JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Phase Equilibrium of the Ternary System Cadmium Chloride + L-Threonine + Water at 298.15 K and Standard Molar Enthalpy of Formation of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$

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ABSTRACT: The equilibrium solubility of the ternary system cadmium chloride + L-threonine + water was determined at 298.15 K, and the corresponding equilibrium diagram was constructed. The ternary system is complicated with four equilibrium solid phases, $CdCl_2 \cdot 2.5H_2O$, $CdCl_2 \cdot H_2O$, $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$, and $C_4H_9NO_3$, of which a new compound of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ was found to be incongruently soluble in the system. The new compound obtained was identified and characterized by the methods of FT-IR, elementary analysis, powder X-ray diffraction, single X-ray diffraction, and thermogravimetric and differential thermal analysis. It belongs to the monoclinic system, space group $P2(1)/$, with $a = 0.7672(4)$ nm, $b = 0.9166(5)$ nm, $c = 1.3787(7)$ nm, $\beta = 96.453(7)°$, $V = 0.9634(8)\ \mathrm{nm}^3$, $Dc = 2.188\ \mathrm{g \cdot cm^{-3}}$, and $Z = 2$. The dissolution enthalpies of $CdCl_2$, $C_4H_9NO_3$, and $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ in 2 $\mathrm{mol \cdot dm^{-3}}$ hydrochloric acid were measured by heat conduction microcalorimetry. By designing an appropriate thermochemical cycle according to Hess's law and through calculation, the reaction enthalpies of formation were found to be $-(9.28 \pm 0.30)\ \mathrm{kJ \cdot mol^{-1}}$ for L-threonine with cadmium chloride, and the standard molar enthalpies of formation were found to be $-(1493.8 \pm 0.4)\ \mathrm{kJ \cdot mol^{-1}}$ for $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$.

INTRODUCTION

Phase diagrams of ternary systems of zinc chloride + amino acids (valine, leucine, threonine, methionine, phenylalanine, histidine, tryptophane) + water at 298.15 K have been investigated, and the corresponding solubilities have been determined in previous studies,[1−4] which is highly valuable and important for us to understand the phase relations and interactions of zinc chloride and amino acids in aqueous media. We can estimate whether new solid phase compounds are formed, and they are congruently and incongruently soluble in aqueous systems. These can provide the fundamental basis and serve as a guide for the preparation of new solid phase compounds. For the zinc chloride + amino acid (AA) (Leu, Try, His) + water systems,[1,4] three equilibrium solid-phase regions $ZnCl_2$, $Zn(AA)Cl_2 \cdot nH_2O$ (1:1 type) (n = 0, 0.5), and AA were observed. In these ternary systems, the new compound $Zn(Try)Cl_2 \cdot 0.5H_2O$ is incongruently soluble, whereas $Zn(Leu)Cl_2$ and $Zn(His)Cl_2 \cdot 0.5H_2O$ are congruently soluble in the aqueous systems. The results show that phase chemical reactions of the three ternary systems are similar (they all have a 1:1 type compound). Li et al. and Gao et al. re-examined the zinc chloride + AA (Val, Thr, Phe, Met) + water systems[1−3] and confirmed the presence of four stable complexes $ZnCl_2$, $Zn(AA)Cl_2 \cdot nH_2O$ (1:1 type), $Zn(AA)_2Cl_2 \cdot nH_2O$ (1:2 type) (n = 0, 0.5, 1, 2) and AA, and the new compounds of the 1:1 and 1:2 types are incongruently soluble in the aqueous systems. Comparing the four ternary systems above,[1−3] we find that the phase chemical behavior of the four ternary systems is very similar because they all have 1:1 type and 1:2 type compounds and are incongruently soluble in the aqueous systems.

Cadmium and zinc are in the same subgroup B. To find out interactions of cadmium chloride with amino acid, contrast the difference of the phase chemical relationship of cadmium chloride and zinc chloride with amino acid in aqueous salt systems, and provide equilibrium data in the aqueous ternary systems of cadmium chloride and amino acid to scientists and engineers using corresponding phase diagrams, Qiao et al. have studied that the cadmium chloride + DL-alanine + water ternary system at 298.15 K and found the presence of three equilibrium solid−phase regions ($CdCl_2 \cdot 2.5H_2O$, $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$, and Ala).[5] Moreover, cadmium is an important environmental and industrial toxin, and it also is a very long half-life multiorgan, multisystem poison.[6,7] Amino acid is an important component of biological organisms, the basic unit of peptide and protein composition, is used in metabolic processes of biological organisms in the basic materials, and has important physiological functions. Therefore, we study the composition and properties of complexes with cadmium and amino acid, which is beneficial to the physiological role of organisms.

Above all, the present paper is concerned with the solubility and phase equilibrium relations of the cadmium chloride + L-threonine + water system at 298.15 K and related measurement of properties of a new solid−phase compound established in the system.

EXPERIMENTAL SECTION

Reagents. Cadmium chloride ($w \geq 0.996$), purchased from Tianjin Yongda Reagent Development Center, Tianjin, China, was analytical reagent grade and crystallized twice before use. L-Threonine ($w \geq 0.998$) was biological reagent grade. Potassium

Received: July 3, 2011
Accepted: October 6, 2011
Published: October 20, 2011

chloride ($w \geq 0.9999$) was spectrum pure grade. Both these reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, and used without further purification. Hydrochloric acid (guaranteed reagent) was purchased from Luoyang Haohua Chemical Reagent Company, Luoyang, China. Quartz sub-boiling distilled water was used (resistivity = 5.7 $M\Omega \cdot cm$).

Investigations on the System at 298.15 K and Analysis Methods. The method of investigation of the solubility of the cadmium chloride + L-threonine + water ternary system has been previously reported.[8] All sealed samples were put in a big water tank with a thermostat fixed at 298.15 K and an electrical stirrer. The precision of the temperature was 0.1 K. The solid−liquid phase equilibrium was established for these samples after (20 to 22) days. The method was as follows: The refractive index of the solution of the sample at 298.15 K was measured, and the values of the refractive index were the same for two continuous days; this result indicated that the phase equilibrium had been established for the solid−liquid system.

The saturated solutions and the corresponding wet solid phases (wet residues) of the samples were separated, taken out, and analyzed. The analysis methods were as follows: (1) The concentration of Cd^{2+} was analyzed by titration with a normal solution of EDTA. (2) The concentration of Cl^- was analyzed by titration with a normal solution of silver nitrate. (3) The concentration of formic acid in formaldehyde solution was first determined by titration with a solution of sodium hydroxide as the blank experiment. Then, the concentration of L-threonine was titrated with sodium hydroxide, and the termination was determined by a pH potentiometer after the amidogen of L-threonine was blanketed with formaldehyde solution and Cd^{2+} was blanketed with a screening agent of 1,10-phenanthroline. The solid-phase compositions in the system were determined graphically by the well-known wet residue method of Schreinemaker.[9] Schreinemaker Method: In a system, every sample consists of two parts, namely, the saturated liquid phase and wet residue (wet residue is the mixture of the saturated liquid and the establishing solid under the condition of equilibrium). For every sample, the saturated liquid phase, the wet residue, and the solid could form a straight line, with the saturated liquid and the solid in the two extreme points and the wet residue inside the line. When the contents of the saturated liquid and the wet residue are known, a radial could be drawn through these two phases. In a system, it is possible that the samples of the different liquid phases possess the same solid phases. Therefore, the radials of the same solid samples are all through one point. The content of this point is what we need to know about the solid.

Equipment and Conditions. C, H, and N analyses were carried out with a Vario EL III CHNOS element analysis instrument. The FT-IR analysis was conducted on a Nicolet 5700 spectrometer (with KBr pellets at room temperature). Thermal characterization of the novel compound was undertaken with an SDT Q600 V8.0 thermal analysis apparatus (TG−DTG) that worked with a heating rate of 10 $K \cdot min^{-1}$ under a N_2 atmosphere with a flow rate of 100 $cm^3 \cdot min^{-1}$. X-ray diffraction (XRD) measurements were performed by a D/Max−3C diffractometer using Cu Kα radiation, 50 kV, and 80 mA, at room temperature. The diffraction data of the structure analysis were collected by a Bruker Smart Apex-II CCD diffractometer using a graphite monochromatized Mo Kα radition (λ = 0.071 073 nm), at room temperature.

An RD496-III-2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used at 298.15 K and was described in detail previously.[10,11]

The enthalpy of solution of KCl in deionized water was measured to verify microcalorimeter calibration. The mean value (17.31 ± 0.06) $kJ \cdot mol^{-1}$ of $\Delta_{sol}H_m$ agrees with the literature value of 17.234 $kJ \cdot mol^{-1}$ reported in ref 12.

Each calorimetric experiment was performed five times. The temperature of the calorimetric experiment was (298.15 ± 0.01) K. The hydrochloric acid solution (2 $mol \cdot dm^{-3}$) was put in the 10 cm^3 Teflon sample cell and reference cell of the calorimeter. After thermal equilibration for at least 1.5 h, the solid sample was pressed into the solvent by a rod. The thermal effect was then recorded automatically on a computer. The total time required for complete dissolution was about 20 min. There were no solid residues observed after the dissolutions.

RESULTS AND DISCUSSION

Cadmium Chloride + L-Threonine + Water System at 298.15 K. The solubility data of the cadmium chloride + L-threonine + water system at 298.15 K are listed in Table 1. The respective concentration values are expressed in mass fraction. Figure 1 depicts the corresponding phase equilibrium diagram.

As can be seen in Figure 1, the curves of solubility in the ternary system consist of four branches of cadmium chloride + L-threonine + water, which correspond to the equilibrium solid phases of $CdCl_2 \cdot 2.5H_2O$ (A), $CdCl_2 \cdot H_2O$ (B), $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ (1:1 type) (C), and L-threonine (D), respectively. This indicates that the phase regions of two new solid-phase compounds of B and C are formed in this system except for initial compounds A and D, of which both compounds of B and C are incongruently soluble in the aqueous system, and the compound of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ has not been reported in the literature. The presence of B in the cadmium chloride + L-threonine + water system implies that $C_4H_9NO_3$ can dehydrate crystal water from $CdCl_2 \cdot 2.5H_2O$.

$Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ obtained from the system was analyzed by a Vario EL III CHNOS element analysis instrument. The contents of C, N, and H are 14.91 %, 4.34 %, and 3.32 %, respectively. These values are also in agreement with theoretical data (14.99 % C, 4.37 % N, and 3.45 % H).

Comparing the reported ternary system,[5] the present system has the different phase chemical reaction. The ternary system (cadmium chloride + DL-alanine + water) presented in the previous paper had a 3:2 type compound, which was congruently soluble. However, an incongruently soluble compound with 1:1 type was obtained in this ternary system.

Characterization of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$. The X-ray powder diffraction pattern of the $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ compound obtained is shown in Figure 2. It is the same as neither $CdCl_2$ nor $C_4H_9NO_3$, nor the simple superposition of $CdCl_2$ and $C_4H_9NO_3$. This demonstrates that $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ is formed from a reaction between $CdCl_2$ and $C_4H_9NO_3$.

The FT-IR spectra of $C_4H_9NO_3$ and $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ were recorded from a KBr tablet in the region of (4000 to 100) cm^{-1}. Compared to that of $C_4H_9NO_3$, the spectrum of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ displays several significant differences: (1) The adsorption peaks at (3160 and 2992) cm^{-1} result from the asymmetrical stretching vibration and the symmetrical stretching vibration of NH_3^+; however, as to the complex, these adsorption bands become broadened and are shifted to

Table 1. Solubility Data (in Mass Fraction) of the Ternary System Cadmium Chloride + L-Threonine + Water at 298.15 K[a]

	composition of composition of saturated solution[b]/%		composition of composition of wet residue/%		
no.	$C_4H_9NO_3$	$CdCl_2$	$C_4H_9NO_3$	$CdCl_2$	solid phase[c]
1	0.00	55.60 ± 0.15	---	---	A
2	1.68 ± 0.15	54.87 ± 0.13	0.76 ± 0.12	76.78 ± 0.20	A
3	4.70 ± 0.19	55.40 ± 0.15	1.51 ± 0.14	75.11 ± 0.18	A
4	8.71 ± 0.18	55.94 ± 0.15	3.21 ± 0.17	73.77 ± 0.14	A+B
5	8.72 ± 0.20	55.94 ± 0.13	4.06 ± 0.19	73.77 ± 0.12	B
6	10.82 ± 0.20	56.57 ± 0.16	4.90 ± 0.20	74.20 ± 0.31	B
7	14.34 ± 0.19	56.50 ± 0.14	6.03 ± 0.18	75.19 ± 0.19	B
8	15.36 ± 0.16	56.71 ± 0.12	17.60 ± 0.25	61.66 ± 0.17	B+C
9	15.75 ± 0.19	54.89 ± 0.14	21.96 ± 0.20	55.93 ± 0.15	C
10	18.55 ± 0.16	50.34 ± 0.12	28.53 ± 0.32	53.94 ± 0.23	C
11	19.28 ± 0.15	48.32 ± 0.11	27.94 ± 0.19	52.25 ± 0.14	C
12	21.48 ± 0.17	46.84 ± 0.14	34.30 ± 0.20	49.40 ± 0.13	C+D
13	21.06 ± 0.19	46.28 ± 0.12	39.20 ± 0.19	45.43 ± 0.14	C+D
14	19.98 ± 0.15	43.71 ± 0.11	61.43 ± 0.35	22.07 ± 0.24	D
15	20.67 ± 0.15	42.01 ± 0.12	56.71 ± 0.29	22.57 ± 0.20	D
16	19.94 ± 0.14	36.99 ± 0.10	63.51 ± 0.42	16.63 ± 0.28	D
17	19.78 ± 0.17	35.09 ± 0.12	65.78 ± 0.37	15.64 ± 0.25	D
18	17.05 ± 0.15	28.96 ± 0.11	67.35 ± 0.34	11.82 ± 0.23	D
19	16.46 ± 0.15	25.13 ± 0.11	74.97 ± 0.39	7.91 ± 0.24	D
20	15.45 ± 0.14	20.79 ± 0.09	76.87 ± 0.46	6.15 ± 0.26	D
21	13.74 ± 0.14	14.93 ± 0.10	75.06 ± 0.36	5.08 ± 0.24	D
22	12.40 ± 0.15	8.85 ± 0.11	73.85 ± 0.36	3.34 ± 0.25	D
23	11.32 ± 0.17	5.46 ± 0.10	78.67 ± 0.39	1.39 ± 0.23	D
24	8.95 ± 0.19	0.00	---	---	D

[a] Uncertainty was twice the standard deviation of the mean. [b] Double saturation point (average): E_1: $CdCl_2$, 55.94 ± 0.15 %; $C_4H_9NO_3$, 8.71 ± 0.18 %. E_2: $CdCl_2$, 56.71 ± 0.12 %; $C_4H_9NO_3$, 15.36 ± 0.16 %. E_3: $CdCl_2$, 46.51 ± 0.18 %; $C_4H_9NO_3$, 21.27 ± 0.25 %. [c] Compounds: A, $CdCl_2 \cdot 2.5H_2O$; B, $CdCl_2 \cdot H_2O$; C, $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$; D, $C_4H_9NO_3$.

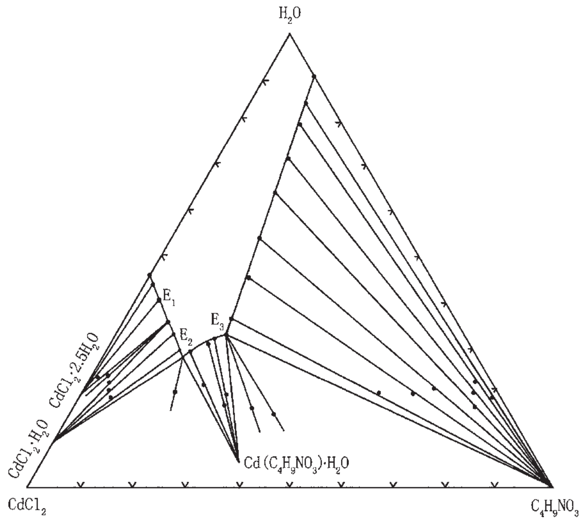

Figure 1. Isothermal solubility diagram of the system cadmium chloride + L-threonine + water at 298.15 K. The E_1, E_2, and E_3 stand for double saturation point, respectively.

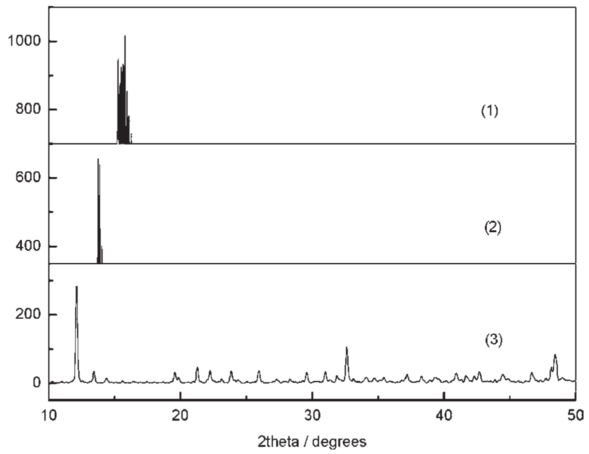

Figure 2. X-ray powder diffraction spectrum of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$. (1) $CdCl_2$, (2) $C_4H_9NO_3$, (3) $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$.

3070 cm^{-1}, which reveals the existence of strong hydrogen bonds between amino groups and H_2O. (2) For the spectrum of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$, the adsorption bands at (1631 and 1450) cm^{-1}, assigned to the asymmetrical and symmetrical stretching vibrations of COO^- in the $C_4H_9NO_3$, are shifted to (1624 and 1414) cm^{-1}, respectively. The results indicate that the carboxyl groups of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$

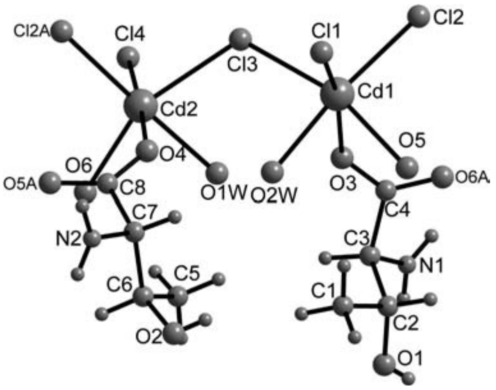

Figure 3. Asymmetric unit structure of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$.

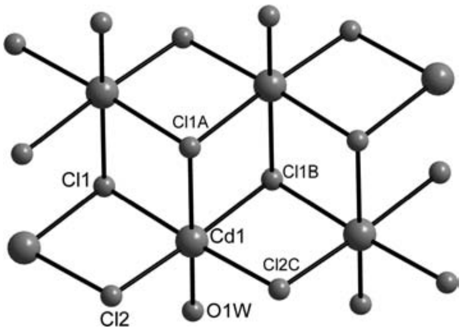

Figure 4. Molecular structure of $CdCl_2 \cdot H_2O$.

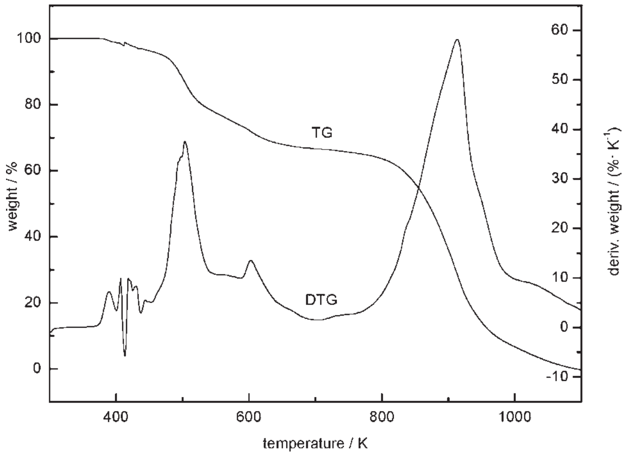

Figure 5. Thermogravimetry and differential thermogravimetry (TG, DTG) curves of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$.

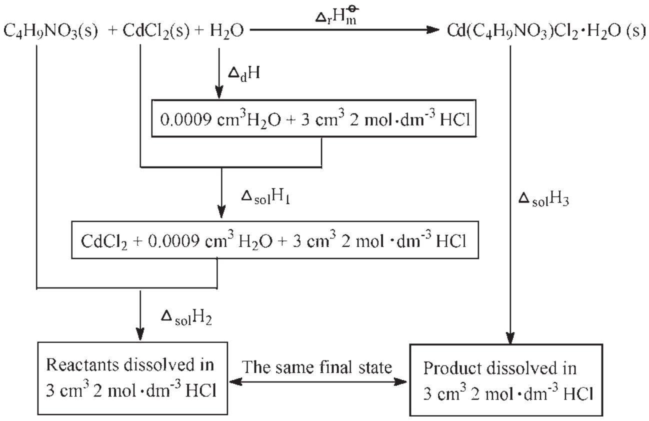

Figure 6. Thermochemical cycle of the reaction enthalpy of L-threonine and cadmium chloride.

are doubly coordinated. (3) The band around 3407 cm^{-1} is attributed to the stretching vibration of −OH in the H_2O molecule. The band observed near 555 cm^{-1} is the wagging vibration of H_2O, which indicates that the H_2O molecule takes part in the coordination. (4) $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ also exhibits some bands in the low wavelength range. For example, the band around 401 cm^{-1} is assigned to the symmetrical stretching vibration of Cd−O (COO^-), and the peak around 328 cm^{-1} is ascribed to the symmetrical stretching vibration of Cd−Cl, which suggest that the oxygen and chlorine also take part in the coordination.

The single crystal of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ with approximate dimension of 0.16 × 0.14 × 0.13 mm^3 was selected for structure analysis. The compound of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ belongs to the monoclinic system, with space group *P*2(1)/, *a* = 0.7672(4) nm, *b* = 0.9166(5) nm, *c* = 1.3787(7) nm, β = 96.453(7)°, *V* = 0.9634(8) nm^3, *Dc* = 2.188 $g \cdot cm^{-3}$, *Z* = 2. R1 = 0.0237($I > 2\sigma$), and wR2 = 0.0612 (all data). The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software. All the non-hydrogen atoms were refined anisotropically. The H1 and H2 atoms bonded to O1 and O2 atoms were located from Fourier difference maps, and the H atoms bonded to other atoms were positioned geometrically. The asymmetric unit structure of the compound is shown in Figure 3. As shown in Figure 3, the H_2O molecule takes part in coordination in $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$.

We also selected the single crystal of $CdCl_2 \cdot H_2O$ with approximate dimensions of 0.18 × 0.15 × 0.12 mm^3 for structure analysis. The compound of $CdCl_2 \cdot H_2O$ belongs to the orthorhombic system, with space group *Pnma*, *a* = 0.9185(1) nm, *b* = 0.3765(5) nm, *c* = 1.1640(1) nm, β = 96.453(7)°, *V* = 0.4025(9) nm^3, *Dc* = 3.817 $g \cdot cm^{-3}$, *Z* = 4, R1 = 0.0506($I > 2\sigma$), and wR2 = 0.1441 (all data). The molecular structure of $CdCl_2 \cdot H_2O$ is shown in Figure 4.

TG−DTG curves for the compound of $CdCl_2 \cdot H_2O$ are presented in Figure 5. It can be seen from the TG curves that there exist three steps in the process of thermal decomposition of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$. The solid complex was stable below 379 K and started decomposition at this point. The first mass loss, 5.55 %, took place in the range of (379 to 476) K, which was associated with the loss of water and can be compared with the calculated value of 5.62 %. The second mass loss occurred in the temperature range from (476 to 698) K, which corresponded to the decomposition of $C_4H_9NO_3$. The third mass loss arose from (793 to 1053) K, which represented the sublimation of cadmium chloride.

Enthalpy of Reaction. HCl(aq) (2 $mol \cdot dm^{-3}$) rapidly dissolves all components of the reaction. According to Hess's law, the reaction enthalpy of L-threonine and cadmium chloride, $\Delta_r H_m{}^{\Theta}(s)$, can be calculated on the basis of thermochemical cycle and is shown in Figure 6.

The molar enthalpy of dilution of 0.9 mg of water in 3.00 cm^3 of [2 $mol \cdot dm^{-3}$ HCl(aq)] at 298.15 K, $\Delta_d H$, was very small, in

Table 2. Molar Enthalpies of Solution of $\Delta_{\text{sol}}H_1$, $\Delta_{\text{sol}}H_2$, and $\Delta_{\text{sol}}H_3$ at 298.15 K[a]

	m	Q_s	$\Delta_{\text{sol}}H_1$	m	Q_s	$\Delta_{\text{sol}}H_2$	m	Q_s	$\Delta_{\text{sol}}H_3$
no.	mg	mJ	kJ·mol^{-1}	mg	mJ	kJ·mol^{-1}	mg	mJ	kJ·mol^{-1}
1	9.21	219.1	4.36	6.02	159.3	3.15	16.16	850.2	16.86
2	9.21	210.0	4.00	6.02	166.8	3.30	16.16	850.4	16.68
3	9.24	204.5	4.06	6.02	168.2	3.33	16.13	841.3	16.71
4	9.25	208.4	4.13	5.98	166.5	3.32	16.15	824.9	16.37
5	9.23	229.5	4.56	5.99	160.9	3.20	16.13	855.4	17.00
mean[b]			4.22 ± 0.21			3.26 ± 0.072			16.76 ± 0.21

[a] $\Delta_{\text{sol}}H_1$, 3.00 cm^3 of [0.0009 cm^3 of H_2O + 2 mol·dm^{-3} HCl(aq)]; $\Delta_{\text{sol}}H_2$, 3.00 cm^3 of [9.23 mg of $CdCl_2$ + 0.0009 cm^3 of H_2O + 2 mol·dm^{-3} HCl(aq)]; $\Delta_{\text{sol}}H_3$, 3.00 cm^3 of [2 mol·dm^{-3} HCl(aq)]. [b] Uncertainty was twice the standard deviation of the mean.

the range of measurement error, and can be ignored.[12,13] The molar enthalpy of solution of 9.23 mg of $CdCl_2$ in 3.00 cm^3 of [0.0009 cm^3 of H_2O + 2 mol·dm^{-3} HCl(aq)] at 298.15 K, $\Delta_{\text{sol}}H_1$, was (4.22 ± 0.21) kJ·mol^{-1}. The molar enthalpy of solution of 6.00 mg of $C_4H_9NO_3$ in 3.00 cm^3 of [9.23 mg of $CdCl_2$ + 0.0009 cm^3 of H_2O + 2 mol·dm^{-3} HCl(aq)] at 298.15 K, $\Delta_{\text{sol}}H_2$, was (3.26 ± 0.072) kJ·mol^{-1}. The molar enthalpy of solution of 16.14 mg of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ in 3.00 cm^3 of [2 mol·dm^{-3} HCl(aq)] at 298.15 K, $\Delta_{\text{sol}}H_3$, was (16.76 ± 0.21) kJ·mol^{-1}. The values of $\Delta_{\text{sol}}H_1$, $\Delta_{\text{sol}}H_2$, and $\Delta_{\text{sol}}H_3$ are listed in Table 2, in which m was the mass of the sample. The uncertainty was estimated as twice the standard deviation of the mean.

The reaction enthalpy of L-threonine and cadmium chloride at 298.15 K can be calculated as

$$\begin{aligned}\Delta_r H_m^{\Theta}(s) &= \Delta_{\text{sol}}H_1 + \Delta_{\text{sol}}H_2 - \Delta_{\text{sol}}H_3\\ &= [(4.22 \pm 0.21) + (3.26 \pm 0.072)\\ &\quad - (16.76 \pm 0.21)]\ \text{kJ}\cdot\text{mol}^{-1}\\ &= -(9.28 \pm 0.30)\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The validity of the thermochemical cycle was proven as follows: The refractive index of the reactants and product in 3.00 cm^3 of [2 mol·dm^{-3} HCl(aq)] at 290 K were measured, namely, 1.3520 and 1.3523, respectively. The values of the refractive index were the same. This suggests that the final thermodynamic state of reactants and product was the same, and the proposed thermochemical cycle is correct.

Standard Molar Enthalpy of Formation. The molar enthalpy of formation of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ can be calculated as shown in following equation:

$$\begin{aligned}\Delta_r H_m^{\Theta}(s) &= \Delta_f H_m^{\Theta}[Cd(C_4H_9NO_3)Cl_2 \cdot H_2O](s)\\ &\quad - \Delta_f H_m^{\Theta}(CdCl_2)(s) - \Delta_f H_m^{\Theta}(C_4H_9NO_3)(s)\\ &\quad - \Delta_f H_m^{\Theta}(H_2O)(l)\end{aligned}$$

The standard molar enthalpy of formation of $CdCl_2$ was taken from the NBS table,[14] namely, −(391.50 ± 0.10) kJ·mol^{-1}. The standard molar enthalpy of formation of $C_4H_9NO_3$(s) was taken from the Lange's Handbook of Chemistry,[15] −(807.2 ± 0.30) kJ·mol^{-1}. The standard molar enthalpy of H_2O(l) was taken from the CODATA Key Values,[16] −(285.830 ± 0.042) kJ·mol^{-1}. Using these scheme and data, the standard molar enthalpy of formation of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ was calculated to be −(1493.8 ± 0.4) kJ·mol^{-1}.

CONCLUSION

The solubility of the ternary system of cadmium chloride + L-threonine + water at 298.15 K was measured, and the corresponding phase diagram was prepared to search for new compounds and obtain equilibrium data for cadmium chloride/L-threonine in aqueous solution. A new solid phase was found to exist in the system, and the composition of the new solid phase compound of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ was determined by the Schrienemaker method. By designing a thermochemical cycle according to Hess's law and through measuring the enthalpy of solution at 298.15 K, the reaction enthalpy of L-threonine with cadmium chloride at 298.15 K and the standard molar enthalpy of formation of the novel compound of $Cd(C_4H_9NO_3)Cl_2 \cdot H_2O$ were obtained.

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REFERENCES

(1) Gao, S. L.; Guo, L. J.; Zhang, F. X.; Ma, Y. Phase Equilibrium of $ZnCl_2$−AA(Leu/Try/Val/Thr) −H_2O (298 K) Systems. *Acta Phys. Chim. Sin.* **2001**, *52*, 573–576 (in Chinese).

(2) Gao, S. L.; Liu, J. R.; Ji, M.; Yang, X. W.; Zhang, F. X.; Li, Z. J. A Study of Coordination Behavior of Zinc Salt with L− a −Methionine. *Chin. Sci. Bull.* **1998**, *43*, 1496–1499 (in Chinese).

(3) Li, H. Y.; Hou, Y. D.; Chen, S. P.; Yu, Y. H.; Gao, S. L. A Study of Coordination Behavior of Zinc Chloride with L-Phenylalanine. *J. Northwest Univ.* **2000**, *30*, 384–387 (in Chinese).

(4) Liu, J. R.; Hou, Y. D.; Gao, S. L.; Ji, M.; Shi, Q. Z. Study on Phase Chemistry of Coordination of Zinc Salts to L−a−Histidine. *Acta Chim. Sin.* **1999**, *57*, 485–490 (in Chinese).

(5) Qiao, Z. P.; Dang, Y. L.; Zhang, S. S. Phase Equilibrium System of Cadmium Chloride + DL-Alanine + Water at 298.15 K and Standard Molar Enthalpy of Formation of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$. *J. Chem. Eng. Data* **2010**, *55*, 2451–2454.

(6) Peng, X. J.; Du, J. J.; Fan, J. L.; Wang, J. Y.; Wu, Y. K.; Zhao, J. Z.; Sun, S. G.; Xu, T. A Selective Fluorescent Sensor for Imaging Cd^{2+} in Living Cells. *J. Am. Chem. Soc.* **2007**, *129*, 1500–1501.

(7) Amit, R. R.; Laran, T. J.; Valeria, C. C. Manganese Homeostasis in Saccharomyces cerevisiae. *Chem. Rev.* **2009**, *109*, 4722–4732.

(8) Wang, H.; Wang, X. F.; Dong, F. X.; Ran, X. Q. Investigation on the Equilibrium Phase Diagrams of the Ternary Systems $CdCl_2$−$RECl_3$−H_2O (RE = La, Nd, Sm, Eu) at 303 K. *J. Chem. Eng. Data* **2007**, *52*, 731–736.

(9) Chen, Y. S. *Analysis of Physical Chemistry*; Higher Education Press: Beijing, 1988; pp 505−506.

(10) Qiao, Z. P.; Xie, H. Q.; Zhuo, L. H.; Chen, X. Study on Phase Equilibrium in the Quaternary System $CsCl-LuCl_3-HCl$ (10.06%)$-H_2O$ at 298.15 ± 0.1 K and New Solid Phase Compounds. *J. Chem. Eng. Data* **2007**, *52*, 1681–1685.

(11) Ji, M.; Liu, M. Y.; Gao, S. L. A New Microcalorimeter for Measuring Thermal Effects. *J. Instrum. Sci. Technol.* **2001**, *29*, 53–57.

(12) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL. 1989.

(13) Lu, J. L.; Liu, B. P.; Tan, Z. C.; Zhang, D. S.; Li, L.; Chen, Y. D.; Shi, Q. Synthesis, Crystal Structure and Thermochemical Study of $[Gd_2(Gly)_6(H_20)_4](ClO_4)_6(H_20)_5$. *Acta Chim. Sin.* **2007**, *21*, 2349–2355 (in Chinese).

(14) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Chumey, K. L.; Nuttal, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data* **1982**, (suppl. 2).

(15) John, A. *Dean Lange's Handbook of Chemistry*, 13th ed.; Mcgraw-Hill, Inc.: New York, 1998.

(16) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.