Preparation and Thermal Chemical Properties of Compounds of Zinc Nitrate with Valine

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The solubility property of the $Zn(NO_3)_2$—Val—H_2O system at 25 °C in the whole composition range has been investigated by the semimicrophase equilibrium method. The corresponding phase diagrams and refractive index diagrams were constructed. From the phase equilibrium results, the incongruently soluble compounds $Zn(Val)(NO_3)_2 \cdot 2H_2O$, $Zn(Val)_2(NO_3)_2 \cdot H_2O$, and $Zn(Val)_3(NO_3)_2 \cdot H_2O$ were synthesized and characterized by IR, XRD, TG—DTG, as well as chemical and elemental analyses. The constant-volume combustion energies of the compounds, $\Delta_c E$, determined by a precision rotating bomb calorimeter at 298.15 K, were (-10064.24 ± 5.41) J g^{-1}, (-13523.98 ± 7.54) J g^{-1}, and (-16116.13 ± 7.58) J g^{-1}, respectively. The standard enthalpies of combustion for these compounds, $\Delta_c H$, were calculated to be (-3442.21 ± 2.25) kJ mol^{-1}, (-5971.2 ± 3.32) kJ mol^{-1}, and (-9007.26 ± 4.24) kJ mol^{-1} while the standard enthalpies of formation were (-1017.34 ± 2.00) kJ mol^{-1}, (-1742.93 ± 3.61) kJ mol^{-1}, and (-2245.70 ± 4.73) kJ mol^{-1}. The enthalpies of solution in condition of simulating human gastric juice (37 °C, pH = 1, the solution of hydrochloric acid), which were also measured by a microcalorimeter, were (22.17 ± 0.05) kJ mol^{-1}, (14.89 ± 0.04) kJ mol^{-1}, and (6.85 ± 0.07) kJ mol^{-1}, respectively.

Zinc is an essential element to the life. Many diseases aroused from the deficiency of zinc have received considerable attention worldwide. L-α-Amino acids are basic units of proteins. L-α-Valine is one of eight species of amino acids that have to be absorbed from food due to being not synthesized by organism. The compounds of L-α-valine and essential elements as additives widely used in such fields as foodstuffs, medicine, and cosmetics [1—3] have a broader prospect for application. Simply put, a better understanding of the research into the compounds of the microelements and L-α-valine is thus of considerable practical and fundamental importance.

In the previous papers, the phase chemistry of the $ZnSO_4/ZnCl_2/ZnAc$—Val—H_2O system and the properties of the corresponding solid compounds have been reported [4—7]. In the forthcoming work, the phase chemistry of the $Zn(NO_3)_2$—Val—H_2O system at 25 °C was investigated by the semimicrophase equilibrium method [8]. Three new solid compounds of zinc with L-α-valine were prepared under the guidance of the phase equilibrium diagram, and thermal chemical properties for these compounds were determined and discussed.

EXPERIMENTAL

$Zn(NO_3)_2 \cdot 6H_2O$ and L-α-valine were B. R. grade (purity > 99.5 %), other regents were A. R. grade. The temperature fluctuation of the constant-temperature water was ± 0.05 °C; WZS-1 Abbe refractometer was made in the Shanghai Shiyan Apparatus Factory, the temperature of that fluctuated within ± 0.2 °C; ZD-2 automatic potentiometric titrator was from the Apparatus Factory of Shanghai. The IR spectra of the compounds were obtained with Bruker EQ UINOX-550 model infrared spectrophotometer (KBr pellets). TG and DTG data were determined by a Perkin—Elmer thermogravimetric analyzer. All TG—DTG tests were performed under a dynamic atmosphere of dry oxygen at a flow rate of 60 cm^3 min^{-1}, the heating rate used was 10 K min^{-1} and sample masses were approximately 1 mg. Carbon, hydrogen, and nitrogen analyses were carried out on a 2400 type elemental analyzer (PE Company, U.S.A.).

Zn^{2+} was determined complexometrically with EDTA. Valine was analyzed by the formalin method. The Zn^{2+} was removed by precipitating with $K_2C_2O_4$ before it was titrated. The solubility of L-α-valine was 4.46 % at 25 °C in our experiment, and the value in Ref. [9] is 8.13 % while the solubility of $Zn(NO_3)_2$ was 55.91 % and the value in Ref. [10] is 55.98 %.

The phase diagram of the ternary system was constructed by the semimicrophase equilibrium method. The constant-volume combustion energies of the compounds have been determined by an RBC-II type ro-

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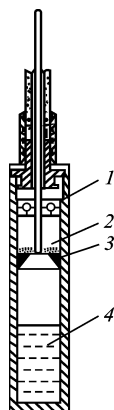*The author to whom the correspondence should be addressed.

Fig. 1. Sketch of calorimetric vessels. *1.* Calorimetric cell, *2.* solid sample, *3.* spacer, *4.* solution.

tating bomb calorimeter [11]. Benzoic acid had an isothermal heat of combustion at 25 °C of −26434 J g^{-1}. The calibration for the apparatus and temperature, the determination processes of the experiment, and the analyses of final products were identical with Refs. [11, 12].

The enthalpies of solution for the compounds were obtained using a microcalorimeter, type RD496-III

(China, Southwest Institute of Electronic Engineering), which was equipped with two 15 cm³ vessels (Fig. 1) [13]. After reaching equilibrium, the spacers of the sample and reference vessels were depressed simultaneously and the samples were mixed. The microcalorimeter was calibrated by the Joule effect [13]. The experimental precision and accuracy were checked by measuring the enthalpy of crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H_m^\circ$ of (17.238 ± 0.048) kJ mol^{-1} was in good agreement with $\Delta_{sol}H_m^\circ$ of (17.241 ± 0.018) kJ mol^{-1} [14]. The measured precision of the microcalorimeter was 0.5 %.

RESULTS AND DISCUSSION

The solubility properties of the ternary system $Zn(NO_3)_2$—Val—H_2O have been investigated in the whole composition range by the semimicrophase equilibrium method at 25 °C. Based on 28 runs (Table 1) of phase equilibrium data, the phase diagram and refractive index diagram have been constructed and are shown in Fig. 2. The solubility and refractive index data of the system are given in Table 1.

Clearly, it is evident for the system $Zn(NO_3)_2$—

Table 1. Solubility and Refractive Index of the $Zn(NO_3)_2$—Val—H_2O System at 25 °C

Run	w(Intermediate)/%		w(Liquid phase)/%		Wet residue/%		w(Dry solid)/%		n_D^{25}	Equilibrium solid phase
	$Zn(NO_3)_2$	Val	$Zn(NO_3)_2$	Val	$Zn(NO_3)_2$	Val	$Zn(NO_3)_2$	Val		
1	–	–	–	4.46	–	–	–	100.0	1.342 5	Val
2	5.01	24.14	6.64	4.12	3.99	43.08	61.64	38.36	1.346 7	Val
3	10.11	22.83	12.88	5.01	8.32	38.04	72.00	28.00	1.354 8	Val
4	15.05	18.85	17.39	6.58	12.81	32.12	72.55	27.45	1.361 0	Val
5	19.93	15.48	21.92	8.89	16.11	32.84	71.15	28.85	1.362 4	Val
6	21.92	22.95	15.10	11.14	17.28	38.55	57.55	42.45	1.369 8	Val + E
7	25.01	21.00	15.10	11.14	24.93	32.16	57.55	42.45	1.369 8	Val + E
8	27.96	24.13	15.10	11.14	29.29	35.65	57.55	42.45	1.369 8	Val + E
9	29.82	14.47	29.31	12.29	30.55	26.58	70.46	29.54	1.410 5	E
10	33.18	20.99	33.12	14.21	33.28	31.97	69.98	30.02	1.402 0	E
11	36.23	19.76	36.75	16.56	35.81	32.10	68.94	31.06	1.428 7	E + D
12	36.98	14.06	36.75	16.56	37.11	33.99	68.94	31.06	1.428 7	E + D
13	38.20	26.01	36.75	16.56	39.85	35.22	68.94	31.06	1.428 7	E + D
14	39.99	22.95	39.31	15.14	40.89	32.04	72.19	27.81	1.430 7	D
15	42.65	20.06	42.66	13.88	42.65	28.87	75.45	24.55	1.435 5	D
16	45.58	20.00	45.92	13.29	44.54	30.05	77.55	22.45	1.452 8	D + C
17	46.99	25.85	45.92	13.29	47.39	32.99	77.55	22.45	1.458 2	D + C
18	49.66	20.97	45.92	13.29	51.98	26.13	77.55	22.45	1.452 8	D + C
19	48.81	14.10	47.96	11.81	51.11	21.00	80.24	18.76	1.456 1	C
20	53.71	14.82	52.91	8.91	54.19	21.98	85.59	14.41	1.478 5	C
21	56.78	9.93	56.82	7.93	56.24	16.96	87.75	12.25	1.483 3	C + S
22	58.62	8.74	56.82	7.93	59.99	9.86	87.75	12.25	1.483 3	C + S
23	59.98	6.78	56.82	7.93	62.13	5.97	87.75	12.25	1.483 3	C + S
24	60.10	4.02	56.82	7.93	61.49	2.31	87.75	12.25	1.483 3	C + S
25	58.18	4.38	55.97	6.21	60.84	2.28	90.01	9.99	1.469 0	S
26	57.98	2.99	55.33	4.24	59.82	2.02	92.88	7.12	1.460 2	S
27	57.86	1.02	55.41	1.78	60.20	0.66	96.89	3.11	1.451 5	S
28	57.96	–	55.91	–	–	–	100.00	–	1.445 0	S
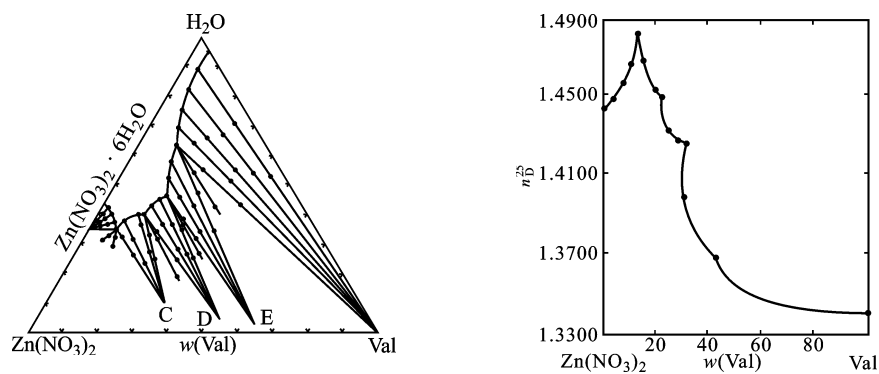
Fig. 2. Solubility diagram and refractive index curve of the ternary system $Zn(NO_3)_2$—Val—H_2O at 25 °C.
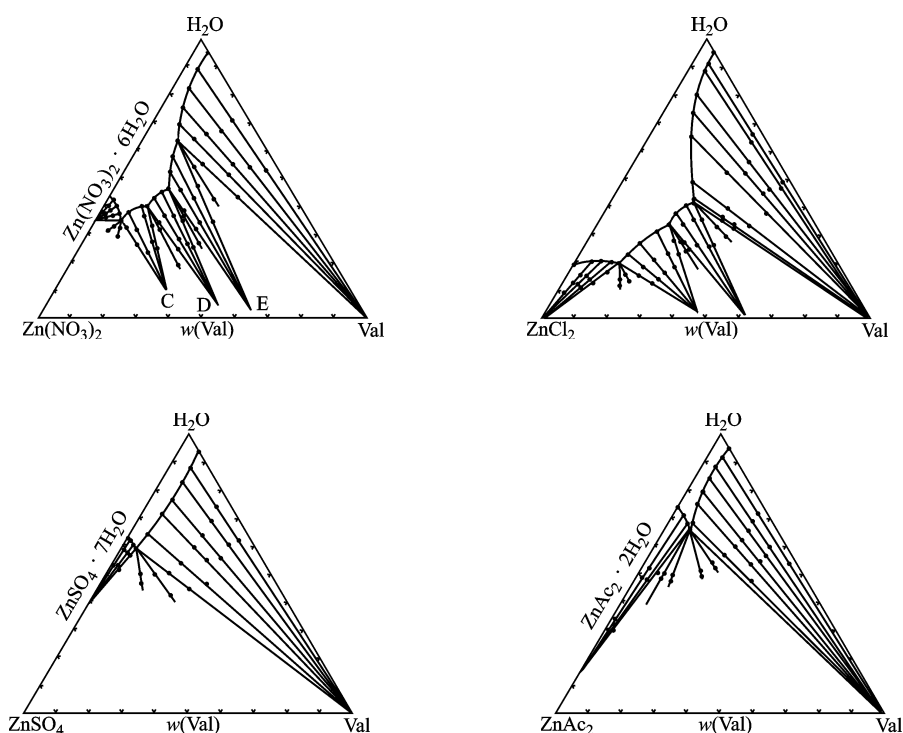
Fig. 3. Comparison of the phase diagrams of the ternary systems $Zn(NO_3)_2/ZnCl_2/ZnSO_4/ZnAc_2$—Val—$H_2O$ at 25 °C.

Val—H_2O that the solubility curves of the systems consist of five branches which correspond to $Zn(NO_3)_2$ ·$6H_2O$ (S), $Zn(Val)(NO_3)_2 \cdot 2H_2O$ (C), $Zn(Val)_2$-$(NO_3)_2 \cdot H_2O$ (D), $Zn(Val)_3(NO_3)_2 \cdot H_2O$ (E), and L-α-val, and C, D, and E are the incongruently soluble compounds which are prepared directly from water. In addition, no new phase regions are formed for the phase diagrams of the $ZnSO_4$—Val—H_2O and $ZnAc_2$—Val—H_2O systems described in Refs. [4, 5], while the incongruently soluble compounds $Zn(Val)Cl_2 \cdot H_2O$ and $Zn(Val)_2Cl_2$ are formed in the $ZnCl_2$—Val—H_2O system [6]. Summarizing the results of ZnX_2 (X = Cl^-, NO_3^-, SO_4^{2-}, and Ac^-)—Val—H_2O system (Fig. 3), we think the reason why the new solid compounds are formed might be the fact that the solubility of the compounds of Cl^- or NO_3^-

with $Zn(Val)^{2+}$ is smaller than those of SO_4^{2-} or Ac^- with $Zn(Val)^{2+}$.

The compounds were prepared by the following procedures: according to the composition of the system point in the phase region of the compounds C, D, and E, the ingredients were sealed in polyethylene tube and put in a thermostat for more than 30 d, then the wet solid was filtered and dried in vacuum, then the final compound was obtained with pale powder, which is insoluble in ethanol and acetone, but soluble in water and its compositional data are listed in Table 2.

The principal IR data of the ligand and the compounds are shown in Table 3 (see also [15]). The absence of the characteristic absorption bands of —COOH group in the compounds at $\bar{\nu}$ = 1700—

**Table 2.** Composition Data (w_i/%) for the Title Compounds C, D, and E*

Compound	Colour	Zn^{2+}	Val	C	H	N
C	Pale	19.14 (19.09)	34.16 (34.20)	17.57 (17.53)	4.44 (4.41)	12.23 (12.27)
D	Pale	14.84 (14.80)	53.10 (53.04)	27.16 (27.19)	5.26 (5.25)	12.71 (12.68)
E	Pale	11.66 (11.70)	62.80 (62.89)	32.27 (32.24)	6.28 (6.31)	12.57 (12.53)

*The data in brackets are calculated values.

Table 3. The Principal IR Data ($\tilde{\nu}_i$/cm^{-1}) of the Ligand and the Title Compounds

Compound	$\nu_{as}(NH_3^+)$	$\nu_s(NH_3^+)$	$\delta_{as}(NH_3^+)$	$\delta_s(NH_3^+)$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\nu(OH)$
L-α-Val	3454.6	2976.9	1614.9	1506.3	1600.3	1425.5	–
C	3414.1	2964.8	1628.7	1498.8	1538.8	1388.1	3545.1
D	3417.5	2971.1	1622.4	1495.4	1558.2	1389.9	3498.7
E	3175.0	2972.1	1622.1	1506.5	1609.6	1390.9	3478.7
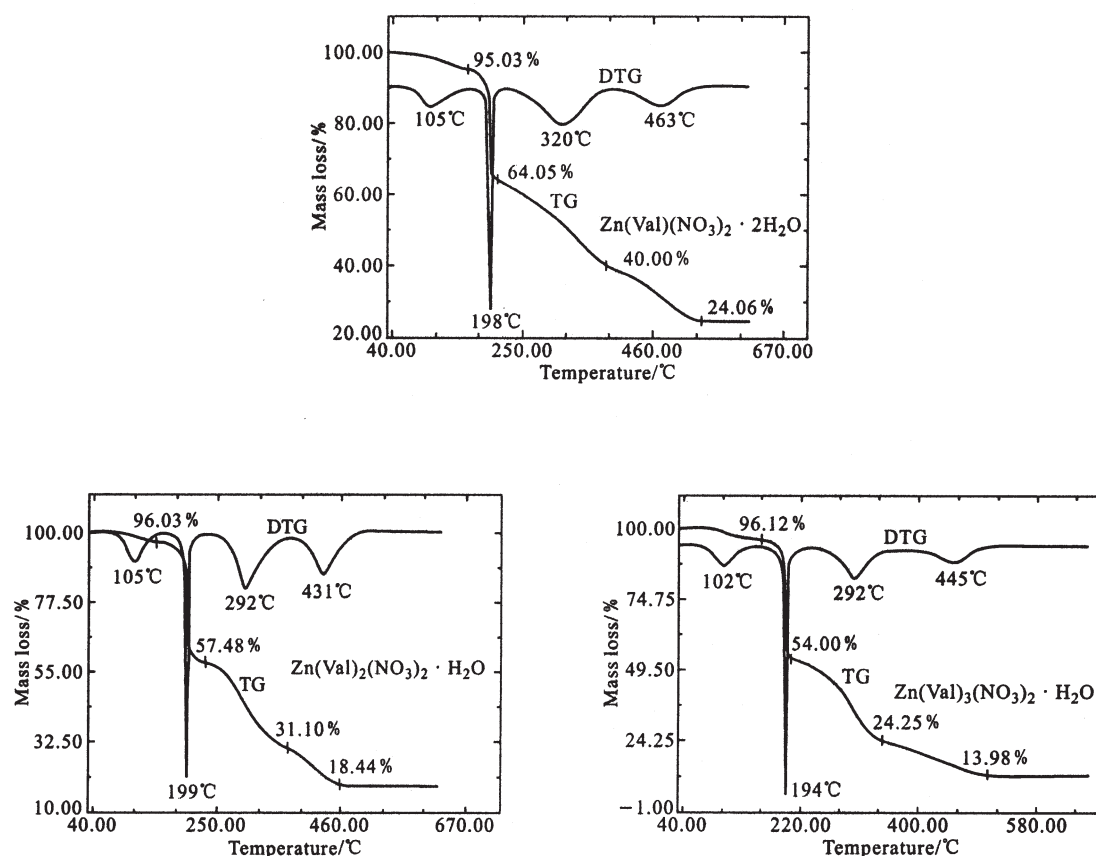
Fig. 4. The TG—DTG curves of the title compounds.

1750 cm^{-1} reveals that valine still maintains zwitterions structure. Considerable shifts of the characteristic absorptions of NH_3^+ and COO^- for the compounds compared with ligand indicate that valine coordinates Zn^{2+} through the N atom of amino and O atom of carboxyl group as bidentate ligand. The characteristic absorption peaks of NO_3^- cannot be identified from the spectrum of the compounds. The wide characteristic absorption band at 3500 cm^{-1} of $\nu_{as}(OH^-)$ re-

veals that the compounds contain H_2O molecule, but the absence of the characteristic peak of Zn—O at 364 cm^{-1} indicates that the water in the compounds is crystallizable, not the coordinated one.
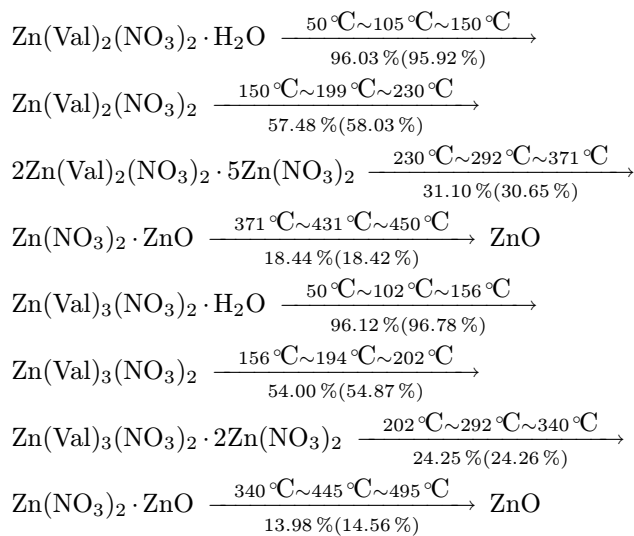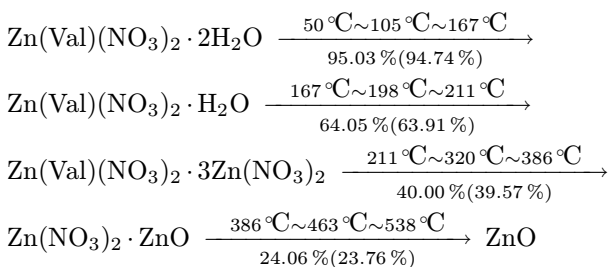
The TG—DTG curves of the compounds are shown in Fig. 4. The compounds decompose in four steps. According to the data from the TG—DTG curves, the first step in the decomposition of the complex C is the loss of one molecule of water, followed

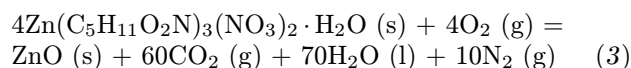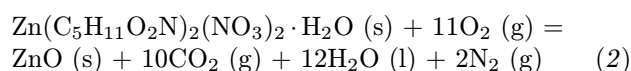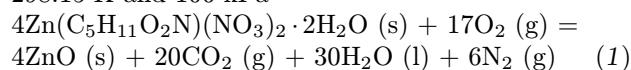**Table 4.** The Constant-Volume Combustion Energies of the Title Compounds

Compound	Run	Mass of complex m/g	Calibrated heat of combustion wire q_c/J	Calibrated heat of acid q_N/J	Calibrated ΔT/K	Combustion energy $-\Delta_c E/(\text{J g}^{-1})$
C	1	1.17140	12.60	33.06	0.6565	10049.35
	2	1.09112	11.70	30.79	0.6137	10085.55
	3	1.09967	11.70	31.04	0.6176	10070.75
	4	1.00212	12.60	28.28	0.5622	10057.80
	5	1.00753	12.60	28.44	0.5658	10067.95
	6	1.06230	10.80	29.98	0.5956	10054.07
	Mean					10064.24±5.41
D	1	1.10260	12.60	48.66	0.8315	13519.26
	2	1.00396	12.69	44.31	0.7579	13532.24
	3	1.07426	12.60	47.41	0.8090	13500.05
	4	1.06359	12.60	46.94	0.8032	13537.76
	5	1.00450	12.60	44.33	0.7569	13507.03
	6	1.00005	10.80	44.13	0.7557	13547.53
	Mean					13523.98±7.52
E	1	1.0056	12.60	52.87	0.9035	16110.21
	2	1.0103	12.60	53.12	0.9072	16099.82
	3	1.0035	12.60	52.75	0.9030	16136.85
	4	1.0002	12.60	52.61	0.9008	16141.19
	5	1.0035	12.60	52.86	0.9027	16097.66
	6	1.0020	12.60	52.71	0.9008	16111.06
	Mean					16116.13±7.58

by another water molecule accompanied with the loss of parts of ligand. The products in these stages are taken out and identified by IR technique analyses. The IR spectra of the products are similar with that of the complex C except the characteristic absorption of water at about 3400 cm^{-1}. As for the compounds D and E, the first decomposition stages are dehydrations which end at 156 °C and 150 °C, followed by losing of parts of the ligand. After these, the decompositions of the compounds C, D, and E proceed in similar steps. Further decomposition of the compounds occurs at 200—400 °C, the product is identified as the compound of $Zn(NO_3)_2$ and ZnO. Subsequently, the compound is completely decomposed into ZnO that coincides with the standard IR spectrum of ZnO. The experimental results of the residual amount are in good agreement with the calculated ones, again confirming the above conclusions.

In accordance with the IR spectra and TG—DTG experiments described above, it is preliminarily assumed that the thermal decomposition processes for these compounds are as follows

$$Zn(Val)(NO_3)_2 \cdot 2H_2O \xrightarrow[\substack{95.03\,\%(94.74\,\%)}]{50\,°C\sim105\,°C\sim167\,°C}$$

$$Zn(Val)(NO_3)_2 \cdot H_2O \xrightarrow[\substack{64.05\,\%(63.91\,\%)}]{167\,°C\sim198\,°C\sim211\,°C}$$

$$Zn(Val)(NO_3)_2 \cdot 3Zn(NO_3)_2 \xrightarrow[\substack{40.00\,\%(39.57\,\%)}]{211\,°C\sim320\,°C\sim386\,°C}$$

$$Zn(NO_3)_2 \cdot ZnO \xrightarrow[\substack{24.06\,\%(23.76\,\%)}]{386\,°C\sim463\,°C\sim538\,°C} ZnO$$

$$Zn(Val)_2(NO_3)_2 \cdot H_2O \xrightarrow[\substack{96.03\,\%(95.92\,\%)}]{50\,°C\sim105\,°C\sim150\,°C}$$

$$Zn(Val)_2(NO_3)_2 \xrightarrow[\substack{57.48\,\%(58.03\,\%)}]{150\,°C\sim199\,°C\sim230\,°C}$$

$$2Zn(Val)_2(NO_3)_2 \cdot 5Zn(NO_3)_2 \xrightarrow[\substack{31.10\,\%(30.65\,\%)}]{230\,°C\sim292\,°C\sim371\,°C}$$

$$Zn(NO_3)_2 \cdot ZnO \xrightarrow[\substack{18.44\,\%(18.42\,\%)}]{371\,°C\sim431\,°C\sim450\,°C} ZnO$$

$$Zn(Val)_3(NO_3)_2 \cdot H_2O \xrightarrow[\substack{96.12\,\%(96.78\,\%)}]{50\,°C\sim102\,°C\sim156\,°C}$$

$$Zn(Val)_3(NO_3)_2 \xrightarrow[\substack{54.00\,\%(54.87\,\%)}]{156\,°C\sim194\,°C\sim202\,°C}$$

$$Zn(Val)_3(NO_3)_2 \cdot 2Zn(NO_3)_2 \xrightarrow[\substack{24.25\,\%(24.26\,\%)}]{202\,°C\sim292\,°C\sim340\,°C}$$

$$Zn(NO_3)_2 \cdot ZnO \xrightarrow[\substack{13.98\,\%(14.56\,\%)}]{340\,°C\sim445\,°C\sim495\,°C} ZnO$$

The data of constant-volume combustion energies of the compounds are listed in Table 4. The standard enthalpies of combustion of the compounds, $\Delta_{c,coor(s)} H_m^\circ$ are referred to the combustion enthalpy change of the following ideal combustion reactions at 298.15 K and 100 kPa

$$4Zn(C_5H_{11}O_2N)(NO_3)_2 \cdot 2H_2O \text{ (s)} + 17O_2 \text{ (g)} = 4ZnO \text{ (s)} + 20CO_2 \text{ (g)} + 30H_2O \text{ (l)} + 6N_2 \text{ (g)} \quad (1)$$

$$Zn(C_5H_{11}O_2N)_2(NO_3)_2 \cdot H_2O \text{ (s)} + 11O_2 \text{ (g)} = ZnO \text{ (s)} + 10CO_2 \text{ (g)} + 12H_2O \text{ (l)} + 2N_2 \text{ (g)} \quad (2)$$

$$4Zn(C_5H_{11}O_2N)_3(NO_3)_2 \cdot H_2O \text{ (s)} + 4O_2 \text{ (g)} = ZnO \text{ (s)} + 60CO_2 \text{ (g)} + 70H_2O \text{ (l)} + 10N_2 \text{ (g)} \quad (3)$$

Table 5. The Standard Combustion Energies, Standard Combustion Enthalpies, and Standard Enthalpies of Formation of the Title Compounds

Compound	$-\Delta_{c,coor(s)}E$	$-\Delta_{c,coor(s)}H_m^\circ$	$-\Delta_{f,coor(s)}H_m^\circ$
C	3447.79±1.85	3442.21±1.85	1017.34±2.00
D	5973.69±3.32	5971.21±3.32	1742.93±3.61
E	9006.64±4.24	9007.26±4.24	2245.70±4.73

Table 6. The Enthalpy of Solution for the Compounds

Complex	Mass of sample m/mg	$\Delta_{sol}H_m^\circ$/(kJ mol^{-1})	Mean of $\Delta_{sol}H_m^\circ$/(kJ mol^{-1})
C	28.46, 33.23, 46.09	22.16, 22.25, 22.14	
	50.55, 66.21, 78.30	22.18, 22.10, 22.17	22.17 ± 0.02
D	32.48, 35.26, 40.36	14.88, 14.95, 14.83	
	45.79, 55.61, 82.90	14.90, 14.86, 14.91	14.89 ± 0.02
E	38.89, 40.17, 45.23	6.90, 6.87, 6.75	
	50.29, 67.00, 84.11	6.94, 6.88, 6.78	6.85 ± 0.03

$\Delta_{c,coor(s)}H_m^\circ$ can be obtained from the equation

$$\Delta_{c,coor(s)}H_m^\circ = \Delta_{c,coor(s)}E + \Delta nRT$$

According to the thermal chemical eqns (*1—3*), the standard enthalpies of formation of the compounds are calculated by the Hess law.

$$\Delta_{f,C(s)}H_m^\circ = [\Delta_{f,ZnO(s)}H_m^\circ + 5\Delta_{f,CO_2(g)}H_m^\circ + \\ + \frac{15}{2}\Delta_{f,H_2O(l)}H_m^\circ] - \Delta_{c,C(s)}H_m^\circ \qquad (4)$$

$$\Delta_{f,D(s)}H_m^\circ = [\Delta_{f,ZnO(s)}H_m^\circ + 10\Delta_{f,CO_2(g)}H_m^\circ + \\ + 12\Delta_{f,H_2O(l)}H_m^\circ] - \Delta_{c,D(s)}H_m^\circ \qquad (5)$$

$$\Delta_{f,E(s)}H_m^\circ = [\Delta_{f,ZnO(s)}H_m^\circ + 15\Delta_{f,CO_2(g)}H_m^\circ + \\ + \frac{35}{2}\Delta_{f,H_2O(l)}H_m^\circ] - \Delta_{c,E(s)}H_m^\circ \qquad (6)$$

where $\Delta_{f,ZnO(s)}H_m^\circ = (-350.46 \pm 0.27)$ kJ mol^{-1}, $\Delta_{f,CO_2(g)}H_m^\circ = (-393.51 \pm 0.13)$ kJ mol^{-1}, $\Delta_{f,H_2O(l)}H_m^\circ = (-285.83 \pm 0.042)$ kJ mol^{-1} [16].

The standard combustion enthalpies and standard enthalpies of formation of the compounds are shown in Table 5.

Under the condition of simulating human gastric juice (37 ℃, pH = 1), the compounds dissolve completely in water and the mole ratio of water to the complex ($n(H_2O)/n$(complex)) is more than 4000. The solution enthalpies of the title compounds in limitless dilution solution are thus obtained and presented in Table 6. The solution is an endothermic reaction, the heat produced by the complex C in solution process is the greatest, and that of the complex E is the lowest.

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