Determination of constant-volume combustion energy for the complexes of zinc amino acids

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Abstract

The eight solid complexes of zinc with L-α-methionine or L-α-histidine were prepared. The constant-volume combustion energies of the complexes, $\Delta_{c,coor}E$, at 298.15 K have been determined by using a precision rotating-bomb calorimeter. The standard enthalpies of combustion, $\Delta_{c,coor}H^{\theta}$, and standard enthalpies of formation, $\Delta_{f,coor}H^{\theta}$, have been calculated for these complexes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The complexes of zinc with α-amino acids as additives, they have vast applied prospects in medicines, foodstuff and cosmetics [1–3]. Preparative methods of zinc amino acids reported in literatures are as follows: adjustment solution pH [4]; treatment with organic solvent [5]; dry reaction [5]; electrolytic process [6]. The drawbacks of above-mentioned methods are low yield and difficult control of reaction conditions. Gao et al. [7] have investigated the solubility properties of $ZnCl_2$/$ZnAc_2$/$ZnSO_4$–Met/His–H_2O systems at 25°C in the whole concentration range by phase equilibrium method. The results indicate that there are some complexes formed in the systems, which are not reported in literatures. However, complexes of zinc with amino acids have not yet been investigated by thermochemical methods. The stan-

dard enthalpies of combustion and standard enthalpies of formation of the complexes have not yet been reported in literature.

In this paper, eight solid complexes of zinc with L-α-histidine or L-α-methionine were prepared. The constant-volume combustion energies have been determined for these complexes. The standard enthalpies of combustion, $\Delta_{c,coor}H^{\theta}$, and standard enthalpies of formation, $\Delta_{f,coor}H^{\theta}$, have been calculated for these complexes. This work not only enriches the thermochemical database, it also provides the theoretical basis for further study on their properties and application.

2. Experimental

2.1. Preparation and composition of the complexes

Referred to literatures [1,5,7], eight solid complexes were prepared, and put into a desiccator containing P_4O_{10} until the weight of the complexes

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became constant. Chemical analysis proved that the composition of the complexes are $Zn(Met)Cl_2(I)$, $Zn(Met)_2Cl_2\cdot2H_2O(II)$, $Zn(Met)$ $SO4\cdot H_2O(III)$, $Zn(Met)_2(IV)$, $Zn(His)Cl_2\cdot1/2H_2O(V)$, $Zn(His)Ac_2\cdot1/2\ H_2O(VI)$, $Zn(His)SO_4\cdot H_2O(VII)$ and $Zn(His)_2\cdot3/2(VIII)$, respectively. The purity of all complexes determined by chemical analysis is >99.9% (analytical error, ≤0.2%).

2.2. Apparatus and experimental procedure

The constant-volume combustion energy of a compound is determined using the precision rotating-bomb (RBC-type 1) [8]. The basic experimental procedure used in this investigation is described as follows: Regulate the room temperature to $25 \pm 1°C$; control the constant-temperature water bath of outer casing of the rotating-bomb to $25.0000 \pm 0.0005°C$; adjust the water temperature in the caloritube lower than that of the water bath of outer casing; and make that the range of the temperature is equal to half the total temperature rise of the calorimeter or so. Add the known amount of pure water to the caloritube; lay the sample into the crucible which is fixed on the support in the rotating-bomb and does not drop into the solution; fix the combustion wire in the bomb; inject the initial bomb-solution into the rotating-bomb; fill of 2533.125 kPa oxygen after sealed the bomb; set up the calorimeter well; begin to experiment; and keep up a constant-rate of temperature change for the calorimeter. In the experimental initial stage; read once the temperature every 30 s; record 10 readings. In the later of eleventh reading; begin to fire; record once the temperature each one minute up to the constant-rate of temperature change; the main period combustion reaction over. Later, read once the temperature every 30 s; record 10 reading as the later stage of the experiment. After the experiment over; analyzes the final products of the combustion reaction.

The energy equivalent of the RBC-type 1 calorimeter was calculated according to the equation

$$W = \frac{Qa + Gb + 5.983c}{\Delta T} \quad (1)$$

where W is the energy equivalent of the RBC-type 1 calorimeter (in JK^{-1}), Q the combustion enthalpy of benzoic acid (in $J\,g^{-1}$), a the mass of determined benzoic acid (in g), G the combustion enthalpy of

Ni–Cr wire for ignition (0.9 J cm^{-1}), b the length of actual Ni–Cr wire consumed (in cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^3 of 0.1000 mol dm^{-3} solution of NaOH (in J cm^{-3}), c the volume (in cm^3) of consumed 0.1000 mol dm^{-3} solution of NaOH and ΔT the correct value of the temperature rise.

The correct value of the heat exchange was calculated by the equation [9]

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{\overline{T}_n - \overline{T}_0}$$
$$\times \left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\overline{T}_0 \right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n the number of readings for the main (or reaction) period, V_0 and V_n the rate of temperature change at the initial and final stages, respectively (V is positive when temperature decreases). $\overline{T}_0, \overline{T}_n$ the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for first and last reading), T_0 the last reading of the initial stage, T_n the first reading of the final stage, $\sum_{i=1}^{n-1} T_i$ the sum of all the readings except the last one of the main period, $(V_n - V_0)/(\overline{T}_n - \overline{T}_0)$ must be constant.

The calorimeter RBC-type 1 was calibrated with benzoic acid of purity 99.999%. Benzoic acid has an isothermal heat of combustion at 25°C of -26476.0 ± 5.8 J g^{-1}. The calibrated experimental results with an uncertainty 0.16% are summarized in Table 1.

2.3. Analysis of final products in oxygen-bomb

2.3.1. Analysis of final gas products
The gases formed in the combustion reaction are collected in a gas-collecting bag. The amount of gas was measured by a gas meter which was joined between the bag and the instrument of gas determination.

The analytical principle and technique of carbon dioxide. The gaseous CO_2 formed in the combustion reaction is absorbed by a weighed absorption pipe with alkali asbestos. The amount of CO_2 can be determined through the weight increment of the pipe after sinking up carbon dioxide. The amount of CO_2 dissolved in the final acidic solution was ignored.

Each measurement must have four absorption pipes connected with each other. The first one is filled with

Table 1
Calibrated experimental results for the energy equivalent of the calorimeter using benzoic acid

No.	Mass of benzoic acid a/g	Calibrated ΔT/K	Calibrated heat of acid containing nitrogen q_N/J	Calibrated heat of combustion wire q_c/J	Energy equivalent of calorimeter W/kJ K^{-1}
1	1.02220	1.5010	17.38	8.55	18.0459
2	1.14830	1.7023	16.83	5.31	17.8708
3	1.06805	1.5870	19.82	7.65	17.8208
4	1.10430	1.6226	33.67	10.80	18.0227
5	0.90470	1.3278	21.72	9.50	18.0513
6	1.04065	1.5352	20.09	7.70	17.9507
7	0.93050	1.3791	25.52	8.10	17.9831
8	0.98310	1.4571	19.82	5.00	17.8665
9	1.08140	1.5978	22.53	9.45	17.9213

$W = 17.9359 \pm 0.0288$ kJ K^{-1}.

P_4O_{10} and $CaCl_2$ (anhydrous) to sink up the water-vapour in gases; the second one is filled with active MnO_2 in order to absorb the nitrogen oxides; the third one is filled with alkali asbestos to absorb the CO_2 which is for determination; the fourth one is also filled with P_4O_{10} and $CaCl_2$ to absorb the water formed in the process of determination.

The analytical principle and technique of sulfur dioxide. A steady complex dichloride sulphurous acid slat forms when sulfur dioxide is absorbed by tetrachloromercurate (TCM). This complex reacts with formalin and pararosaniline producing a purplish red complex. The amount of sulfur dioxide can be determined through TCM–Pararosaniline colorimetric analysis method.

The analytical principle and technique of nitrogen oxides (NO$_x$). Azo dyes forms when the NO_2 is sunk up by the absorption solution in the first flask. The NO does not react with the absorption solution but becomes NO_2 when it passes through an oxide pipe. The formed NO_2 is absorbed by the absorption solution in the second flask. The amount of NO_2 and NO can be got by determination of the absorbance at wavelength between 540 and 545 nm (Saltzman colorimetric analysis method).

2.3.2. Analysis of the final solution

Wash the fittings and the inside wall of the bomb using quadratic distilled water, then transfer the bomb solution (including the washing solution) to a cone bottle completely, heat to boiling to remove CO_2, titrate the solution to the final point of phenolphthalein using the standard solution of NaOH to get the total amount of acids. The solution after neutralization

cooled to the room temperature is transferred to a volumetric flask. If a compound contains chlorine, sulfur and nitrogen, the final bomb-solution contains HCl(aq), H_2SO_4(aq) and HNO_3(aq). In analysis, the total amount of acids must be measured first. The amount of HNO_3 can be obtained using the weight method of $BaSO_4$. The amount of HNO_3 can be determined by using the Devarda's alloy method. The amount of HCl in the solution is corrected through the difference value of the total amount of acids and the amount of HNO_3 and H_2SO_4 in solution. Then, the corrected heat of acid is obtained based on the results.

2.3.3. Analysis of final solid products

Since the crucible in the rotating-bomb is fixed up the support and does not drop into the solution, the final solid products are in the crucible after the experiment over. It is proved that the final product is only ZnO by IR spectra and chemical analyses.

The analytical results of the final products show that the combustion reaction is complete, neither carbon deposits or carbon monoxide formed during the combustion reaction, and the amount of NO$_x$ in the final gas phase is insignificant.

3. Results and discussion

3.1. Combustion energy of sample of the complexes (in solid)

The method of determining the combustion energy for samples is the same as for the calibration of the

Table 2
Combustion energy, standard combustion enthalpy and standard enthalpy of formation of the complexes (in kJ mol^{-1})

Complex	No. of experiments	$-\Delta_{c,coor}E$	$-\Delta_{c,coor}H^{\theta}$	$-\Delta_{f,coor}H^{\theta}$
Zn(Met)CL$_2$	6	3356.72 ± 2.14	3354.86 ± 2.14	730.82 ± 2.27
Zn(Met)$_2$Cl$_2$·2H$_2$O	6	7472.93 ± 6.48	7474.17 ± 6.48	1019.59 ± 6.65
Zn(Met)SO$_4$·H$_2$O	6	2231.71 ± 3.11	2231.09 ± 3.11	2538.44 ± 3.32
Zn(Met)$_2$	6	6413.52 ± 4.41	6419.73 ± 4.41	1317.75 ± 4.64
Zn(His)Cl$_2$·$\frac{1}{2}$H$_2$O	6	3065.78 ± 1.76	3060.20 ± 1.76	979.26 ± 1.95
Zn(His)Ac$_2$·$\frac{1}{2}$H$_2$O	6	4907.80 ± 2.98	4907.18 ± 2.98	1665.02 ± 3.28
Zn(His)SO$_4$·H$_2$O	6	2789.44 ± 3.31	2785.10 ± 3.31	1795.30 ± 3.43
Zn(His)$_2$·$\frac{3}{2}$H$_2$O	6	5848.95 ± 2.37	5847.71 ± 2.37	1940.26 ± 2.88

calorimeter with benzoic acid. The sample weights were determined in vacuo. The combustion energies of the samples were calculated according to the formula
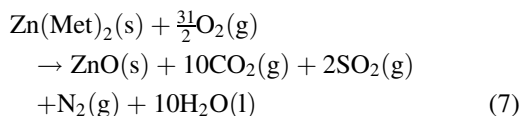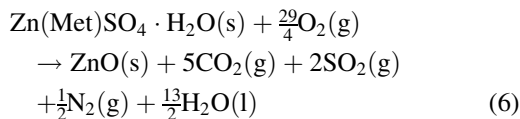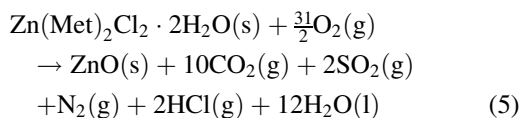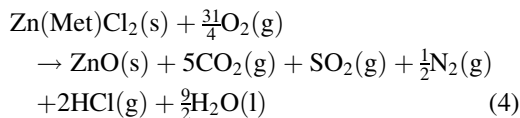
$$\Delta_{c,coor}E = \frac{W\Delta T - Gb - 5.983c}{m} \qquad (3)$$

where $\Delta_{c,coor}E$ (in J g^{-1}) denotes the constant-volume combustion energy of the sample, and m the mass (in g) of the determined sample. The other symbols are as in Eq. (1). The results of the calculations are given in Table 2, respectively.

3.2. Standard combustion enthalpies of the complexes

The standard combustion enthalpy of the complexes, $\Delta_{c,coor}H^{\theta}$, refers to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa

$$Zn(Met)Cl_2(s) + \tfrac{31}{4}O_2(g)$$
$$\rightarrow ZnO(s) + 5CO_2(g) + SO_2(g) + \tfrac{1}{2}N_2(g)$$
$$+2HCl(g) + \tfrac{9}{2}H_2O(l) \qquad (4)$$

$$Zn(Met)_2Cl_2 \cdot 2H_2O(s) + \tfrac{31}{2}O_2(g)$$
$$\rightarrow ZnO(s) + 10CO_2(g) + 2SO_2(g)$$
$$+N_2(g) + 2HCl(g) + 12H_2O(l) \qquad (5)$$

$$Zn(Met)SO_4 \cdot H_2O(s) + \tfrac{29}{4}O_2(g)$$
$$\rightarrow ZnO(s) + 5CO_2(g) + 2SO_2(g)$$
$$+\tfrac{1}{2}N_2(g) + \tfrac{13}{2}H_2O(l) \qquad (6)$$

$$Zn(Met)_2(s) + \tfrac{31}{2}O_2(g)$$
$$\rightarrow ZnO(s) + 10CO_2(g) + 2SO_2(g)$$
$$+N_2(g) + 10H_2O(l) \qquad (7)$$

$$Zn(His)Cl_2 \cdot \tfrac{1}{2}H_2O(s) + \tfrac{29}{4}O_2(g)$$
$$\rightarrow ZnO(s) + 6CO_2(g) + \tfrac{3}{2}N_2(g)$$
$$+2HCl(g) + 4H_2O(l) \qquad (8)$$

$$Zn(His)Ac_2 \cdot \tfrac{1}{2}H_2O(s) + \tfrac{45}{4}O_2(g)$$
$$\rightarrow ZnO(s) + 10CO_2(g) + \tfrac{3}{2}N_2(g)$$
$$+8H_2O(l) \qquad (9)$$

$$Zn(His)SO_4 \cdot H_2O(s) + \tfrac{27}{4}O_2(g)$$
$$\rightarrow ZnO(s) + 6CO_2(g) + \tfrac{3}{2}N_2(g)$$
$$+SO_2(g) + \tfrac{11}{2}H_2O(l) \qquad (10)$$

$$Zn(His)_2 \cdot \tfrac{3}{2}H_2O(s) + \tfrac{29}{2}O_2(g)$$
$$\rightarrow ZnO(s) + 12CO_2(g)$$
$$+3N_2(g) + \tfrac{19}{2}H_2O(l) \qquad (11)$$

The standard combustion enthalpies of the complexes were calculated from the combustion energy by the equations

$$\Delta_{c,coor}H^{\theta} = \Delta_{c,coor}E + \Delta nRT \qquad (12)$$

$$\Delta n = n_{gas}(products) - n_{gas}(reactants) \qquad (13)$$

where n_{gas} is the total amount (in moles) of gas present as products or as reactants, $R = 8.314$ J mol^{-1} K^{-1}, $T = 298.15$ K. The results of the calculations are also shown in Table 2.

3.3. Standard formation enthalpies of the complexes

The standard formation enthalpies of the complexes, $\Delta_{f,coor}H^{\theta}$, were calculated by Hess's law according to the thermochemical equations

a. The standard formation enthalpy of Zn(Met)Cl$_2$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 5\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ \Delta_{\text{f,SO}_2\text{(g)}}H^{\theta} + 2\Delta_{\text{f,HCl(g)}}H^{\theta}$$
$$+ \tfrac{9}{2}\Delta_{\text{f,H}_2\text{O(l)}}H^{\alpha}) - \Delta_{\text{c,ccor(s)}}H^{\theta} \qquad (14)$$

b. The standard formation enthalpy of $Zn(Met)_2$-$Cl_2 \cdot 2H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 10\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ 2\Delta_{\text{f,SO}_2\text{(g)}}H^{\theta} + 2\Delta_{\text{f,HCl(g)}}H^{\theta}$$
$$+ 12\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta}) - \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (15)$$

c. The standard formation enthalpy of $Zn(Met)$-$SO_4 \cdot H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 5\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ 2\Delta_{\text{f,SO}_2\text{(g)}}H^{\theta} + 10\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta})$$
$$- \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (16)$$

d. The standard formation enthalpy of $Zn(Met)_2$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 10\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ 2\Delta_{\text{f,SO}_2\text{(g)}}H^{\theta} + 10\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta})$$
$$- \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (17)$$

e. The standard formation enthalpy of $Zn(His)Cl_2 \cdot 1/2H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 6\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ 2\Delta_{\text{f,HCl(g)}}H^{\theta} + 4\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta})$$
$$- \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (18)$$

f. The standard formation enthalpy of $Zn(His)Ac_2 \cdot 1/2H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 10\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ 8\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta}) - \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (19)$$

g. The standard formation enthalpy of $Zn(His)$-$SO_4 \cdot H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{f,ZnO(s)}}H^{\theta} + 6\Delta_{\text{f,CO}_2\text{(s)}}H^{\theta}$$
$$+ \Delta_{\text{f,SO}_2\text{(s)}}H^{\theta} + \tfrac{11}{2}\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta})$$
$$- \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (20)$$

h. The standard formation enthalpy of $Zn(His)_2 \cdot 3/2H_2O$

$$\Delta_{\text{f,coor(s)}}H^{\theta} = (\Delta_{\text{ZnO(s)}}H^{\theta} + 12\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta}$$
$$+ \tfrac{19}{2}\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta}) - \Delta_{\text{c,coor(s)}}H^{\theta} \qquad (21)$$

Where $\Delta_{\text{f,ZnO(s)}}H^{\theta} = -350.46 \pm 0.27 \text{ kJ mol}^{-1}$, $\Delta_{\text{f,CO}_2\text{(g)}}H^{\theta} = -393.51 \pm 0.13 \text{ kJ mol}^{-1}$, $\Delta_{\text{f,H}_2\text{O(l)}}H^{\theta} = -285.83 \pm 0.042 \text{ kJ mol}^{-1}$, $\Delta_{\text{f,HCl(g)}}H^{\theta} = -92.31 \pm 0.03 \text{ kJ mol}^{-1}$, $\Delta_{\text{f,SO}_2\text{(g)}}H^{\theta} = -296.81 \pm 0.20 \text{ kJ mol}^{-1}$ [10]. The results of the calculations are also shown in Table 2.

Acknowledgements

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