

# Thermodynamics of the coordination compound $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ (Met = L- $\alpha$ -methionine)

## Low temperature heat capacities and the standard molar enthalpy of formation

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**Abstract** Low temperature heat capacities of the solid coordination compound,  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ , have been measured by a precision automated adiabatic calorimeter over the temperature range 78–371 K. The initial dehydration temperature of the coordination compound is determined to be,  $T_D = 325.05$  K, by analysis of the heat-capacity curve. The experimental values of molar heat capacities in the temperature region have been fitted to a polynomial equation of heat capacities with the reduced temperature ( $X$ ), [ $X = f(T)$ ], by a least squares method. Smoothed heat capacities and thermodynamic functions relative to the standard reference temperature 298.15 K of the compound are derived from the fitted polynomial equation and listed at 5 K intervals. Enthalpies of dissolution of  $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\}$  and  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$  in  $100 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3}$   $\text{HCl}(\text{aq})$  at  $T = 298.15$  K have been determined to be  $\Delta_d H_{m,1}^0 = (56.929 \pm 0.051) \text{ kJ mol}^{-1}$  and  $\Delta_d H_{m,2}^0 = (37.337 \pm 0.029) \text{ kJ mol}^{-1}$ , respectively, with an isoperibol solution-reaction calorimeter. The standard molar enthalpy of formation of the compound is determined to be  $\Delta_f H_m^0 [\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}, \text{s}] = -(1327.08 \pm 0.75) \text{ kJ mol}^{-1}$  from the enthalpies of dissolution of the reactants and products and other thermodynamic data by a Hess' thermochemical cycle.

**Keywords** Adiabatic calorimetry · Heat capacity · Standard molar enthalpy of formation · Amino acids · Isoperibol solution-reaction calorimetry

## Introduction

Because L- $\alpha$ -amino acids act as basic building blocks in protein molecules and hormones and the transition metal ions play an important role in living organisms, many efforts have been focused on study of the system of amino acids–metal ions [1–4]. Consequently, a fundamental thermodynamics for complexes based on L- $\alpha$ -amino acids is of paramount importance.

The essential trace element Zn is a structural constituent in numerous proteins, including growth factors, cytokines, receptors, enzymes, and transcription factors belonging to cellular signaling pathways, and is essential for their biological activity [5, 6], especially in intelligence development. Many diseases result from deficiency of zinc in the human body, such as dwarfism, hypertension, rheumatoid arthritis, sugar diabetes, and cardiovascular diseases, etc. Complexes of zinc with L- $\alpha$ -amino acids are considered to be one of the most efficient zinc tonics because they have a higher absorption ratio in the human body than traditionally inorganic and organic weak-acid zinc tonics. Such coordination compounds of zinc have found wide application in medicine, foodstuff, animal feed, and cosmetic as nutrient additives [7–9]. Gao et al. [10] have investigated the phase chemistry of the coordination behavior of zinc salts with L- $\alpha$ -methionine 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 on refractive indices in ternary systems. The compound,  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ , has been synthesized in a 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 reported the initial decomposition temperature of

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the solid complex to be  $T_D = 323.15$  K according to the results of thermogravimetry.

It is noteworthy that various thermodynamic properties of the complex have not been reported so far. Extensive research on the complexes of zinc with L- $\alpha$ -amino acid, the low temperature heat capacities over the temperature range 78–371 K and the standard molar enthalpy of formation of the title compound at  $T = 298.15$  K have been measured by adiabatic calorimetry and isoperibol solution-reaction calorimetry, respectively. The experimental values of molar heat capacities have been fitted to a polynomial equation of heat capacities ( $C_{p,m}$ ) as a function of reduced temperature ( $X$ ), [ $X = f(T)$ ], by a least squares method so as to calculate smoothed heat capacities and various thermodynamic functions of the coordination compound.

## Experimental

### Synthesis and characterization of the sample

$ZnSO_4 \cdot 7H_2O(s)$ ,  $NaNO_3(s)$ , L- $\alpha$ -methionine(s),  $\alpha-Al_2O_3(s)$ , and  $HCl(aq)$  used as the reagents in the experiments were of analytical grade and obtained from Shanghai Reagent Factory, PR China.  $KCl(s)$  as Standard Reference Material 1655 was obtained from the National Institute of Standards and Technology. The solid complex,  $Zn(Met)(NO_3)_2 \cdot 1/2H_2O(s)$ , was a white crystal with a lumpy shape. The sample used for the measurements was prepared by a semi-micro phase equilibrium method [10, 11]. The solid complex obtained was kept in a desiccator containing  $P_4O_{10}$  until the mass of the complex became constant. The results of chemical and elemental analyses, IR spectra, TG/DTG, and XRD indicated that the composition of the complex was  $Zn(Met)(NO_3)_2 \cdot 1/2H_2O(s)$ . The purity of the complex determined by chemical and elementary analyses was higher than 99.90% mass fraction (analytical uncertainty in mass fraction  $\leq 0.2$ ).

### Adiabatic calorimetry

A high-precision automatic adiabatic calorimeter was used to measure the heat capacities over the temperature range  $78 \leq (T/K) \leq 371$ . The calorimeter was fabricated in the Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China. The principle and structure of the adiabatic calorimeter are described in detail elsewhere [12, 13]. In brief, the calorimeter comprised of a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junction chromel-constant 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, Shanghai Institute of Industrial Automatic Meters, 16-mm length, 1.6-mm dia., and a nominal resistance of 100  $\Omega$ ) was used 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, PR China. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded using 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 of the reference standard material ( $\alpha-Al_2O_3$ ) was measured over the temperature range  $78 \leq (T/K) \leq 373$ . The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass,  $M(Al_2O_3) = 101.9613$  g mol<sup>-1</sup>. The experimental molar heat capacities of  $\alpha-Al_2O_3$  were fitted by a least squares method to a polynomial. Deviations of the experimental results from those of the smoothed curve lie within  $\pm 0.2\%$ , while the uncertainty is within 0.3%, as compared with the values given by the former National Bureau of Standards [14] over the entire 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 controlled at 0.1–0.4 K min<sup>-1</sup> and 1–3 K, respectively. The heating duration was 10 min, and the temperature drift rate of the sample cell measured in an equilibrium period was always kept within  $10^{-3}$  to  $10^{-4}$  K min<sup>-1</sup> during acquisition of the 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 [12, 13]. The sample mass of  $Zn(Met)(NO_3)_2 \cdot 1/2H_2O(s)$  used for the calorimetric measurement was 3.6546 g, which is equivalent to 0.0105 mol in terms of its molar mass,  $M = 347.622$  g mol<sup>-1</sup>.

### 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 have been described in detail elsewhere [15]. The reliability of the calorimeter was verified initially [15] by measuring the dissolution enthalpies of KCl (calorimetric primary standard) in doubly

distilled water at  $T = 298.15$  K. The mean dissolution enthalpy was  $(17547 \pm 13)$  J mol<sup>-1</sup> for KCl, which compares well with the corresponding published data [16],  $(17536 \pm 3.4)$  J mol<sup>-1</sup>. In all dissolution experiments, 100 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the mixtures  $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\}$  and  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$ . The solids,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ ,  $\text{NaNO}_3(\text{s})$ , and  $\text{L-Met}(\text{s})$ , were ground in an agate mortar to a fine powder. The solid compounds were weighed on parchment paper separately to avoid mixing before dissolution. The mixture of  $\sim 0.288$  g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ ,  $\sim 0.171$  g of  $\text{NaNO}_3(\text{s})$ , and  $\sim 0.150$  g of  $\text{L-Met}(\text{s})$  at a mole ratio of  $n(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}):n(\text{NaNO}_3):n(\text{L-Met}) = 1:2:1$  was dissolved in 100 mL of 2 mol dm<sup>-3</sup> HCl at  $T = 298.15$  K. The final solution obtained was designated as solution A. The solids,  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ , and  $\text{Na}_2\text{SO}_4(\text{s})$ , were ground to a fine powder and dried in a vacuum drying oven in order to remove additional adsorbed water. The solid compounds were weighed on parchment paper separately to avoid mixing before dissolution. The dissolution enthalpy of the mixture of  $\sim 0.35$  g of  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  and  $\sim 0.14$  g of  $\text{Na}_2\text{SO}_4(\text{s})$  at a mole ratio of  $n(\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}):n(\text{Na}_2\text{SO}_4) = 1:1$  in 100 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> HCl was determined under the same conditions as above. The final solution obtained was named as solution A'. Finally, the UV/vis spectra and the data of the refractive indices were used to confirm whether solution A was in the same thermodynamic state as that of solution A'. The results indicate that chemical components and physicochemical properties of solution A are consistent with those of solution A'.

## Results and discussion

### Low-temperature heat capacity

The structure of the coordination compound was shown to be stable over the temperature range 78–325 K, as shown in Table 1 and Fig. 1. No phase change, association nor thermal decomposition is seen to occur. However, at temperatures above 325 K, the heat capacity curve rises steeply. The phenomenon is associated with the dehydration or thermal decomposition of the compound, as shown by TG analysis [10]. In addition, the initial dehydration temperature ( $T_D$ ) has been obtained by analysis of the heat capacity curve. Two sections of the heat capacity curves, i.e., 78–325 and 326–371 K were extrapolated linearly. The intersection point of these two straight lines is the initial decomposition temperature,  $T_D = 325.05$  K (Fig. 1). TG analysis shows the initial dehydration temperature to be 323.15 K, the final

dehydration temperature as 458.15 K and the mass loss as 3.01%. The mass loss was identical with the percentage of the water molecule in the coordination compound (the theoretical mass loss during dehydration was 2.99%). The initial dehydration temperature obtained from TG analysis was in agreement with that from the heat capacity curve. The main reason for the difference (1.90 K) between the two results is that the surface of the sample absorbed some additional moisture in the air during TG analysis. The removal of the adsorbed water in the sample occurred before that of crystal water. This reduces the initial dehydration temperature and increases the actual mass loss of the sample. However, during the adiabatic calorimetric measurements, when the sample was put into the sample cell, the air pressure within the sample cell was vacuumed to below 100 Pa with a vacuum pump to prevent moisture from being absorbed on the surface of the sample. Then, about 100 kPa of high purity helium was filled in the sample cell to increase the rate of heat conduction of sample cell during low-temperature heat capacity measurements and also to reduce the time to reach thermal equilibrium. The sample cell was sealed by soldering. In the temperature range, 78–325 K, the rise in heat capacity curve was steady. However, at 326–371 K, the curve rises very steeply, indicating the thermal decomposition of the compound into another substance, which has properties different from the original compound. The results above 325 K are thus not relevant to the present studies. The experimental points in the temperature range of 78–325 K were fitted by a least-squares method, and a polynomial equation of experimental molar heat capacities ( $C_{p,m}$ ) versus reduced temperature ( $X$ ),  $X = f(T) = [T - (T_1 + T_2)/2]/[(T_1 - T_2)/2]$  where  $T_1 = 325$  K and  $T_2 = 78$  K, is obtained (Eq. 1),

$$C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1}) = 198.536 + 203.077X + 81.520X^2 - 8.313X^3 - 13.589X^4 + 23.420X^5 + 33.901X^6 \quad (1)$$

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  $\pm 0.3\%$  except for some points around the lower and upper temperature limits. In addition, it can be seen from Fig. 1 that a slow process of dehydration occurs after 325 K rather than an obvious peak of dehydration. There are two possible reasons for this phenomenon. On the one hand, the crystal water possesses a large percentage in the complex; on the other hand, the mass of the sample is large. Since the sample cell is sealed during the entire calorimetric experiment, after the dehydration occurs, the speed of dehydration should accelerate with the rise in temperature. However, the rate of the dehydration is also inhibited as a result of the rapid increase of vapor pressure of the water in the sample cell.

**Table 1** The experimental molar heat capacities of  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$  ( $M_{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})} = 347.622 \text{ g mol}^{-1}$ )

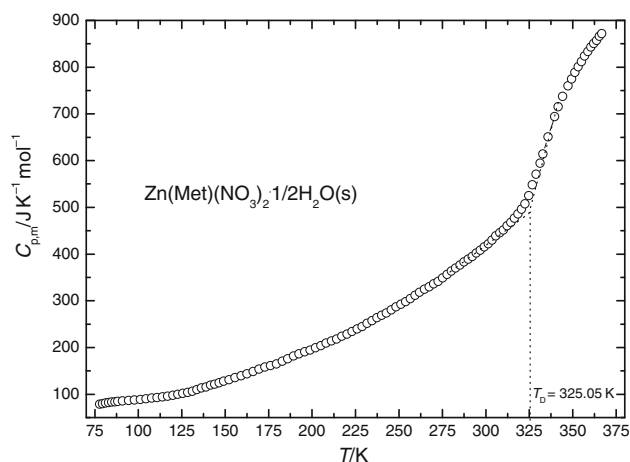
$T/\text{K}$	$C_{p,m}/\text{J K}^{-1}\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}/\text{J K}^{-1}\text{mol}^{-1}$	$T/\text{K}$	$C_{p,m}/\text{J K}^{-1}\text{mol}^{-1}$
77.705	78.555	186.027	175.798	292.135	394.833
79.312	79.864	189.321	181.894	294.506	402.369
81.161	81.178	192.455	186.373	296.809	408.425
82.929	82.074	195.669	190.727	299.113	415.472
84.696	83.169	198.804	194.211	301.348	421.765
86.464	83.965	201.938	199.561	303.584	430.071
88.152	84.741	205.015	203.968	305.752	439.132
90.804	85.756	208.045	209.389	307.987	445.662
94.339	86.692	211.112	213.918	310.019	451.466
97.795	87.687	214.161	218.182	312.255	460.779
101.169	88.981	217.142	224.104	314.355	467.575
104.464	90.354	220.122	228.546	316.455	476.636
107.679	91.688	222.991	234.024	318.420	485.949
110.813	93.022	225.881	239.799	320.521	496.017
113.866	94.475	228.794	244.892	322.552	507.596
116.919	95.908	231.571	251.584	324.653	525.215
119.813	97.640	234.484	257.507	326.726	548.371
122.705	99.571	237.262	263.844	328.853	571.025
125.518	101.801	240.039	268.878	331.156	594.775
128.331	104.050	242.749	273.971	332.849	614.402
131.063	106.399	245.594	280.604	335.830	651.139
133.714	109.664	248.304	286.882	339.556	694.419
136.286	113.217	251.082	292.686	341.656	715.305
138.943	115.457	253.859	298.194	344.231	737.655
141.514	119.338	256.569	304.768	347.347	760.095
144.043	121.628	259.347	311.815	349.379	774.689
146.571	124.415	261.921	318.093	351.276	789.032
149.143	127.799	264.698	324.667	353.173	800.859
152.207	131.183	267.340	329.893	355.069	812.137
155.657	135.363	269.915	336.186	356.831	824.008
159.107	139.344	272.489	341.220	358.728	833.511
162.557	143.425	275.131	348.771	360.489	843.162
166.029	148.402	277.638	356.322	362.048	850.933
169.393	153.776	280.144	363.369	363.674	857.475
172.843	158.056	282.583	369.914	365.299	866.533
176.144	161.142	285.089	376.710	366.654	872.069
179.529	164.725	287.461	383.003		
182.813	170.821	289.832	389.044		

Smoothed heat capacity and thermodynamic functions of the sample

The smoothed values of molar heat capacities and thermodynamic functions of the complex,  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  were derived according to the following thermodynamic equations (Eqs. 2–4).

$$H_{(T)} - H_{(298.15 \text{ K})} = \int_{298.15}^T C_{p,m} dT \quad (2)$$

$$S_{(T)} - S_{(298.15 \text{ K})} = \int_{298.15}^T C_{p,m} T^{-1} dT \quad (3)$$

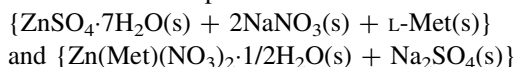


**Fig. 1** Plot of heat capacities ( $C_{p,m}$ ) against temperature ( $T$ ) for the coordination compound  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$

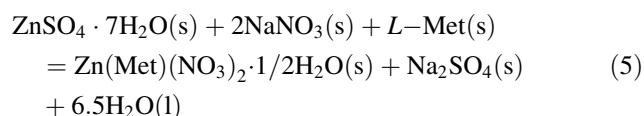
$$G_{(T)} - G_{(298.15\text{ K})} = \int_{298.15}^T C_{p,m} dT - T \cdot \int_{298.15}^T C_{p,m} \cdot T^{-1} dT \quad (4)$$

The fitted polynomial values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature, 298.15 K are tabulated at an interval of 5 K (Table 2).

Dissolution enthalpies of the mixtures



The complex,  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ , is one of the products in the following reaction (Eq. 5).



The enthalpy change of the above proposed reaction and standard molar enthalpy of formation of the complex  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  were determined by a designed Hess thermochemical cycle using the experimental data of isoperibol calorimetry and other thermodynamic data.

If “s” = calorimetric solvent,  $2 \text{ mol dm}^{-3}$  HCl (aq), the dissolution process of the mixture of reactants in reaction (5) is expressed as  $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\} + \text{“s”}$  to give solution A. The experimental results of the process are listed in Table 3. The dissolution process of the products,  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$ , in reaction (5) may be expressed as  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\} + \text{“s”}$  to give solution A'. The results of the dissolution experiments are shown in Table 4. Solution A' +  $\{6.5\text{H}_2\text{O}(\text{l})\} = \text{Solution A}$ . The enthalpy of

**Table 2** Thermodynamic functions of the complex  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$

$T/\text{K}$	$C_{p,m}/$ $\text{J K}^{-1} \text{mol}^{-1}$	$[H_{(T)} -$ $H_{(298.15 \text{ K})}]/$ $\text{J mol}^{-1}$	$[S_{(T)} -$ $S_{(298.15 \text{ K})}]/$ $\text{J K}^{-1} \text{mol}^{-1}$	$[G_{(T)} -$ $G_{(298.15 \text{ K})}]/$ $\text{J mol}^{-1}$
298.15	412.970	0	0	0
300	418.929	769.112	2.5717	-2.4052
305	435.811	2904.26	9.6279	-32.239
310	453.981	5126.61	16.853	-97.941
315	473.656	7443.05	24.268	-201.26
320	495.085	9861.59	31.889	-343.18
325	518.552	12391.6	39.739	-523.77

dissolution of  $\{6.5\text{H}_2\text{O}(\text{l})\}$  ( $\Delta_d H_{m,3}$ ) as one of the products in reaction (5) in the solvent was within the range of experimental error, and may be omitted since the amount of  $\text{H}_2\text{O}(\text{l})$  was very small according to the stoichiometric number of  $\text{H}_2\text{O}(\text{l})$  in reaction (5), i.e.,  $\Delta_d H_{m,3}$  ( $\text{kJ mol}^{-1}$ ) = 0. The change in enthalpy of reaction (5),  $\Delta_r H_m(5)$ , can be calculated in accordance with the above designed Hess thermochemical cycle, and experimental results listed in Tables 3 and 4 by the Eq. 6:

$$\Delta_r H_m(5) = \Delta_d H_{m,1}^0 - (\Delta_d H_{m,2}^0 + \Delta_d H_{m,3}^0) \quad (6)$$

$$= (19.592 \pm 0.059) \text{ kJ mol}^{-1}.$$

A reaction scheme used to derive the standard molar enthalpy of formation of the complex  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  is given in Table 5. The enthalpy change of reaction (5) obtained from experimental values of the dissolution enthalpies of  $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\}$  and  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$  in  $100 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3}$  hydrochloric acid combined with some auxiliary thermodynamic data [17–20]:  $\Delta_f H_m^0[\text{Na}_2\text{SO}_4, \text{s}] = -1383.16 \text{ kJ mol}^{-1}$  [17],  $\Delta_f H_m^0[\text{NaNO}_3, \text{s}] = -466.24 \text{ kJ mol}^{-1}$  [18],  $\Delta_f H_m^0[\text{L-Met}, \text{s}] = -(577.50 \pm 0.70) \text{ kJ mol}^{-1}$  [19]  $\Delta_f H_m^0[\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}] = -(285.83 \pm 0.04) \text{ kJ mol}^{-1}$  [20], have been used to calculate the standard molar enthalpy of formation of the complex  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  as follows:

$$\Delta_f H_m^0[\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}, \text{s}] = \Delta H_9 = \Delta H_1$$

$$- (\Delta H_2 + \Delta H_3) + (2\Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_7 - 6.5\Delta H_8)$$

$$= \Delta_r H_{m,9} + 2\Delta_f H_m^0(\text{NaNO}_3, \text{s}) + \Delta_f H_m^0(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}, \text{s})$$

$$+ \Delta_f H_m^0(\text{L-Met}, \text{s}) - \Delta_f H_m^0(\text{Na}_2\text{SO}_4, \text{s})$$

$$- 6.5\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) = -(1327.08 \pm 0.75) \text{ kJ mol}^{-1}. \quad (7)$$

where  $\Delta H_1 - \Delta H_9$  is the change in molar enthalpy of the corresponding reactions in Table 5. The results of UV/vis spectrum and refractive index are important for detecting

**Table 3** Dissolution enthalpy of  $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\}$  mixture at a mole ratio of  $n(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}):n(\text{NaNO}_3):n(\text{L-Met}) = 1:2:1$  in  $100 \text{ cm}^3$  of  $2 \text{ mol L}^{-1}$  HCl at  $T = 298.15 \text{ K}^a$ 

No.	$W_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{g}}$	$W_{\text{NaNO}_3}/\text{g}$	$W_{\text{Met}}/\text{g}$	$\Delta E_c/\text{mv}$	$\Delta E_s/\text{mv}$	$t_e/\text{s}$	$Q_s/\text{J}$	$\Delta_d H_{m,1}^0/\text{kJ mol}^{-1}$
1	0.2887	0.1707	0.1498	2.4276	2.4095	543.25	56.963	56.738
2	0.2892	0.1710	0.1501	2.4259	2.4231	551.11	57.423	57.098
3	0.2888	0.1707	0.1499	2.4515	2.4268	544.41	57.234	56.989
4	0.2886	0.1706	0.1498	2.4194	2.4260	549.67	57.050	56.845
5	0.2884	0.1705	0.1496	2.4259	2.4187	546.92	57.090	56.924
6	0.2893	0.1710	0.1501	2.4263	2.4184	549.06	57.328	56.984

Avg. ( $56.929 \pm 0.051$ )

<sup>a</sup>  $m$  Mass of sample,  $t_e$  Heating period of electrical calibration,  $Q_s$  Heat effect during the sample dissolution,  $\Delta E_s$  The voltage change during the sample dissolution,  $\Delta E_c$  The voltage change during the electrical calibration,  $\Delta_s H_m^0 = Q_s / n = (\Delta E_s / \Delta E_c) \cdot I^2 R t (M/m)$ , where  $R$  is the electro-resistance ( $R = 1017.2 \Omega$  at  $T = 298.15 \text{ K}$ ),  $I$  is the current ( $I = 10.115 \text{ mA}$ ), and  $M$  is the molar mass of the sample. The purities for the samples involved in the calorimetric experiments are above 0.995 mass fraction

**Table 4** Dissolution enthalpy of  $\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$  mixture at a mole ratio of  $n(\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}):n(\text{Na}_2\text{SO}_4) = 1:1$  in  $100 \text{ cm}^3$  of  $2 \text{ mol L}^{-1}$  HCl at  $T = 298.15 \text{ K}^a$ 

No.	$W_{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}/\text{g}}$	$W_{\text{Na}_2\text{SO}_4}/\text{g}$	$\Delta E_c/\text{mv}$	$\Delta E_s/\text{mv}$	$t_e/\text{s}$	$Q_s/\text{J}$	$\Delta_d H_{m,2}^0/\text{kJ mol}^{-1}$
1	0.3490	0.1427	2.4046	2.4453	365.29	37.384	37.237
2	0.3496	0.1430	2.5979	2.6132	363.37	37.596	37.383
3	0.3491	0.1428	2.3622	2.4317	371.67	37.574	37.413
4	0.3489	0.1427	2.5361	2.5743	364.81	37.404	37.269
5	0.3486	0.1426	2.5683	2.6120	365.78	37.431	37.322
6	0.3497	0.1430	2.4166	2.4690	369.32	37.621	37.395

Avg. ( $37.337 \pm 0.029$ )

<sup>a</sup>  $m$  Mass of sample,  $t_e$  Heating period of electrical calibration,  $Q_s$  Heat effect during the sample dissolution,  $\Delta E_s$  The voltage change during the sample dissolution,  $\Delta E_c$  The voltage change during the electrical calibration,  $\Delta_s H_m^0 = Q_s / n = (\Delta E_s / \Delta E_c) \cdot I^2 R t (M/m)$ , where  $R$  is the electro-resistance ( $R = 1017.2 \Omega$  at  $T = 298.15 \text{ K}$ ),  $I$  is the current ( $I = 10.115 \text{ mA}$ ), and  $M$  is the molar mass of the sample. The purities for the samples involved in the calorimetric experiments are above 0.995 mass fraction

**Table 5** Reaction scheme used to determine the standard molar enthalpy of formation of  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  at  $T = 298.15 \text{ K}$ 

No.	Reactions	Formed solution	$(\Delta_f H_m^0 \text{ or } \Delta_d H_m^0 \pm \sigma_a)/\text{kJ mol}^{-1}$
1	$\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + \text{L-Met}(\text{s})\} + \text{“s”} =$	A	$(56.929 \pm 0.051) (\Delta H_1)$
2	$\{\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\} + \text{“s”} =$	A'	$(37.337 \pm 0.029) (\Delta H_2)$
3	Solution A + $\{6.5\text{H}_2\text{O}(\text{l})\} =$ Solution A		0 ( $\Delta H_3$ )
4	$\text{Na}(\text{s}) + (1/2)\text{N}_2(\text{g}) + (3/2)\text{O}_2(\text{g}) = \text{NaNO}_3(\text{s})$		$-466.24 (\Delta H_4)$
5	$\text{Zn}(\text{s}) + \text{S}(\text{s}) + (11/2)\text{O}_2(\text{g}) + 7\text{H}_2(\text{g}) = \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$		$-3077.75 (\Delta H_5)$
6	$5\text{C}(\text{s}) + 1/2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 11/2\text{H}_2(\text{g}) + \text{S}(\text{s}) = \text{Met}(\text{s})$		$-(577.50 \pm 0.70) (\Delta H_6)$
7	$2\text{Na}(\text{s}) + \text{S}(\text{s}) + 2\text{O}_2 = \text{Na}_2\text{SO}_4(\text{s})$		$-1383.16 (\Delta H_7)$
8	$\text{H}_2(\text{g}) + (1/2)\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$		$-(285.830 \pm 0.042) (\Delta H_8)$
9	$\text{Zn}(\text{s}) + 5\text{C}(\text{s}) + 6\text{H}_2(\text{g}) + (9/2)\text{O}_2(\text{g}) + (3/2)\text{N}_2(\text{g})$ $= \text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$		$-(1327.08 \pm 0.75) (\Delta H_9)$

the differences of the structure and composition between the two solutions. In the present study, all the reactants and products of reaction (5) can be easily dissolved in the selected solvent. The measured values of the refractive indices of solution A and solution A' are  $1.3538 \pm 0.0005$

and  $1.3540 \pm 0.0008$ , respectively. The results of UV/vis spectroscopy UV/vis spectrum and the data of the refractive indices of solution A obtained agree with those of solution A'. No difference exists in the structure and chemical composition between the two solutions. These

results have demonstrated that the solutions A and A' are same and the designed Hess thermochemical cycle can be used reliably to derive the standard molar enthalpy of formation of the coordination compound  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ .

## Conclusions

The article provided the low temperature heat capacities of the coordination compound  $\text{Zn}(\text{Met})(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  by adiabatic calorimetry. The smoothed heat capacities and thermodynamic functions of the title compound were also obtained. In addition, the standard molar enthalpy of formation of the title compound was determined to be  $-(1327.08 \pm 0.75) \text{ kJ mol}^{-1}$  in accordance with a Hess's law.

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