Thermochimica Acta 400 (2003) 43–49

thermochimica acta

www.elsevier.com/locate/tca

Low-temperature heat capacity and standard molar enthalpy of formation of the complex $Zn(Thr)SO_4 \cdot H_2O$ (s)

You-Ying Di [a], Zhi-Cheng Tan [a,*], Guo-Qi Zhang [b],
San-Ping Chen [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 Science, Wuhan University, Wuhan 430072, PR China
[c] Department of Chemistry, Northwest University, Xi'an 710069, PR China

Received 19 June 2002; accepted 6 September 2002

Abstract

Low-temperature heat capacities of the complex $Zn(Thr)SO_4 \cdot H_2O$ (s) have been precisely measured with a small sample adiabatic calorimeter over the temperature range from 78 to 373 K. The initial dehydration temperature of the complex ($T_d = 325.50$ K) has been obtained by analysis of the heat-capacity curve. The experimental values of molar heat capacities have been fitted to a polynomial equation by least square method. The standard molar enthalpy of formation of the complex has been determined from the enthalpies of dissolution ($\Delta_d H_m^\ominus$) of [$ZnSO_4 \cdot 7H_2O$ (s) +Thr (s)] and $Zn(Thr)SO_4 \cdot H_2O$ (s) in 100 ml of 2 mol dm^{-3} HCl solvent as: $\Delta_f H^\ominus_{m,Zn(Thr)SO_4 \cdot H_2O} = -2111.7 \pm 3.4\,\mathrm{kJ\,mol^{-1}}$. These experiments were made by using an isoperibol solution calorimeter at 298.15 K.

Keywords: Low-temperature heat capacity; Isoperibol solution calorimetry; Dissolution enthalpy; Standard molar enthalpy of formation; $Zn(Thr)SO_4 \cdot H_2O$

1. Introduction

Zinc is one of the trace elements necessary for the human body, and α-amino acids are the basic units which constitute the proteins demanded for the life activity. The complexes of zinc with α-amino acid have vast application prospects in medicines, foodstuffs and cosmetics [1–3]. Gao et al. [4] have studied the coordination behavior of zinc with L-threonine through the method of semi-micro phase equilibrium. They have characterized the structure and other properties of the complex of zinc with L-threonine, $Zn(Thr)SO_4 \cdot H_2O$ (s), by means of FTIR, X-ray diffraction analysis, TG and DTA, and pointed out that the initial decomposition temperature of the solid complex is 323.20 K. For the purpose of the application of the compound, its low-temperature heat capacities over the temperature range from 78 to 373 K have been measured by adiabatic calorimetry. The standard molar enthalpy of formation of the complex has been determined by isoperibol solution calorimetry.

2. Experimental

All the chemicals ($ZnSO_4 \cdot 7H_2O$ (s), Thr (s), α-Al_2O_3, KCl, THAM and HCl) used were of

---

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

0040-6031/03/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00477-X

analytical grade and obtained from the Shanghai Reagent Factory, PR China.

$Zn(Thr)SO_4{\cdot}H_2O$ (s) forms white crystals. The sample used for the measurements was prepared by semi-micro phase equilibrium method [5]. The solid complex obtained was put into a desiccator containing P_4O_{10} until the weight of the complex became constant. The results of chemical and elemental analysis, IR spectra, TG–DTG and X-ray diffraction have proved that the composition of the complex was $Zn(Thr)SO_4{\cdot}H_2O$ (s), as shown in the literature [4]. The purity of the complex determined by chemical and elementary analysis was higher than 99.9% (analytical error, $\leq$0.2 mass%).

The heat-capacity measurements were made by an adiabatic calorimeter for small sample masses over the temperature range from 78 to 373 K. The calorimeter was established in thermochemistry laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR China. The construction of the calorimeter has been described earlier in detail in literature [6,7]. It briefly consists of a sample cell, a thermometer, a heater, two (inner and outer) adiabatic shields, two sets of differential thermocouples, a vacuum can and a Dewar vessel. Liquid nitrogen was used as the cooling medium. The calorimeter cell was made of 0.3 mm thick gold-plated copper, 20 mm long, 20 mm in diameter, with internal volume of about 6 cm^3. When the temperature of the sample cell increases due to heating, the differential thermocouples measure the temperature differences. This signal is used to control the heaters distributed on the walls of the inner and outer shields, respectively. Both shields were heated under the control of the signal and kept at the same temperatures as that of the sample cell. At the same time, the vacuum can where the sample cell housed was evacuated to be 10^{-3} Pa. In this way, the heat loss of the sample cell caused by the radiation and convection is greatly reduced.

The sample was heated using the standard discrete heating method and the temperature of the sample cell was alternately measured. The energy introduced into the sample cell was supplied by a dc voltage supplier with a stability of 5 ppm. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were usually within 0.1 mK min^{-1}. During the heat-capacity measurements, the temperature difference between the inner adiabatic shield and the sample cell was automatically kept within 1 mK in order to obtain a satisfactory adiabatic condition. The data of heat capacities and corresponding equilibrium temperatures were corrected for heat exchange with the surroundings [6,7].

The mass of the sample measured was 4.1302 g, which was equivalent to 0.0139 mol based on its molar mass of 296.6182 g mol^{-1}.

The molar heat capacities of α-Al_2O_3 used as the standard substance were measured in the same temperature range as that of the sample measurement in order to confirm the reliability of the calorimeter. The sample mass used for the measurements was 1.8219 g, which is equivalent to 0.0179 mol based on its molar mass, $M(Al_2O_3) = 101.9613$ g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.5%, as compared with those of the former National Bureau of Standards [8] over the whole temperature range.

The isoperibol reaction calorimeter used for this study was constructed in thermochemistry laboratory of Wuhan University in PR China and has been used for measuring enthalpies of solid–liquid, liquid–liquid reactions [9,10]. The volume of the reaction vessel is 100 cm^3. The precisions of controlling and measuring the temperatures are ±0.001 and ±0.0001 K, respectively.

The calorimeter was tested by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.1 mol l^{-1} HCl and the KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies are $-29,776 \pm 16$ J mol^{-1} for THAM and $17,597 \pm 17$ J mol^{-1} for KCl, which are in conformity with the respective published data [11,12]. Deviations of dissolution enthalpies of KCl in twice distilled water and THAM in 0.1 mol l^{-1} HCl obtained by the homemade calorimeter from the corresponding values of literature [11,12] are within 0.30%.

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

The electrical current (I) was 10.269 mA, which was controlled by a precision electric source with stepwise constant currents, and the resistance of the electrical heater was 1350.6 Ω during every electrical energy calibration.

The solid $ZnSO_4 \cdot 7H_2O$ (s) was ground into a fine powder in an agate motar. The mixture of about 0.1440 g Thr (s) and 0.06 g $ZnSO_4 \cdot 7H_2O$ (s) at mole ratio of $n(ZnSO_4 \cdot 7H_2O):n(\mathrm{Thr}) = 1:1$ was dissolved in 100 ml of 2 mol dm^{-3} HCl at 298.15 K. The final solution obtained was named as Solution A.

The complex $Zn(Thr)SO_4 \cdot H_2O$ (s) was dried in a vacuum desiccator in order to take off some additional adsorbing water. Then, it was ground into a fine powder. Dissolution enthalpy of about 0.1490 g $Zn(Thr)SO_4 \cdot H_2O$ (s) in 100 ml of 2 mol 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 refrangibility 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 from 78 to 325 K: no phase change, association nor thermal decomposition occurred. However, at temperatures above 325 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 78–325 and 325–373 K were extrapolated linearly. The

Table 1
The experimental molar heat capacities of the complex $Zn(Thr)SO_4 \cdot H_2O$ ($M = 296.6182\ \mathrm{g\,mol^{-1}}$)

T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,m}$ ($\mathrm{J\,K^{-1}\,mol^{-}}$)
78.071	113.96	152.491	202.06	275.710	296.82
80.135	117.81	156.468	203.69	280.529	301.55
81.971	122.69	160.369	206.20	285.118	306.29
84.266	128.77	164.193	210.35	289.707	311.47
86.560	133.65	168.018	212.42	294.296	314.14
89.008	136.47	171.766	215.98	298.809	318.88
91.455	139.87	175.437	220.27	303.245	323.02
93.826	142.98	179.261	222.49	307.681	326.58
96.045	146.09	182.856	226.19	311.964	333.55
98.263	148.61	186.451	229.89	316.401	338.42
100.481	150.98	190.046	231.37	320.684	345.08
102.699	153.05	195.935	235.67	324.967	352.19
104.764	155.86	201.678	240.70	329.174	362.56
107.212	158.68	207.485	244.97	331.927	373.22
109.659	161.79	213.068	249.85	335.216	385.06
112.412	164.59	218.728	253.88	338.735	402.09
115.166	167.56	224.159	257.73	342.637	419.41
117.690	170.67	229.665	260.54	346.539	435.40
120.826	174.67	235.096	263.06	350.361	451.39
123.809	176.15	240.374	268.24	354.185	467.23
127.404	179.55	245.651	272.24	358.009	481.15
131.840	184.14	250.929	274.90	361.604	492.70
136.046	187.69	255.977	279.06	365.199	502.62
140.329	191.69	261.101	283.49	368.794	509.28
144.383	194.66	266.073	288.37	372.159	515.35
148.437	198.21	270.892	291.93		

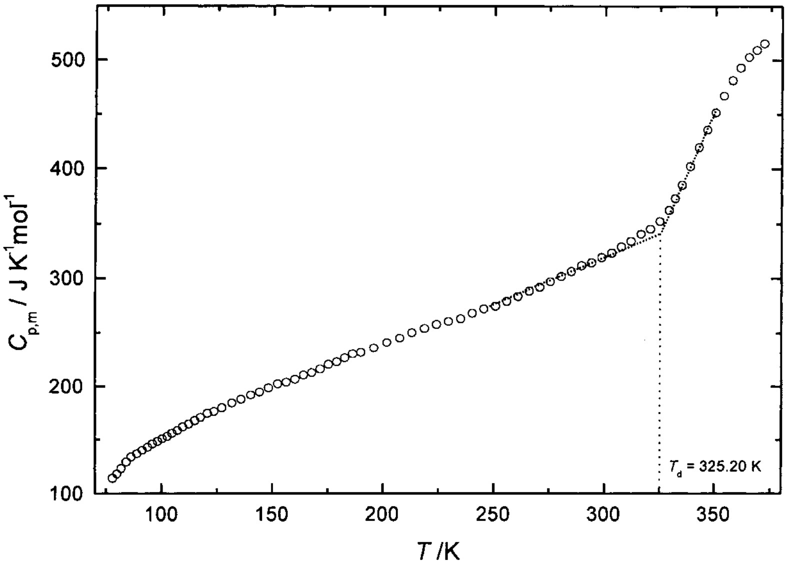

Fig. 1. The curve of the experimental molar heat capacities of the complex Zn(Thr)SO_4·H_2O vs. the temperature (T).

intersection point of these two straight lines is the initial decomposition temperature, $T_d = 325.50$ K (see Fig. 1). TG analysis has given the initial dehydration temperature (323.2 K), the final dehydration temperature (417 K) of the compound and the loss-mass percentage (6.38%). The loss-mass percentage was identical with the percentage of the water molecule in the coordination compound, i.e. the theoretical loss-mass percentage (6.10%). The initial dehydration temperature obtained from TG analysis was in agreement with that obtained from the heat-capacity curve.

Sixty-four experimental points in the region from 78 to 325 K were fitted by means of the least square method and a polynomial equation of experimental molar heat-capacities ($C_{p,\mathrm{m}}$) versus temperature (T) has been obtained:

$$\begin{aligned} C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) &= 240.255 + 93.399X - 16.512X^2 + 2.312X^3 \\ &\quad +37.309X^4 + 22.380X^5 - 28.039X^6 \end{aligned}$$

where $X = (T - 201.5)/123.5$. The standard deviations of experimental molar heat-capacities from the smoothed heat-capacities calculated by the polynomial equation were within ±0.3% except for some points around the lower and upper temperature limits.

3.2. The standard molar enthalpy of formation of the complex Zn(Thr)SO_4·H_2O (s)

The coordination compound Zn(Thr)SO_4·H_2O may be seen to be formed in the following reaction:

$$\begin{aligned} &\mathrm{ZnSO_4 \cdot 7H_2O\,(s) + Thr\,(s)} \\ &\quad = \mathrm{Zn\,(Thr)SO_4 \cdot H_2O\,(s) + 6H_2O\,(l)} \qquad (1) \end{aligned}$$

The enthalpy change of above reaction and standard molar enthalpy of formation of Zn(Thr)SO_4·H_2O were determined through a Hess thermochemical cycle using experimental data of isoperibol solution calorimetry and auxillary thermodynamic data.

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

$$\{\mathrm{ZnSO_4 \cdot 7H_2O\,(s)\ and\ Thr\,(s)}\} + \text{‘s’} = \text{Solution A}$$

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

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

$$\{\mathrm{Zn(Thr)SO_4 \cdot H_2O(s)}\} + \text{‘s’} = \text{Solution A}'$$

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

No.	W_{Thr} (g)	$W_{ZnSO_4\cdot 7H_2O}$ (g)	ΔE_e (mV)	ΔE_s (mV)	t (s)	Q_s (J)	$\Delta_d H^\theta_{m,1}$ (kJ mol^{-1})
1	0.1439	0.0599	1.220	1.562	190.29	34.710	69.420
2	0.1439	0.0599	1.200	1.600	190.94	36.259	72.518
3	0.1438	0.0599	1.300	1.575	205.27	35.419	70.838
4	0.1438	0.0596	1.375	1.625	218.12	36.713	73.426
5	0.1441	0.0598	1.312	1.625	208.58	36.779	73.558
Average							72.0 ± 1.6

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; $\Delta_d H^\theta_m$: dissolution enthalpy, $\Delta_d H^\theta_m = (\Delta E_e/\Delta E_s)I^2Rt(M/W)$, where R is the electrical resistance of the heater in the reaction vessel ($R = 1350.6\,\Omega$); I is electrical current through the heater ($I = 10.269$ mA) and M is molar mass of the sample.

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

The dissolution enthalpy of H_2O (l) as one of the products in the reaction (1) under the same condition 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 (1).

The enthalpy change of the reaction (1) can be calculated in accordance with a thermochemical cycle and experimental results listed in Tables 2 and 3 as follows:

$$\begin{aligned}\Delta_r H_m(\mathrm{l}) &= \Delta_d H^\theta_{m,1}\{ZnSO_4\cdot 7H_2O\,(s)\ \text{and Thr (s)}\}\\ &\quad -\Delta_d H^\theta_{m,2}\{Zn(Thr)SO_4\cdot H_2O\,(s)\}\\ &= 55.1 \pm 1.8\ \text{kJ mol}^{-1}\end{aligned}$$

A reaction scheme used to derive the standard molar enthalpy of formation of the complex Zn(Thr) $SO_4{\cdot}H_2O$ (s) is given in Table 4. The experimental values of the dissolution enthalpies of the reactants and products in the reaction (1) were combined with auxiliary thermodynamic data, $\Delta_f H^\theta_m[ZnSO_4\cdot 7H_2O(s)] = -3077.75$ kJ mol^{-1} [13,14], $\Delta_f H^\theta_m$[Thr (s)] = -693.6 ± 2.9 kJ mol^{-1} [13,14] and $\Delta_f H^\theta_m[H_2O\,(l)] = -285.83 \pm 0.04$ kJ mol^{-1} [13,14], to calculate the standard molar enthalpy of formation of the complex $Zn(Thr)SO_4{\cdot}H_2O$ (s) as follows:

$$\begin{aligned}\Delta_f H^\theta_m&\{Zn(Thr)SO_4\cdot H_2O\,(s)\}\\ &= \Delta_r H_m(\mathrm{l}) + \Delta_f H^\theta_m[ZnSO_4\cdot 7H_2O\,(s)]\\ &\quad +\Delta_f H^\theta_m[\text{Thr (s)}] - 6\Delta_f H^\theta_m[H_2O\,(l)]\\ &= \Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 - 6\Delta H_5\\ &= \Delta H_6 = 2111.7 \pm 3.4\ \text{kJ mol}^{-1}\end{aligned}$$

in which $\Delta H_1 \sim \Delta H_6$ are the molar enthalpy changes of the corresponding reactions in Table 4.

In this paper, all of the reactants and products of the reaction (1) can be easily dissolved in the selected solvent. The measured refrangibility values of solutions A and A′ were 1.3494 ± 0.0004 and 1.3497 ± 0.0003, respectively. The results of UV-Vis spectroscopy were shown in Fig. 2. UV-Vis spectrum and the data of

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

No.	$W_{Zn(Thr)SO_4\cdot H_2O}$ (g)	ΔE_e (mV)	ΔE_s (mV)	t (s)	Q_s (J)	$\Delta_d H^\theta_{m,2}$ (kJ mol^{-1})
1	0.1488	0.5700	0.575	58.94	8.468	16.936
2	0.1489	0.6050	0.663	56.23	8.769	17.538
3	0.1495	0.5875	0.585	57.47	8.150	16.300
4	0.1492	0.6950	0.650	67.17	8.947	17.894
5	0.1496	0.5700	0.550	58.11	7.916	15.832
Average						16.9 ± 0.8

Table 4
Reaction scheme used to determine the standard molar formation enthalpy of the Zn(Thr)$SO_4 \cdot H_2O$ (s) at 298.15 K

No.	Reaction scheme	$\Delta_f H^\theta_m$ or $\Delta_d H^\theta_m \pm \sigma_a$ (kJ mol^{-1})
1	{$ZnSO_4 \cdot 7H_2O$ (s) and Thr (s)} + 's' = Solution A	72 ± 1.6 (ΔH_1)
2	{Zn(Thr)$SO_4 \cdot H_2O$ (s)} + 's' = Solution A′	16.9 ± 0.8 (ΔH_2)
3	Zn (s) + S (s) + 11/2O_2 (g) + 7H_2 (g) = $ZnSO_4 \cdot 7H_2O$ (s)	−3077.75 (ΔH_3)
4	4C (s) + 1/2N_2 (g) + 3/2O_2 (g) + 4H_2 (g) = Thr (l)	−693.9 ± 2.9 (ΔH_4)
5	2O_2 (g) + H_2 (g) = H_2O (l)	−285.83 ± 0.04 (ΔH_5)
6	Zn (s) + S (s) + 4O_2 (g) + 4C (s) + 5H_2 (g) = Zn(Thr)$SO_4 \cdot H_2O$ (s)	−2111.9 ± 3.4 (ΔH_6)

In which 's' is the calorimetric solvent, 2 mol dm^{-3} hydrochloric acid, $\sigma_a = \sqrt{\sum_{i=1}^{5}(x_i - \bar{x})^2/n(n-1)}$ where n is experimental number; x_i is a single value in a set of dissolution measurements; and $\bar{x}$ is the mean value of a set of measurement results.

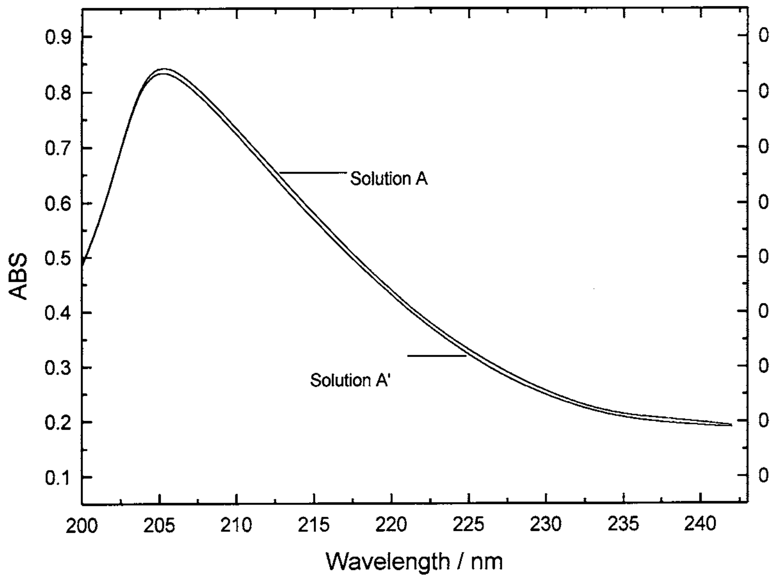

Fig. 2. UV-Vis spectrum of solutions A and A′ obtained from the dissolution of the reactants and products in the reaction (1) in 2 mol dm^{-3} HCl (diluted into 1:20).

the refrangibility of Solution A obtained agreed with those of Solution A′. These results have demonstrated that the designed thermochemical cycle is reasonable and reliable, and can be used to calculate the standard molar enthalpy of formation of Zn(Thr)$SO_4 \cdot H_2O$ (s).

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 Methionisne 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 4 830 716, 1989-05-16 (Chem. Absrt. 110 (1989) 219070).
[4] S.L. Gao, X.Y. Zhang, X.W. Yang, Q.Z. Shi, Acta Chim. Sinica 59 (2001) 73.

[5] H.Y. Jiang, D.H. Ren, H.F. Xie, Chin. J. Northwest Univ. (Natural Science Edition) 22 (1986) 1.
[6] Z.C. Tan, G.Y. Sun, Y. Sun, J. Therm. Anal. 45 (1995) 59.
[7] Z.C. Tan, L.X. Zhou, S.X. Chen, et al., Sci. Sinica, Ser. B 26 (1983) 1014.
[8] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Natl. Bur. Stand. 87 (1982) 159.
[9] C.X. Wang, Z.H. Song, W.G. Xiong, S.S. Qu, Acta Physio-Chim. Sinica 7 (5) (1991) 586.
[10] T.Z. Wang, Y. Yu, Y. Liu, P.J. Zhou, S.S. Qu, Thermochim. Acta 333 (1999) 1.
[11] R.L. Montgomery, R.A. Melaugh, C.C. Lau, G.H. Meier, H.H. Chan, F.D. Rossini, J. Chem. Thermodyn. 9 (1977) 915.
[12] P. Pychly, V. Pekarek, J. Chem. Thermodyn. 9 (1977) 391.
[13] 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.
[14] J.A. Dean, Lange's Handbook of Chemistry (Trans. by J.F. Shang, S.J. Cao, W.M. Xin, et al., The Scientific Press), Thirteenth ed., vol. 9, Beijing, Science Press, 1991, pp. 1986.