Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 412 (2004) 171–177

thermochimica acta

www.elsevier.com/locate/tca

Low-temperature heat capacities and standard molar enthalpy of formation of the coordination compound $Zn(His)SO_4{\cdot}H_2O(s)$ (His = L-α-histidine)

You-Ying Di [a], Zhi-Cheng Tan [a,*], Hua-Guang Yu [b], Sheng-Li Gao [c], Yi Liu [b], Li-Xian Sun [a]

[a] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*
[b] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China*
[c] *Department of Chemistry, Northwest University, Xi-an 710069, PR China*

Received 4 June 2003; received in revised form 18 September 2003; accepted 29 September 2003

Abstract

Low-temperature heat capacities of the solid coordination compound $Zn(His)SO_4{\cdot}H_2O(s)$ were precisely measured by a precision automated adiabatic calorimeter over the temperature range between $T = 78$ and 373 K. The initial dehydration temperature of the coordination compound was determined to be, $T_d = 324.20$ K, by analysis of the heat-capacity curve. The experimental values of molar heat capacities were fitted to a polynomial equation of heat capacities ($C_{p,m}$) with the reduced temperatures, x ($x = f(T)$), by least square method. Enthalpies of dissolution of the $ZnSO_4 \cdot 7H_2O(s) + His(s)$ ($\Delta_d H^\circ_{m,1}$) and the $Zn(His)SO_4{\cdot}H_2O(s)$ ($\Delta_d H^\circ_{m,2}$) in 100.00 ml of 2 mol l^{-3} HCl(aq) at $T = 298.15$ K were determined to be, $\Delta_d H^\circ_{m,1} = -(13.129 \pm 0.013)$ kJ mol^{-1} and $\Delta_d H^\circ_{m,2} = -(11.271 \pm 0.012)$ kJ mol^{-1}, by means of a homemade isoperibol solution-reaction calorimeter. The standard molar enthalpy of formation of the compound was determined as: $\Delta_f H^\circ_m$ ($Zn(His)SO_4 \cdot H_2O$, s, 298.15 K) $= -(1827.61 \pm 2.31)$ kJ mol^{-1} from the enthalpies of dissolution and other auxiliary thermodynamic data through a Hess thermochemical cycle by using the homemade isoperibol calorimeter. Furthermore, the reliability of the designed Hess thermochemical cycle was verified by comparing between UV/Vis spectra and the refractive indexes of Solution A (from dissolution of the [$ZnSO_4 \cdot 7H_2O(s) + His(s)$] mixture in 2 mol l^{-3} hydrochloric acid) and Solution A′ (from dissolution of the complex $Zn(His)SO_4{\cdot}H_2O(s)$ in 2 mol l^{-3} hydrochloric acid).

Keywords: $Zn(His)SO_4{\cdot}H_2O(s)$; Adiabatic calorimetry; Isoperibol solution-reaction calorimetry; Standard molar enthalpy of formation; UV/Vis spectroscopy

1. Introduction

It is well known that zinc is one of the trace elements necessitated for the human body. It plays an important role in human's physical growth, especially intelligence development. Many kinds of diseases will be brought about owing to the shortage of the zinc as one of bioelements in the human body. The L-α-amino acids are indispensable nutrients in the organism and the basic units that constitute the proteins demanded for the life activity. The complexes of zinc with L-α-amino acid have been considered to be one of the most efficient zinc-tonics because it has been verified experimentally that this kind of complex has a higher absorption ratio in the human body than that of traditionally inorganic and organic weak-acid zinc-tonics. It is well established that this kind of coordination compound has found wide application in medicines, foodstuffs, forages and cosmetics as nutrient additives [1–3]. Gao et al. [4] have investigated phase chemistry of coordination behavior of zinc salts with L-α-histidine by the method of semi-micro-phase equilibrium, the corresponding equilibrium phase diagram and refractive index diagram have been constructed from the compositions of saturated solutions and the data of refractive indexes in ternary systems, and finally synthesized the coordination compound $Zn(His)SO_4{\cdot}H_2O(s)$ in the mixed solution of water and acetone under the guidance of equilibrium phase diagram. They have characterized the structure and other properties of the complex by means of FTIR, XRD, TG and DTA, and pointed out that the initial decomposition temperature of the solid complex is $T_d = 323.15$ K according to the result of the thermogravimetry.

However, up to now, various thermodynamic properties of the complex were not reported in literature. As one project of the research program about the complexes of zinc with L-α-amino acid, for the purposes of further investigation and

---

[*] Corresponding author. Fax: +86-411-4691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

0040-6031/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/j.tca.2003.09.022

application of the coordination compound, in the present work, the low-temperature heat capacities over the temperature range between $T = 78$ and 373 K and the standard molar enthalpies of formation at $T = 298.15$ K were measured by adiabatic calorimetry and isoperibol solution-reaction calorimetry, respectively. The experimental values of molar heat capacities were fitted to a polynomial equation of heat capacities ($C_{\mathrm{p,m}}$) versus reduced temperatures, x ($x = f(T)$), by least square method so as to calculate various thermodynamic properties of the coordination compound.

The isoperibol solution-reaction calorimetry is a universal technique used for the measurements of enthalpies of reaction, dissolution, dilution, mixing, formation, and excess enthalpies [5–18] in a thermochemistry laboratory. Especially the solution calorimetry is often applied to determine the standard molar enthalpies of formation of many important substances in industry and scientific research based on the data of enthalpies of dissolution, reaction and some auxiliary thermodynamic quantities. The standard molar enthalpies of formation, together with the standard or specified entropy, are equally important data in determining any chemical equilibrium. The solution-reaction calorimeter has been established in our thermochemistry laboratory on the basis of other investigations [5–15] and our previous works [16–18]. At the same time, the molar enthalpies of dissolution of KCl(s) (Standard Reference Material 1655) in double distilled water and reaction of THAM(s) (NBS 742a standard substance) with 0.1000 mol l^{-1} HCl(aq) at $T = 298.15$ K have been measured so that the reliability of the calorimeter is confirmed. In view of the importance of the standard molar enthalpy of formation and the enthalpy of dissolution in industrial production, theoretical research and application development of the compound $\mathrm{Zn(His)SO_4{\cdot}H_2O(s)}$, in this paper, these thermodynamic data of the complex has been derived by means of a designed Hess thermochemical cycle through the homemade isoperibol solution-reaction calorimeter.

2. Experimental

2.1. Reagents and sample

All the chemicals ($\mathrm{ZnSO_4{\cdot}7H_2O(s)}$, histidine(s), α-$\mathrm{Al_2O_3}$(s) and HCl(aq)) used were the reagents of analytical grade and obtained from the Shanghai Reagent Factory, PR China. KCl(s) was provided from the National Institute of Standards and Technology, Standard Reference Material 1655. THAM(s) was a NBS 742a standard substance and provided from the formerly National Bureau of Standardization.

The solid complex $\mathrm{Zn(His)SO_4{\cdot}H_2O(s)}$ was a white crystal with a lumpy shape. The sample used for the measurements was prepared by semi-micro phase equilibrium method [4,19]. The solid complex obtained was put into a desiccator containing $\mathrm{P_4O_{10}}$ until the weight of the complex became constant. The results of chemical and elemental analysis, IR spectra, TG-DTG and XRD have proved that the composition of the complex was $\mathrm{Zn(His)SO_4{\cdot}H_2O(s)}$, as indicated in the literature [4]. The purity of the complex determined by chemical and elementary analysis was higher than 99.90% (analytical error, $\leq$0.2 mass%).

2.2. Adiabatic calorimetry

A high-precision automatic adiabatic calorimeter was used to measure the heat capacities over the temperature range $78 \leq (T/\mathrm{K}) \leq 373$. The calorimeter was established in thermochemistry laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [20–22]. Briefly, the calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, the inner and the outer adiabatic shields, two sets of six-junctions 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 at $T = 273.15$ K) 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 picked up by use of the Data Acquisition/Switch Unit (Model 34970A, Agilent, USA), and processed on line by a computer.

To verify the accuracy of the calorimeter, the heat-capacity measurements of the reference standard material, α-$\mathrm{Al_2O_3}$, were made over the temperature range $78 \leq (T/\mathrm{K}) \leq 373$. The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(\mathrm{Al_2O_3}) = 101.9613$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.3%, as compared with those of the former National Bureau of Standards [23] 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 0.1–0.4 K min^{-1} and 1–3 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 [19–21]. The sample mass used for calorimetric measurements was 4.3511 g, which was equivalent to 0.01300 mol in terms of its molar mass, $M = 334.6269\ \mathrm{g\,mol^{-1}}$.

2.3. Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter was mainly composed of the precision temperature controlling system, the electric energy calibration system, the calorimetric body, the electric stirring system, the thermostatic bath made by transparent silicate glass, the precision temperature measuring system and the data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [16–18].

The thermostatic bath was made by transparent silicate glass and surrounded by the air layer formed by the organic glass of 4 mm in thickness. The total resistance of the heater in the thermostatic bath was about 80 Ω. During whole experiment, the water thermostat was automatically maintained at $T = (298.150 \pm 0.001)$ K by regulating an adjustable precision resistor linked in the Wheatstone bridge. The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. Experiments have demonstrated that the precision of temperature controlling of this kind of system can reach $\pm 1 \times 10^{-3}$ K at least.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the temperature measurement system and the sampling system. The temperature measurement system consisted of a wheatstone electric bridge similar to that of the temperature controlling system and another thermistor with large negative temperature coefficient of resistance. A Data Acquisition/Switch Unit (Model 34970 A, Agilent, USA) was used to measure the temperature of the solution in the chamber with an accuracy of 0.1 mK. The unbalanced voltage signal of the electric bridge was linear response to the change of temperature over the temperature range between $T = 290$ and 305 K. The signal from the electric bridge of measuring the temperature was amplified and automatically picked up by use of the Agilent data acquisition system mentioned above, and processed on line by a computer. Measurements indicated that the precision of measuring the temperature reached $\pm 1 \times 10^{-4}$ K at least and the time constant of the calorimeter was about 2.9 s.

The system of electric energy calibration contained the electric heater and the precision power source with stepwise constant currents. During each electrical energy calibration, the electrical current (I) was set at 10.115 mA, and the resistance of the electrical heater was 1017.2 Ω at $T = 298.15$ K.

The reliability of the calorimeter was verified by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in $0.1\ \mathrm{mol\,l^{-1}}$ hydrochloric acid and KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. The mean dissolution enthalpies were—$(29\,776 \pm 16)\ \mathrm{J\,mol^{-1}}$ for THAM and $(17\,597 \pm 17)\ \mathrm{J\,mol^{-1}}$ for KCl, which compared with corresponding published data [24,25],—$(29\,765 \pm 10)\ \mathrm{J\,mol^{-1}}$ for THAM and $(17\,536 \pm 3.4)\ \mathrm{J\,mol^{-1}}$ for KCl.

In all dissolution experiments of the sample, $2\ \mathrm{mol\,l^{-3}}$ HCl was chosen as calorimetric solvent for measuring the dissolution enthalpies of the [His(s) and $ZnSO_4{\cdot}7H_2O(s)$] mixture and the complex $Zn(His)SO_4{\cdot}H_2O(s)$, respectively.

The solid $ZnSO_4{\cdot}7H_2O(s)$ was ground within an agate mortar into fine powder. The mixture of about 0.158 g of His(s) and about 0.285 g of $ZnSO_4{\cdot}7H_2O(s)$ at mole ratio of $n(ZnSO_4{\cdot}7H_2O){:}n(His) = 1{:}1$ was dissolved in 100 ml of $2\ \mathrm{mol\,l^{-3}}$ HCl at $T = 298.15$ K. The final solution obtained was named as Solution A.

The solid complex $Zn(His)SO_4{\cdot}H_2O(s)$ was dried in a vacuum desiccator in order to take off some additional adsorbing water. Then, it was ground into fine powder. Dissolution enthalpy of about 0.3320 g of $Zn(His)SO_4{\cdot}H_2O(s)$ in 100 ml of $2\ \mathrm{mol\,l^{-3}}$ hydrochloric acid was determined under the same condition as the above. The final solution obtained was named as Solution A′.

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

3. Results and discussion

3.1. Low-temperature heat capacities

All experimental results, listed in Table 1 and plotted in Fig. 1, showed that the structure of the coordination compound was stable over the temperature range between $T = 78$ and 324 K: no phase change, association nor thermal decomposition occurred. However, at temperatures above 324 K, the heat-capacity curve steeply began to rise. The phenomenon was associated with the dehydration or thermal decomposition of the compound, as shown by TG analysis [4]. In addition, the initial dehydration temperature (T_d) has been obtained by means of the analysis of heat-capacity curve. Two sections of the heat-capacity curves for 78–324 and 324–373 K were extrapolated linearly. The intersection point of these two straight lines was the initial decomposition temperature, $T_d = 324.20$ K (see Fig. 1). TG analysis has given the initial dehydration temperature (323.15 K), the final dehydration temperature (515.15 K) and the loss-mass percentage (5.22%) of the compound. The loss-mass percentage was identical with the percentage of the water molecule in the coordination compound (the theoretical loss-mass of the dehydration was 5.35%). 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 324.20 K, the section of the heat-capacity curve in the temperature range $324 \le (T/\mathrm{K}) \le 373$ was corresponding to the thermal anomaly of the compound on the

Table 1
Experimental molar heat capacities of the complex Zn(His)$SO_4 \cdot H_2O$(s) ($M = 334.6269\,\mathrm{g\,mol^{-1}}$)

T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
78.135	101.321	171.469	259.945	277.576	426.229
80.164	105.431	168.941	254.037	280.682	430.621
82.007	108.385	173.934	264.055	283.864	436.768
84.299	111.725	176.507	268.036	286.969	442.916
86.591	115.449	178.924	271.889	290.076	447.892
89.044	119.688	181.585	276.385	292.955	449.356
91.412	123.413	184.036	280.495	295.909	457.845
93.812	127.651	186.371	284.092	298.864	463.407
96.035	131.376	188.957	288.334	301.742	468.677
98.315	135.358	191.465	292.569	304.621	478.337
100.493	138.183	193.915	296.807	307.561	484.018
102.634	142.165	196.469	300.147	310.483	490.248
104.807	146.275	198.925	303.743	313.409	499.122
107.224	150.128	201.969	308.367	316.364	505.269
109.652	155.395	205.046	314.147	319.167	511.709
112.409	159.761	208.14	320.697	322.121	521.077
115.125	164.642	211.168	324.037	325.101	532.201
116.702	167.596	214.131	328.532	327.955	543.911
119.369	172.349	217.289	332.514	330.929	556.253
121.997	176.844	220.227	336.651	333.643	567.834
124.526	181.339	223.106	340.749	336.429	580.925
127.148	185.321	226.288	344.262	339.143	594.268
129.721	189.431	229.319	348.653	342.002	611.388
131.243	191.358	232.348	352.459	344.643	627.502
133.93	195.339	235.227	356.850	346.571	642.354
136.504	201.633	238.182	361.241	348.502	655.697
139.012	205.101	241.212	366.218	350.512	669.543
141.456	209.982	244.242	370.316	352.643	681.628
143.161	213.064	247.273	375.293	354.786	695.474
145.901	216.917	250.152	379.977	357.071	706.803
148.472	222.055	253.106	382.611	358.929	718.888
151.238	223.468	256.061	387.295	361.013	730.787
153.761	229.119	259.015	392.564	363.071	741.179
156.533	234.004	262.197	396.956	364.857	750.861
158.983	237.725	265.227	403.396	366.429	756.560
161.433	241.706	268.333	408.665	368.643	765.714
163.962	246.073	271.439	413.642	371.429	774.274
166.491	249.284	274.545	419.789		

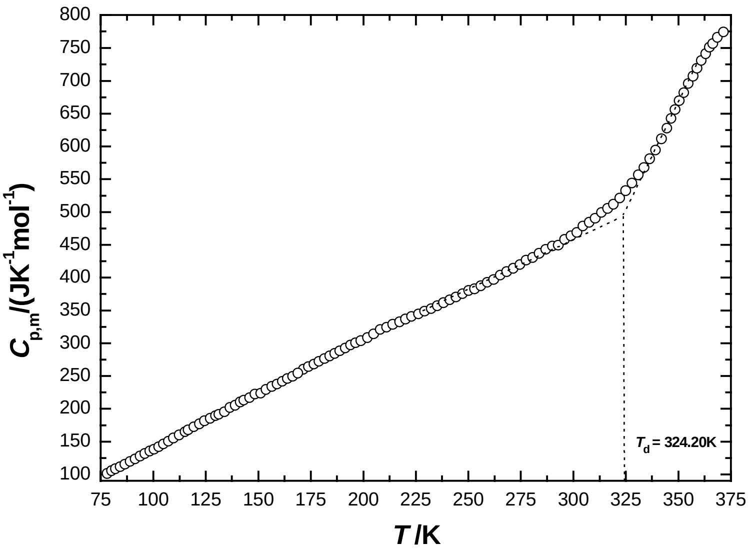

Fig. 1. The curve of the experimental molar heat capacities of the complex Zn(His)$SO_4 \cdot H_2O$(s) vs. the temperature (T).

Table 2
Dissolution enthalpy of the [$ZnSO_4{\cdot}7H_2O$(s) and His(s)] mixture [n($ZnSO_4{\cdot}7H_2O$):n(His) = 1:1] in 100 ml of 2 mol l^{-3} hydrochloric acid at $T = 298.15$ K[a]

Number	W_{His} (g)	$W_{\mathrm{ZnSO_4\cdot 7H_2O}}$ (g)	ΔE_s (mV)	ΔE_e (mV)	t (s)	Q_s (J)	$\Delta_d H^\circ_{m,1}$ (kJ mol^{-1})
1	0.1551	0.2836	−1.9658	1.9942	124.3	−13.123	−13.128
2	0.1558	0.2851	−2.1238	2.1311	126.4	−13.201	−13.146
3	0.1548	0.2832	−1.9311	1.9831	122.3	−13.071	−13.101
4	0.1556	0.2846	−2.0733	2.0994	124.7	−13.141	−13.104
5	0.1561	0.2858	−2.0996	2.1301	125.4	−13.240	−13.168
Average							−(13.129 ± 0.013)

[a] In which: W—mass of sample; ΔE_e—the voltage change during the electrical calibration; ΔE_s—the voltage change during the sample dissolution; t—heating duration of electrical calibration; Q_s—heat effect of sample dissolution; $\Delta_d H^\circ_{m,1}$—dissolution enthalpy, $\Delta_d H^\circ_m = (\Delta E_s/\Delta E_e) I^2 Rt(M/W)$, where R is the electrical resistance of the heater in the reaction vessel ($R = 1017.2\,\Omega$ at $T = 298.15$ K); I the electrical current through the heater ($I = 10.115$ mA) and M the molar mass of the sample.

basis of the above analysis. Therefore, the useful and real section of heat-capacity curve of the compound itself was in the temperature region $78 \leq (T/\mathrm{K}) \leq 324$. Ninety-two experimental points in the temperature region between $T = 78$ and 324 K were fitted by means of the least square method and a polynomial equation of experimental molar heat capacities ($C_{p,m}$) versus reduced temperature, x ($x = f(T)$), has been obtained:

$$C_{p,m}\ (\mathrm{J\,K^{-1}\,mol^{-1}}) = 307.0213 + 189.2737x - 30.8171x^2 + 13.1675x^3 + 50.2504x^4 + 9.9280x^5 - 13.3360x^6$$

in which $x = (T–201)/123$. 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.

3.2. *The standard molar enthalpy of formation of the complex Zn(His)$SO_4{\cdot}H_2O$(s)*

The complex Zn(His)$SO_4{\cdot}H_2O$(s) was one of the products in the following reaction:

$$ZnSO_4 \cdot 7H_2O(s) + His(s) = Zn(His)SO_4 \cdot H_2O(s) + 6H_2O(l) \quad (1)$$

The enthalpy change of the above supposed reaction and standard molar enthalpy of formation of the complex Zn(His)$SO_4{\cdot}H_2O$(s) were determined through a designed Hess thermochemical cycle using experimental data of isoperibol calorimetry and other auxiliary thermodynamic data.

If ‘s’ = calorimetric solvent, 2 mol l^{-3} HCl(aq), the dissolution process of the mixture of reactants in the reaction (1) was expressed into: {$ZnSO_4{\cdot}7H_2O$ (s) and His (s)} + ‘s’ = Solution A.

The experimental results of the process were listed in Table 2.

The dissolution process of the product, Zn(His)$SO_4{\cdot}H_2O$(s), in the reaction (1) may be expressed as follows: {Zn(His)$SO_4 \cdot H_2O$(s)} + ‘s’ = Solution A′.

The results of the dissolution experiments were shown in Table 3.

The dissolution enthalpy of {$6H_2O$(l)} as one of the products in the reaction (1) in the solvent was within the range of experimental error and may be omitted because the amount of H_2O(l) was very small according to the stoichiometric number of H_2O(l) in the reaction.

The enthalpy change of the reaction (1), $\Delta_r H_m(1)$, can be calculated in accordance with the above designed Hess thermochemical cycle and experimental results listed in Tables 1 and 2 by means of the following equation as follows:

$$\begin{aligned}\Delta_r H_m(1) &= \Delta_d H^\circ_{m,1}\{ZnSO_4 \cdot 7H_2O(s)\ \text{and}\ His(s)\} - \Delta_d H^\circ_{m,1}\{Zn(His)SO_4 \cdot H_2O(s)\} \\ &= -(1.858 \pm 0.018)\ \mathrm{kJ \cdot mol^{-1}}\end{aligned}$$

A reaction scheme used to derive the standard molar enthalpy of formation of the complex Zn(His)$SO_4{\cdot}H_2O$(s) has been given in Table 4. The enthalpy change of the reaction (1) obtained from experimental values of the dissolution

Table 3
Dissolution enthalpy of the Zn(His)$SO_4{\cdot}H_2O$(s) in 100 ml of 2 mol l^{-3} hydrochloric acid at $T = 298.15$ K

Number	$W_{\mathrm{Zn(His)SO_4\cdot H_2O}}$ (g)	ΔE_s (mV)	ΔE_e (mV)	t (s)	Q_s (J)	$\Delta_d H^\circ_{m,1}$ (kJ mol^{-1})
1	0.3318	−3.5890	3.3974	113.3	−11.162	−11.257
2	0.3321	−3.5991	3.4006	113.5	−11.151	−11.236
3	0.3322	−3.6072	3.4287	113.9	−11.198	−11.280
4	0.3316	−3.6144	3.3578	115.7	−11.186	−11.288
5	0.3321	−3.6698	3.4016	116.2	−11.209	−11.294
Average						−(11.271 ± 0.012)

Table 4
Reaction scheme used to determine the standard molar enthalpy of formation of the complex $Zn(His)SO_4 \cdot H_2O(s)$ at $T = 298.15\,K$[a]

Number	Reaction scheme	$\Delta_f H^\circ_m$ or $\Delta_d H^\circ_m \pm \sigma_a$ (kJ mol^{-1})
1	$\{ZnSO_4 \cdot 7H_2O(s)$ and His $(s)\}$ + ‘s’ = Solution A	$-(13.129 \pm 0.013)$ (ΔH_1)
2	$\{Zn(His)SO_4 \cdot H_2O\ (s)\}$ + ‘s’ = Solution A′	$-(11.271 \pm 0.012)$ (ΔH_2)
3	$Zn(s) + S(s) + \frac{11}{2}O_2(g) + 7H_2(g) = ZnSO_4 \cdot 7H_2O(s)$	-3077.75 (ΔH_3)
4	$6C(s) + \frac{3}{2}N_2(g) + O_2(g) + \frac{9}{2}H_2(g) = His(s)$	$-(466.70 \pm 2.30)$ (ΔH_4)
5	$\frac{1}{2}O_2(g) + H_2(g) = H_2O(l)$	$-(285.83 \pm 0.04)$ (ΔH_5)
6	$Zn(s) + S(s) + \frac{7}{2}O_2(g) + 6C(s) + \frac{11}{2}H_2(g) = \frac{1}{2}N_2(g)Zn(His)SO_4 \cdot H_2O(s)$	$-(1827.61 \pm 2.31)$ (ΔH_6)

[a] In which ‘s’ is the calorimetric solvent, $2\,mol\,l^{-3}$ hydrochloric acid;

$$\sigma_a = \left(\sum_{i=1}^{5} (x_i - \bar{x})^2 / n(n-1) \right)^{1/2},$$

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.

enthalpies of the [His(s) and $ZnSO_4 \cdot 7H_2O(s)$] mixture and the complex $Zn(His)SO_4 \cdot H_2O(s)$ in $100\,cm^3$ of $2\,mol\,l^{-3}$ hydrochloric acid were combined with some auxiliary thermodynamic data, $\Delta_f H^\circ_m[ZnSO_4 \cdot 7H_2O, s, 298.15\,K] = -3077.75\,kJ\,mol^{-1}$ [26], $\Delta_f H^\circ_m[His, s, 298.15\,K] = -(466.70 \pm 2.30)\,kJ\,mol^{-1}$ [26] and $\Delta_f H^\circ_m[H_2O, l, 298.15\,K] = -(285.83 \pm 0.04)\,kJ\,mol^{-1}$ [27], to calculate the standard molar enthalpy of formation of the complex $Zn(His)SO_4 \cdot H_2O(s)$ as follows:

$$\begin{aligned}
&\Delta_f H^\circ_m\{Zn(His)SO_4 \cdot H_2O, s, 298.15\,K\} \\
&\quad = \Delta_r H_m(1) + \Delta_f H^\circ_m[ZnSO_4 \cdot 7H_2O, s, 298.15\,K] \\
&\qquad + \Delta_f H^\circ_m[His, s, 298.15\,K] \\
&\qquad - 6\Delta_f H^\circ_m[H_2O, l, 298.15\,K] \\
&\quad = \Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 - 6\Delta H_5 \\
&\quad = \Delta H_6 = -(1827.61 \pm 2.31)\,kJ\,mol^{-1}
\end{aligned}$$

in which ΔH_1–ΔH_6 are the molar enthalpy changes of the corresponding reactions are given in Table 4.

The results of UV/Vis spectra and refrangibility (refractive index) are two important bases for detecting whether the two kinds of solutions are the same or not in structure and composition. In this paper, all of the reactants and products of the reaction (1) can be easily dissolved in the selected solvent. The measured values of the refractive indexes of Solution A and Solution A′ were (1.3728 ± 0.0005) and (1.3733 ± 0.0008), respectively. The results of UV/Vis spectroscopy were shown in Fig. 2. UV/Vis spectrum and the data of the refrangibility of Solution A obtained agreed with those of Solution A′, no difference in the structure and chemical composition of the two solutions appeared. These results have demonstrated that the designed Hess thermochemical cycle was reasonable and reliable, and can be used to derive the standard molar enthalpy of formation of the coordination compound $Zn(His)SO_4 \cdot H_2O(s)$.

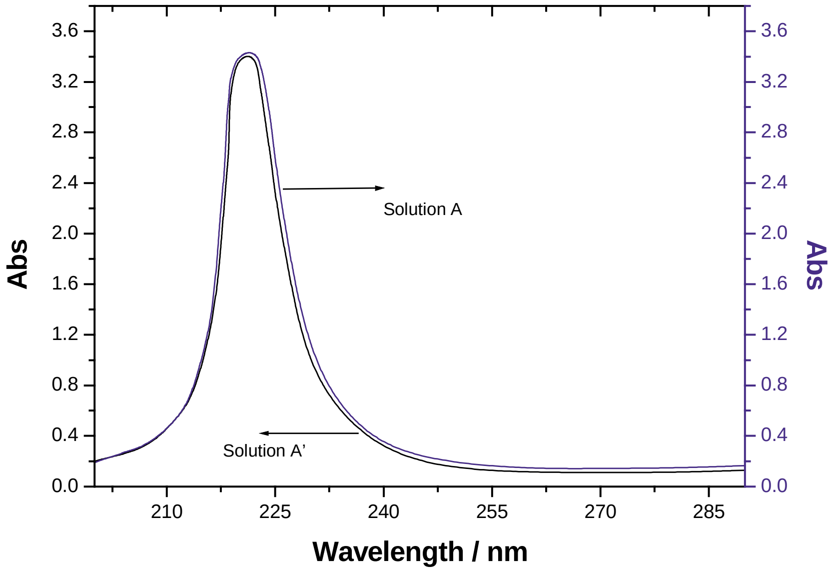

Fig. 2. UV/Vis spectra of Solution A and Solution A′ obtained from the dissolution of the $[ZnSO_4 \cdot 7H_2O(s)$ and His(s)] mixture and the $Zn(His)SO_4 \cdot H_2O(s)$ in the supposed reaction (1) in $100\,cm^3$ of $2\,mol\,l^{-3}$ HCl (diluted into 1:20).

The equilibrium constant (*K*) and the yield of the chemical reaction in which the coordination compound $Zn(His)SO_4 \cdot H_2O(s)$ is involved can be determined based on the standard molar enthalpies of formation and the specified entropies of the reactants and products in the reaction used in industry. In addition, histidine is one of the L-α-amino acids necessary for human body. Good coordination behavior of zinc salts with the histidine and other amino acids is probably due to the existence of the amino group in the amino acids. By using the same methods as that applied in the present paper, the heat capacities and standard molar enthalpies of other complexes of zinc salts with L-α-amino acids can be determined.

Acknowledgements

This work was financially supported by the National Science Foundation of China under the contract NSFC No. 20073047.

References

[1] M. Mahmoud, S. Abdel-monem, M. Paul, Method of nutritional supplementation for zinc and methionine by ingesting 1:1 zinc methionine complex, US Patent US 4-039-681, 1977-08-02; Chem. Abstr. 87 (1977) 15196.
[2] S. Taguchi, M. Inokuchi, N. Nakajima, M. Inomata, Y. Natitoh, Antipruritic drug and antipruritic composition, WO Patent 10 178, 1992-06-25; Chem. Abstr. 117 (1992) 258218.
[3] H. Harvey, Ashmed, U. Kaysville, Pure amino acid chelates, US Patent US 4-830-716, 1989-05-16; Chem. Abstr. 110 (1989) 219070.
[4] J.R. Liu, Y.D. Hou, S.L. Gao, M. Ji, Q.Z. Shi, Acta Chim. Sin. 57 (1999) 485–490.
[5] H.J. Seifert, S. Funke, Thermochim. Acta 320 (1998) 1–7.
[6] J.R. Payne, Thermochim. Acta 242 (1994) 13–19.
[7] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, L.C.M. da Silva, F. Dietze, E. Hoyer, Thermochim. Acta 378 (2001) 45–49.
[8] M. Jemal, A.B. Cherifa, I. Khattech, I. Ntahomvukiye, Thermochim. Acta 259 (1995) 13–18.
[9] P. Venkatesu, M.V. Prabhakara Rao, D.H.L. Prasad, Y.V.L. Ravi Kumar, Thermochim. Acta 342 (1999) 73–76.
[10] M. Schlegel, A. Lowe, Chem. Eng. Proc. 37 (1998) 61–77.
[11] S. Sunner, I. Sci. Tools 13 (1966) 1–13.
[12] J.K. Grime, in: J.K. Grime (Ed.), General Analytical Applications of Solution Calorimetry, Chem. Anal. (New York), 79 (Anal. Solution Calorim.), 1985, Chapter 6, pp. 163–298.
[13] H.F. Ferguson, D.J. Frurip, A.J. Pastor, L.M. Peerey, L.F. Whiting, Thermochim. Acta 363 (2000) 1–9.
[14] K.C. Thompson, Thermochim. Acta 355 (2000) 83–87.
[15] H.C. Dickinson, Bull. Natl. Bur. Stand. (US) 11 (1914) 189–196.
[16] L.Z. Zou, Z.H. Zhang, G.D. Xu, S.S. Qu, Chem. J. Chin. Uni. 10 (1989) 1211–1216.
[17] C.X. Wang, S.H. Song, W.G. Xong, S.S. Qu, Acta Phys.-Chim. Sin. 7 (1991) 586–589.
[18] H.G. Yu, Y. Liu, Z.C. Tan, J.X. Dong, T.J. Z, X.M. Huang, S.S. Qu, Thermochim. Acta 401 (2003) 217–224.
[19] H.Y. Jiang, D.H. Ren, H.F. Xie, Chin. J. Northwest Uni. (Natural Science Edition) 22 (1986) 1–6.
[20] Z.C. Tan, G.Y. Sun, Y. Sun, J. Therm. Anal. 45 (1995) 59–67.
[21] Z.C. Tan, G.Y. Sun, Y.J. Song, L. Wang, J.R. Han, Y.S. Liu, et al., Thermochim. Acta 252–253 (2000) 247–253.
[22] Z.C. Tan, L.X. Sun, S.H. Meng, L. Li, P. Yu, B.P. Liu, J.B. Zhang, J. Chem. Thermodyn. 34 (2002) 1417–1429.
[23] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stand 87 (1982) 159–163.
[24] R.L. Montgomery, R.A. Melaugh, C.C. Lau, G.H. Meier, H.H. Chan, F.D. Rossini, J. Chem. Thermodyn. 9 (1977) 915–936.
[25] P. Pychly, V. Pekarek, J. Chem. Thermodyn. 9 (1977) 391–396.
[26] D.D. Waeman, W.H. Evans, V.B. Paskes, et al., The NBS tables of chemical thermodynamic properties, Phys. Chem. Ref. Data 11 (Suppl. 2) (1982) 38, 140.
[27] J.A. Dean, in: J.F. Shang, S.J. Cao, W.M. Xin, et al. (Transl.), Lange's Handbook of Chemistry, 13th ed., Science Press, Beijing, 1991, pp. 1986.