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Low-Temperature Heat Capacities and Standard Molar Enthalpy of Formation of the Coordination Compound $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ (Leu = L-α-Leucine)

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Low-temperature heat capacities of the solid coordination compound $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ were measured by a precision automated adiabatic calorimeter over the temperature range between $T = 78$ K and $T = 371$ K. The initial dehydration temperature of the coordination compound was determined to be $T_D = 326.50$ 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-squares method. Enthalpies of dissolution of the [$ZnSO_4 \cdot 7H_2O(s)$ + Leu(s)] ($\Delta_{sol}H^\circ_{m,1}$) and the $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ ($\Delta_{sol}H^\circ_{m,2}$) in 100.00 mL of 2 mol·dm^{-3} HCl(aq) at $T = 298.15$ K were determined to be $\Delta_{sol}H^\circ_{m,1} = -(85.80 \pm 0.09)$ kJ·mol^{-1} and $\Delta_{sol}H^\circ_{m,2} = (55.97 \pm 0.06)$ kJ·mol^{-1} by means of a homemade isoperibol solution−reaction calorimeter. The standard molar enthalpy of formation of the compound was determined as $\Delta_f H^\circ_m(Zn(Leu)SO_4 \cdot 1/2H_2O$, s, 298.15 K) = $-(1999.0 \pm 0.9)$ kJ·mol^{-1} from the enthalpies of dissolution and other auxiliary thermodynamic data through a Hess thermochemical cycle. Furthermore, the reliability of the Hess thermochemical cycle was verified by comparing UV/Vis spectra and the refractive indexes of solution A (from dissolution of the [$ZnSO_4 \cdot 7H_2O(s)$ + Leu(s)] mixture in 2 mol·dm^{-3} hydrochloric acid) and solution A′ (from dissolution of the complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ in 2 mol·dm^{-3} hydrochloric acid).

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 diseases result from 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 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.[1,2,3] Yang et al.[4] and Jiang et al.[5] have investigated phase chemistry of coordination behavior of zinc salts with L-α-leucine by the method of semi-microphase 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 $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ 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 thermogravimetry.

However, up to now, various thermodynamic properties of the complex have not been reported in the literature. As one project of the research program about the complexes of zinc with L-α-amino acid, the low-temperature heat capacities over the temperature range between $T = 78$ K and $T = 371$ 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 ($C_{p,m}$) as a function of reduced temperatures (x), [$x = f(T)$], by a least-squares method so as to calculate various thermodynamic properties of the coordination compound.

Exprimental Section

Reagents and Sample. $ZnSO_4 \cdot 7H_2O(s)$, leucine(s), α-Al_2O_3(s), and HCl(aq) used were the reagents of analytical grade and obtained from the Shanghai Reagent Factory, People's Republic of 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 $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ was a white crystal with a lumpy shape. The sample used for the

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measurements was prepared by a semi-microphase equilibrium method.[4,5] The solid complex obtained was put into a desiccator containing P_4O_{10} until the mass of the complex became constant. The results of chemical and elemental analysis, IR spectra, TG-DTG, and XRD indicated that the composition of the complex was $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$.[4] The purity of the complex determined by chemical and elementary analysis was higher than 99.9 % mass fraction (analytical uncertainty in mass fraction $\leq$ 0.1 %).

Adiabatic Calorimetry. A high-precision automatic adiabatic calorimeter was used to measure the heat capacities over the temperature range $78 \leq (T/\mathrm{K}) \leq 371$. The calorimeter was established in the Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, People's Republic of China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere.[6,7] Briefly, the calorimeter mainly comprised a sample cell; a platinum resistance thermometer; an electric heater; inner and 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) 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 the data acquisition/switch unit (model 34970A, Agilent, USA) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat-capacity measurements of the reference standard material, α-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, $M(Al_2O_3) = 101.9613\ \mathrm{g \cdot mol^{-1}}$. Deviations of the experimental results from those of the smoothed curve lie within ± 0.2 %, while the uncertainty is within ± 0.3 %, as compared with the values given by the former National Bureau of Standards[8] 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.[6,7] The sample mass used for calorimetric measurements was 4.3511 g, which was equivalent to 0.01300 mol in terms of its molar mass, $M = 334.6269\ \mathrm{g \cdot mol^{-1}}$.

Isoperibol Solution−Reaction Calorimetry. The isoperibol solution−reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, 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.[9,10]

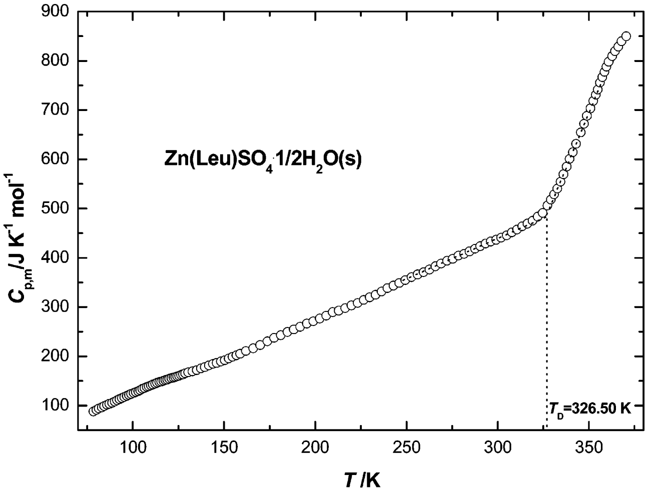

Figure 1. Curve of the experimental molar heat capacities of the complex Zn (Leu) $SO_4 \cdot 1/2H_2O(s)$ vs the temperature (T).

The reliability of the calorimeter was verified previously[10] by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.1 $\mathrm{mol \cdot dm^{-3}}$ hydrochloric acid and KCl (calorimetrically primary standard) in double-distilled water at $T = 298.15$ K.

In all dissolution experiments of the sample, 2 $\mathrm{mol \cdot dm^{-3}}$ HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the [Leu(s) and $ZnSO_4 \cdot 7H_2O(s)$] mixture and the complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$, respectively.

The solid $ZnSO_4 \cdot 7H_2O(s)$ was ground within an agate mortar into fine powder. The mixture of about 0.132 g of Leu(s) and about 0.288 g of $ZnSO_4 \cdot 7H_2O(s)$ at mole ratio of $n(ZnSO_4 \cdot 7H_2O){:}n(\mathrm{Leu}) = 1{:}1$ was dissolved in 100 mL of 2 $\mathrm{mol \cdot dm^{-3}}$ HCl at $T = 298.15$ K. The final solution obtained was designated as solution A.

The solid complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ was dried in a vacuum desiccator in order to take off some additional adsorbing water. Then, it was ground into fine powder. The dissolution enthalpy of about 0.303 g of $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ in 100 mL of 2 $\mathrm{mol \cdot dm^{-3}}$ 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 used 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′.

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 $T = 326$ K, no phase change, and no association nor thermal decomposition occurred. However, at temperatures above 326 K, the heat-capacity curve began to rise steeply. The phenomenon was associated with the dehydration or thermal decomposition of the compound, as shown by TG analysis.[3] 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 to 326) K and (327 to 371) K were extrapolated linearly. The intersection point of these two straight lines

Table 1. Experimental Molar Heat Capacities of the Complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$ ($M = 301.638\ g \cdot mol^{-1}$)

T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$
78.451	87.827	108.789	139.02	139.502	178.08	206.055	282.38	278.563	404.53	336.104	569.41
79.972	90.762	109.925	140.61	141.718	181.23	209.493	289.73	281.624	407.94	337.861	584.95
81.439	93.655	111.078	142.54	143.945	184.28	213.008	292.52	284.680	413.05	339.542	600.46
82.959	96.547	112.230	144.18	146.073	186.49	216.447	297.35	287.660	418.17	341.289	614.20
84.409	98.866	113.366	146.11	148.299	189.54	219.885	303.04	290.487	423.57	342.969	631.26
85.858	101.42	114.518	147.57	150.429	192.10	223.245	308.16	293.391	428.97	345.568	654.48
87.238	103.24	115.671	148.87	152.557	195.44	226.609	314.41	296.218	432.95	347.336	671.89
88.687	105.51	116.736	150.23	154.719	199.17	229.894	319.80	299.198	436.36	349.017	688.11
90.065	108.03	117.872	151.61	156.781	201.84	233.104	324.93	302.025	440.34	350.916	703.16
91.447	110.41	118.954	152.76	158.909	205.14	236.389	331.47	304.929	445.75	352.488	718.08
92.739	112.81	120.019	154.16	161.955	210.44	239.675	338.29	307.756	451.61	353.907	730.99
94.032	114.92	121.186	155.64	166.016	216.19	242.884	343.41	310.583	457.29	354.977	741.65
95.342	117.00	122.233	156.81	169.913	222.78	246.093	348.81	313.486	463.45	356.112	755.39
96.636	119.40	123.314	157.84	173.744	230.05	249.455	354.47	316.314	469.01	357.335	766.53
97.935	121.39	124.362	159.12	177.477	237.37	252.817	360.63	319.141	475.31	358.579	777.19
99.158	123.38	125.443	160.40	181.145	242.72	256.103	365.95	321.968	483.27	359.714	787.73
100.459	125.42	126.523	162.07	184.736	249.45	259.389	370.78	324.719	490.66	360.937	798.03
101.681	127.19	127.582	163.22	188.328	254.43	262.674	376.10	327.317	506.01	362.836	809.29
102.904	129.17	128.652	165.12	191.842	259.88	265.883	382.50	329.172	518.02	364.452	819.35
104.039	131.13	130.420	167.23	195.434	266.27	269.093	388.04	330.897	528.68	366.219	828.48
105.271	133.61	132.712	169.36	199.025	270.77	272.302	393.72	332.665	540.12	367.966	839.37
106.502	135.53	135.005	171.92	202.539	276.46	275.435	397.70	334.423	554.05	370.499	849.44
107.639	137.59	137.297	175.26								

Table 2. Thermodynamic Functions of the Complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$

T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	$[H_{(T)}-H_{(298.15K)}]$/$J \cdot mol^{-1}$	$[S_{(T)}-S_{(298.15K)}]$/$J \cdot K^{-1} \cdot mol^{-1}$	T/K	$C_{p,m}$/$J \cdot K^{-1} \cdot mol^{-1}$	$[H_{(T)}-H_{(298.15K)}]$/$J \cdot mol^{-1}$	$[S_{(T)}-S_{(298.15K)}]$/$J \cdot K^{-1} \cdot mol^{-1}$
80	90.016	−56420	−293.01	210	288.23	−31905	−125.39
85	99.951	−55947	−287.24	215	296.71	−30443	−118.51
90	109.04	−55426	−281.28	220	305.20	−28938	−111.58
95	117.44	−54861	−275.17	225	313.69	−27391	−104.62
100	125.29	−54256	−268.96	230	322.16	−25801	−97.624
105	132.70	−53612	−262.68	235	330.59	−24169	−90.599
110	139.78	−52932	−256.33	240	338.98	−22495	−83.545
115	146.63	−52216	−249.96	245	347.32	−20780	−76.467
120	153.34	−51467	−243.57	250	355.61	−19023	−69.365
125	159.96	−50685	−237.17	255	363.85	−17224	−62.243
130	166.57	−49869	−230.75	260	372.05	−15385	−55.102
135	173.21	−49020	−224.33	265	380.21	−13504	−47.943
140	179.92	−48138	−217.90	270	388.37	−11583	−40.767
145	186.74	−47221	−211.47	275	396.53	−9621.3	−33.573
150	193.69	−46270	−205.02	280	404.73	−7618.7	−26.361
155	200.78	−45285	−198.55	285	413.01	−5575.1	−19.129
160	208.03	−44263	−192.07	290	421.40	−3489.9	−11.876
165	215.45	−43204	−185.57	295	429.96	−1362.4	−4.5988
170	223.03	−42108	−179.03	298.15	435.49	0	0
175	230.76	−40974	−172.46	300	438.78	808.28	2.7063
180	238.64	−39800	−165.86	305	447.88	3023.5	10.042
185	246.66	−38587	−159.22	310	457.36	5285.0	17.413
190	254.80	−37334	−152.54	315	467.31	7594.8	24.821
195	263.05	−36039	−145.82	320	477.81	9955.5	32.269
200	271.38	−34703	−139.05	325	488.98	12370	39.762
205	279.78	−33325	−132.24				

was the initial decomposition temperature, $T_D = 326.50$ K (see Figure 1). TG analysis had given the initial dehydration temperature (323.15 K), the final dehydration temperature (458.15 K), and the loss-mass percentage (3.01 %) 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 2.99 %). 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 326.50 K, the section of the heat-capacity curve in the temperature range $327 \leq (T/K) \leq 371$ 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 $78 \leq (T/K) \leq 326$. The 107 experimental points in the temperature region between $T = 78$ K and $T = 326$ K were fitted by means of the least-squares method and a polynomial equation of experimental molar heat-capacities ($C_{p,m}$) versus reduced temperature (x), $x = f(T)$, has been obtained:

$$C_{p,m}/J \cdot K^{-1} \cdot mol^{-1} = 275.575 + 209.210x + 18.120x^2 - 49.787x^3 - 0.216x^4 + 44.522x^5 - 3.766x^6$$

In which $x = (T/K - 202.5)/124.5$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ± 0.3 % except for several points around the lower and upper temperature limits.

Thermodynamic Functions of the Complex $Zn(Leu)SO_4 \cdot 1/2H_2O(s)$. The smoothed molar heat capacities and thermodynamic functions of the complex $Zn(Leu)SO_4 \cdot 1/$

Table 3. Dissolution Enthalpy of [$ZnSO_4·7H_2O$(s) and Leu(s)] Mixture [$n(ZnSO_4·7H_2O):n$(Leu) = 1:1] in 100 mL of 2 mol·dm^{-3} HCl at 298.15 K[a]

no.	m_{Leu} g	$m_{ZnSO4·7H2O}$ g	ΔE_e mV	ΔE_s mV	t s	Q_s J	$\Delta_{sol}H^\circ_{m,1}$ kJ·mol^{-1}
1	0.1316	0.2883	1.5622	−1.5941	809.7	−85.982	−85.70
2	0.1317	0.2889	1.6877	−1.7223	812.8	−86.320	−85.97
3	0.1320	0.2891	1.5346	−1.5659	813.5	−86.389	−85.85
4	0.1319	0.2896	1.6476	−1.6812	810.4	−86.058	−85.58
5	0.1321	0.2890	1.6685	−1.7026	811.5	−86.180	−85.57
6	0.1315	0.2882	1.6564	−1.6902	813.1	−86.347	−86.13
	avg $\Delta_{sol}H^\circ_{m,1}$= − (85.80 ± 0.09) kJ·mol^{-1}						

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

Table 4. Dissolution Enthalpy of Zn(Leu)$SO_4·1/2H_2O$(s) in 100 mL of 2 mol·dm^{-3} HCl at 298.15 K

no.	$m_{Zn(Leu)SO4·1/2H2O}$ g	ΔE_e mV	ΔE_s mV	t s	Q_s J	$\Delta_{sol}H^\circ_{m,2}$ kJ·mol^{-1}
1	0.3026	2.1995	2.1555	528.2	56.085	55.90
2	0.3029	2.3762	2.3287	530.2	56.305	56.08
3	0.3035	2.1606	2.1174	530.6	56.351	56.00
4	0.3033	2.3197	2.2733	528.6	56.134	55.82
5	0.3038	2.3492	2.3022	529.4 -	56.214	55.82
6	0.3024	2.3322	2.2855	530.4	56.323	56.18
	avg $\Delta_{sol}H^\circ_{m,2}$ = (55.97 ± 0.06) kJ·mol^{-1}					

$2H_2O$(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:

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

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

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 the interval of 5 K. The uncertainties of ($H_{(T)} - H_{(298.15K)}$) and ($S_{(T)} - S_{(298.15K)}$) were evaluated to be ± 0.45 % and ± 0.48 %, respectively.

Standard Molar Enthalpy of Formation of the Complex Zn(Leu)$SO_4·1/2H_2O$(s). The complex Zn(Leu)$SO_4·1/2H_2O$(s) was one of the products in the following reaction:

$$ZnSO_4·7H_2O(s) + Leu(s) = Zn(Leu)SO_4·1/2H_2O(s) + 6.5H_2O(l) \quad (1)$$

The enthalpy change of the above supposed reaction and standard molar enthalpy of formation of the complex Zn(Leu)$SO_4·1/2H_2O$(s) were determined through a designed Hess thermochemical cycle using the experimental data of isoperibol calorimetry and other auxiliary thermodynamic data.

If ‘s’ = calorimetric solvent, 2 mol·dm^{-3} HCl(aq), the dissolution process of the mixture of reactants in reaction 1 was expressed into:

$$\{ZnSO_4·7H_2O(s)\text{ and }Leu(s)\} + \text{‘s’} = \text{solution A}$$

The experimental results of the process were listed in Table 3.

The dissolution process of the product, Zn(Leu)$SO_4·1/2H_2O$(s), in reaction 1 may be expressed as follows:

$$\{Zn(Leu)SO_4·1/2H_2O(s)\} + \text{‘s’} = \text{solution A}'$$

The results of the dissolution experiments were shown in Table 4.

The dissolution enthalpy of {$6.5H_2O$(l)} ($\Delta_{sol}H^\circ_{m,3}$) as one of the products in reaction 1 in the solvent was within the range of experimental error cannot be detected 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, namely, $\Delta_f H^\circ_{m,3}$/kJ·mol^{-1} = 0.

The enthalpy change of 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:

$$\Delta_r H_m(1) = \Delta_{sol}H^\circ_{m,1} - (\Delta_{sol}H^\circ_{m,2} + \Delta_{sol}H^\circ_{m,3}) = -(141.\ 8 \pm 0.1)\text{ kJ·mol}^{-1}$$

A reaction scheme used to derive the standard molar enthalpy of formation of the complex Zn(Leu)$SO_4·1/2H_2O$(s) has been given in Table 5. The enthalpy change of reaction 1 obtained from experimental values of the dissolution enthalpies of the [Leu(s) and $ZnSO_4·7H_2O$(s)] mixture and the complex Zn(Leu)$SO_4·1/2H_2O$(s) in 100 cm^3 of 2 mol·dm^{-3} hydrochloric acid were combined with some auxiliary thermodynamic data, $\Delta_f H^\circ_m$[$ZnSO_4·7H_2O$, s, 298.15 K]] = −3077.75 kJ·mol^{-1},[11] $\Delta_f H^\circ_m$[Leu, s] = −(637.4±0.9) kJ·mol^{-1},[12] and $\Delta_f H^\circ_m$[H_2O, l, 298.15K] = −(285.83 ± 0.04) kJ·mol^{-1},[13] to calculate the standard

Table 5. Reaction Scheme Used To Determine the Standard Molar Enthalpy of Formation of the Zn(Leu)$SO_4·1/2H_2O$(s) at 298.15 K[a]

no.	reaction scheme	$\Delta_{sol}H^\circ_m$ or $\Delta_{sol}H^\circ_m \pm \sigma_a$/kJ·mol^{-1}
1	{$ZnSO_4·7H_2O$(s) and Leu(s)} + ‘s’ = solution A	−(85.80 ± 0.09) (ΔH_1)
2	{Zn(Leu)$SO_4·H_2O$(s)} + ‘s’ = solution A′	(55.97 ± 0.06) (ΔH_2)
3	solution A + {$6.5H_2O$(l)} = solution A	0 (ΔH_3)
4	Zn(s) + S(s) + $11/2O_2$(g) + $7H_2$(g) = $ZnSO_4·7H_2O$(s)	−3077.75 (ΔH_4)
5	6C(s) + $1/2N_2$(g) + O_2(g) + $13/2H_2$(g) = Leu(s)	−(637.39 ± 0.92) (ΔH_5)
6	$1/2O_2$(g) + H_2(g) = H_2O(l)	−(285.83 ± 0.04) (ΔH_6)
7	Zn(s) + S(s) + $15/2O_2$(g) + 6C(s) + $14H_2$(g) + $1/2N_2$(g) = Zn(Leu)$SO_4·1/2H_2O$(s)	−(1999.0 ± 0.9)(ΔH_7)

[a] In which ‘s’ is the calorimetric solvent, 2 mol·dm^{-3} hydrochloric acid; $\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i is a single value in a set of dissolution measurements; $\bar{x}$ is the mean value of a set of measurement results.

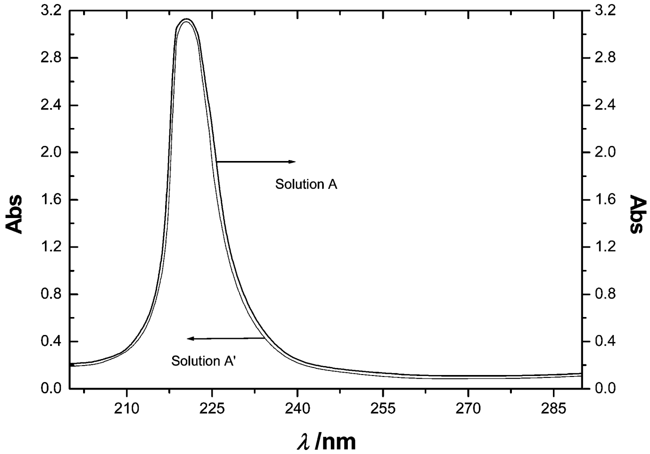

Figure 2. UV/Vis spectra of solution A and solution A′ obtained from the dissolution of the [$ZnSO_4{\cdot}7H_2O$(s) and Leu(s)] mixture and the Zn(Leu)$SO_4{\cdot}1/2H_2O$(s) in the supposed reaction 1 in 100 cm^3 of 2 $mol{\cdot}dm^{-3}$ HCl (diluted into 1:20).

molar enthalpy of formation of the complex Zn(Leu)$SO_4{\cdot}1/2H_2O$(s) as follows:

$$\Delta_f H^\circ_m\ [\mathrm{Zn(Leu)SO_4{\cdot}1/2H_2O,\ s}] = \Delta H_7 = \Delta H_1 - (\Delta H_2 + \Delta H_3) + (\Delta H_4 + \Delta H_5 - 6.5\Delta H_6) = \Delta_r H_m(1) + (\Delta^\circ_{fm}[\mathrm{ZnSO_4{\cdot}7H_2O,\ s}] + \Delta^\circ_{fm}\ [\mathrm{L\text{-}Leu,\ s}] - 6.5\Delta^\circ_{fm}\ [\mathrm{H_2O,\ l}]) = -(1999.0 \pm 0.9)\ \mathrm{kJ{\cdot}mol^{-1}}$$

in which ΔH_1, ΔH_2, ..., ΔH_7 are the molar enthalpy changes of the corresponding reactions in Table 5.

The results of UV−Vis spectra and refrangibility (refractive index) were two important information for detecting the differences of the structure and composition between two kinds of solutions. In this paper, all of the reactants and products of 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 Figure 2. UV/Vis spectrum and the data of the refractive indexes of solution A obtained agreed with those of solution A′, no difference in the structure and chemical composition existed between the two solutions. These results have demonstrated that solutions A and A′ were same and 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(Leu)$SO_4{\cdot}H_2O$(s).

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