)$ + 2Gly(s)	2 mol·L^{-1} HCl	1	0.326 9	2.78	2.77	12.804	12.758	13.66
		2	0.330 3	2.78	2.82	12.726	12.909	13.67
		3	0.332 4	2.53	2.77	11.464	12.552	13.52
		4	0.333 7	2.76	2.86	12.447	12.898	13.52
		5	0.328 9	2.96	2.84	13.298	12.759	13.56
			$\Delta_S H_m$ (2) = −(0.93 ± 0.03) kJ·mol^{-1}					
HAc (l)	2 mol·L^{-1} HCl	1	0.205 2	1.00	1.70	4.508	−3.156	−0.93
		2	0.206 0	1.19	1.06	5.292	−4.714	−0.93
		3	0.206 4	1.05	1.06	4.696	−4.741	−0.93
		4	0.201 4	1.02	1.11	4.541	−4.942	−0.95
		5	0.205 6	0.96	1.04	4.287	−4.644	−0.91
			$\Delta_S H_m$ (3) = −(14.64 ± 0.02) kJ·mol^{-1}					
trans-$Cu(Gly)_2 \cdot H_2O(s)$	HAc (l) + 2 mol·L^{-1} HCl	1	0.229 4	3.13	3.09	13.830	−14.009	−14.67
		2	0.228 1	3.12	3.07	13.660	−13.883	−14.62
		3	0.235 7	2.85	2.55	11.736	−13.117	−14.65
		4	0.228 9	2.84	2.69	12.531	−13.230	−14.69
		5	0.233 8	2.83	2.82	13.073	−13.027	−14.59

[a] R = 1666.0 Ω, I = 10.000 mA. [b] m/g is the mass of the sample; ΔE_e/mV, the voltage change during the electrical calibration; ΔE_s/mV, the voltage change during the sample dissolution; Q_e/J, the electrical energy of electrical calibration; Q_s/J, the heat effect; $\Delta_S H_m = (\Delta E_s/\Delta E_e) \times I^2 R t_e (M/m)$, where R is the electroresistance, I, the electrical current, M, the molar mass, and t_e, the heating period of electrical calibration.

Table 4. Reaction Scheme Used To Determine the Standard Molar Formation Enthalpy of the Complex *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ at 298.15 K[a]

no.	reactions	solution	$\Delta_f H_m$° or $\Delta_S H_m \pm \sigma_a$/kJ ·mol^{-1} [c]
1	{$Cu(Ac)_2 \cdot H_2O(s)$ + 2Gly(s)} + "s" =	A	ΔH_1 = (13.59 ± 0.03)
2	2HAc(l) + "s" =	A_1	ΔH_2 = −(0.93 ± 0.03)
3	*trans*-$Cu(Gly)_2 \cdot H_2O(s)$ + "A_1" =	A′	ΔH_3 = −(14.64 ± 0.02)
4	$2H_2(g) + O_2(g) + 2C(s) = HAc(l)$		ΔH_4 = −484.5
5	$Cu(s) + 4 H_2(g) + 5/2O_2(g) + 4 C(s) = Cu (Ac)_2 \cdot H_2O(s)$		ΔH_5 = −1193.7
6	$2C(s) + 5/2 H_2(g) + O_2(g) + 1/2 N_2(g) = Gly(s)$		ΔH_6 = −(528.5 ± 0.5)
7	$Cu(s) + N_2(g) + 6H_2(g) + 5/2O_2(g) + 4C(s) =$ *trans*-Cu $(Gly)_2 \cdot H_2O(s)$		ΔH_7 = −(1251.7 ± 1.0)

[a] The solvent "s" is 2 mol·L^{-1} HCl ($\Delta H_7 = \Delta H_1 - 2\Delta H_2 - \Delta H_3 - 2\Delta H_4 + \Delta H_5 + 2\Delta H_6$). [b] According to ref 7. [c] $\sigma_a = \sqrt{(\sum_{i=1}^{5}(x_i - \bar{x})^2)/(n(n-1))}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

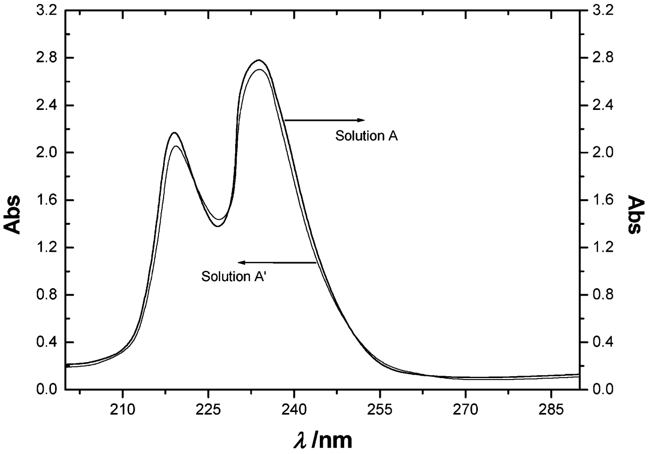

Figure 2. UV−vis spectra of solution A and solution A′ obtained from the dissolution of the {$Cu(Ac)_2 \cdot H_2O(s)$ + 2Gly(s)} mixture in 100 cm^3 of 2 $mol \cdot dm^{-3}$ HCl and {*trans*-$Cu(Gly)_2 \cdot H_2O(s)$} in solution A_1 (diluted into 1:20).

solid-state coordination reaction of $Cu(Ac)_2 \cdot H_2O(s)$ with glycine is shown as follows

$$Cu(Ac)_2 \cdot H_2O(s) + 2Gly(s) \rightarrow Cu(Gly)_2 \cdot H_2O(s) + 2HAc(l) \tag{1}$$

The enthalpy change of reaction 1 was determined by measuring the enthalpies of dissolution of {$Cu(Ac)_2 \cdot H_2O(s)$ + 2Gly(s)}[$\Delta_s H_m$ (1)] and HAc(l) [$\Delta_s H_m$ (2)] in 2 $mol \cdot dm^{-3}$ and the *trans*-Cu(Gly) $2 \cdot H_2O(s)$ [$\Delta_s H_m$ (3)] in the solvent [HAc(l) + 2 $mol \cdot L^{-1}$ HCl] at 298.15 K.

The measurement results of dissolution enthalpies for the reactants and products of reaction 1 are listed in Table 3. The enthalpy change of the solid-state coordination reaction 1 can be calculated according to a thermochemical cycle and the experimental results of the dissolution enthalpies as follows

$$\Delta_r H_m (1) = \Delta_s H_m (1) - 2\Delta_s H_m (2) - \Delta_s H_m (3) = (30.09 \pm 0.05)\ \mathrm{kJ \cdot mol^{-1}}$$

Standard Molar Formation Enthalpy of trans-$Cu(Gly)_2 \cdot H_2O$ (s). One reaction scheme used to derive the standard molar formation enthalpy of *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ has been given in Table 4. The experimental values of the dissolution enthalpies of the reactants and products in the solid-state coordination reaction 1 were combined with auxiliary thermodynamic data of $\Delta_f H_m$°[$Cu(Ac)_2 \cdot H_2O(s)$] = −1193.7 kJ·mol^{-1} [8], $\Delta_f H_m$°[HAc(l)] = −484.5 kJ·mol^{-1} [9], and $\Delta_f H_m$°[Gly(s)] = −528.5 ± 0.5 kJ·mol^{-1} [10] to derive the standard molar formation enthalpy of *trans*-$Cu(Gly)_2 \cdot H_2O$ (s)

$$\Delta_f H_m°[trans\text{-}Cu(Gly)_2 \cdot H_2O(s)] = \Delta_r H_m (1) - 2\Delta_f H_m°(HAc, l) + 2\Delta_f H_m°(Gly, s) + \Delta_f H_m°[Cu(Ac)_2 \cdot H_2O, s] = \Delta H_7 = \Delta H_1 - 2\Delta H_2 - \Delta H_3 - 2\Delta H_4 + \Delta H_5 + 2\Delta H_6$$

$$= -(1251.6 \pm 1.0)\ \mathrm{kJ \cdot mol^{-1}}$$

in which $\Delta H_1 - \Delta H_7$ are the enthalpy changes of the corresponding reactions in Table 4.

In this paper, all of the reactants and products of the solid-state coordination reaction can be easily dissolved in the corresponding solvents. Solution A is in a thermodynamic equivalent state to solution A′, which has been verified by UV spectroscopy, as shown in Figure 2.

4. Conclusions

This paper reports low-temperature heat capacities measured by adiabatic calorimetry and the dissolution enthalpies of the reactants and the products of the solid-state coordination reaction of copper(II) acetate with L-α-glycine by isoperibol solution calorimetry. Additionally, the initial dehydration temperature, thermodynamic functions, and standard molar enthalpy of formation of the product [*trans*-Cu(Gly)$_2$·H$_2$O(s)] were derived from these experimental results.

The reliability of the designed thermochemical cycle has been verified by UV spectroscopy. It is shown that the cycle is reasonable and can be used to determine the standard molar enthalpy of formation of the product [*trans*-Cu(Gly)$_2$·H$_2$O(s)]. The uncertainty of the standard molar enthalpy of formation obtained by isoperibol solution calorimetry was estimated to be between 0.5 % and 1 %, chiefly considering the measurements of voltage changes E_s and E_e, duration time of electric calibration t, final data processing, and so on.

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