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A thermochemical study of the solid-state coordination reactions of two α-amino acids with copper(II) acetate

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Abstract

The two solid-state coordination reactions

$$\mathrm{CuAc_2 \cdot H_2O(s) + 2Ala(s) \rightarrow \mathit{trans}\text{-}Cu(Ala)_2(s) + 2HAc(l) + H_2O(l)} \tag{1}$$

$$\mathrm{CuAc_2 \cdot H_2O(s) + 2Gly(s) \rightarrow \mathit{trans}\text{-}Cu(Gly)_2 \cdot H_2O(s) + 2HAc(l)} \tag{2}$$

have been studied by solution calorimetry. The molar dissolution enthalpies of the reactants and the products in some solvents (such as 2 mol l^{-1} HCl or its solutions) of these solid–solid coordination reactions have been measured by an isoperibol solution calorimeter. The standard molar formation enthalpies of [*trans*-Cu(Ala)$_2$(s), 298.15 K] and [*trans*-Cu(Gly)$_2$(s), 298.15 K] have been determined to be -1015.42 ± 0.06 and 1252.36 ± 0.05 kJ mol^{-1}, respectively, from the results of the molar dissolution enthalpies and other auxiliary thermodynamic data.

Keywords: Copper(II) acetate; Glycine; Alanine; Isoperibol solution calorimetry; Standard molar formation enthalpy

1. Introduction

Solid-state chemical synthesis is an important and promising method in the field of synthetic chemistry. The method [1] has been widely used to synthesize various solid-state coordination compounds of many metal salts with α-amino acids because it avoids complicated experimental operations and harsh reaction conditions. It is well-known that α-amino acids are basic structural units which constitute the proteins and copper(II) is one of the trace elements necessary for the human body. It was early established that the complex of α-amino acids with copper(II) is one of the complexes with *cis*- and *trans*-geometric isomers, which has extensive application in food, cosmetics and medicines as a nutrient.

In 1993, Zheng and Xin [2] synthesized a series of complexes (including *trans*-Cu(Ala)$_2$(s), *trans*-Cu(Gly)$_2$·H$_2$O(s) and others) by means of solid-state coordination reactions of copper(II) acetate with α-amino acids at ambient temperature. XRD, IR, DTA and elemental analysis were employed to characterize their structures. However, up till now, the enthalpies of solid-state coordination reactions involved in the syntheses of these complexes and their respective standard molar formation enthalpy have not been reported in literature. The purpose of the present study

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is to determine the dissolution enthalpies of the reactants and the products of two solid-state coordination reactions of copper(II) acetate with α-alanine and α-glycine, respectively, by isoperibol solution calorimetry. In addition, the standard molar formation enthalpies of the products [*trans*-Cu(Ala)$_2$(s) and *trans*-Cu(Gly)$_2$·H$_2$O(s)] of the two solid-state coordination reactions were derived from the respective dissolution enthalpies.

2. Experimental

2.1. Chemicals

Copper(II) acetate [Cu(Ac)$_2$·H$_2$O(s)], alanine(s), glycine(s) and other reagents used in these experiments were of analytical grade and obtained from Shanghai Reagent Factory. KCl(s) used for calibration of the isoperibol solution calorimeter was of a purity greater than 99.99%, and dried in a vacuum oven for 6 h at 135–140 °C prior to use. The water used in measurements was twice distilled.

2.2. Sample preparations and characterization

The samples used in the present measurements were prepared according to the method given in the literature [1,2], in which 5 mmol Cu(Ac)$_2$·H$_2$O(s) of 80–100 mesh was mixed and ground with certain amount of alanine and glycine, respectively, in 1:2 mole ratio. These were retained for 4 h at ambient temperature. If subsequent XRD measurement showed that the refraction peaks of the two reactants in the system of every solid-state coordination reaction have disappeared, the reactions have been completed. The products were washed for three times with absolute ethyl alcohol, and for once with ethyl ether of analytical grade. Finally, these were placed in a vacuum desiccator at ambient temperature to vacuum dry for 4 h. Chemical and element analyses (model: PE-2400, Perkin-Elmer, USA) have shown that the purity of the samples prepared were higher than 99.98 mol%.

2.3. Calorimeter and calibration

The isoperibol solution calorimeter used was adapted for measuring enthalpies of solid–liquid and liquid–liquid reactions [3,4]. The volume of the reaction vessel was 100 cm^3. The precisions of controlling and measuring the temperature were ±0.001 and ±0.0001 K, respectively.

The reliability of the calorimeter was confirmed by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.1 mol l^{-1} HCl and KCl (calorimetric primary standard) in twice distilled water at 298.15 K. The mean dissolution enthalpies are $-29\,776 \pm 16$ J mol^{-1} for THAM and $17\,597 \pm 17$ J mol^{-1} for KCl, which are well in conformity with the corresponding published data [5,6], $-29\,766 \pm 31.5$ J mol^{-1} for THAM and $17\,536 \pm 9$ J mol^{-1} for KCl.

3. Results and discussion

3.1. The calorimetric solvent

In these experiments, 2 mol l^{-1} HCl were chosen as calorimetric solvents for measurements of the dissolution enthalpies of the reactants and products in the reactions of Cu(Ac)$_2$·H$_2$O(s) with alanine and with glycine.

3.2. The determination of enthalpy change for the solid-state coordination reaction of Cu(Ac)$_2$·H$_2$O(s) with alanine

Of about 0.31 g sample of Cu(Ac)$_2$(s) and Ala(s) mixture at mole ratio of n(*trans*-Cu(Ala)$_2$)/n(Ala) = 1:2 were dissolved in 100 ml of 2 mol l^{-1} HCl at 298.15 K.

If ‘s’ = calorimetric solvent of 2 mol l^{-1} HCl, then,

$$\{\mathrm{Cu(Ac)_2 \cdot H_2O(s)} + 2\mathrm{Ala(s)}\} + \text{‘s’} = \text{solution A}$$

The dissolution enthalpies of HAc(aq) [n(HAc)/n(H$_2$O) = 2:1] in 100 ml of 2 mol l^{-1} HCl were measured under the same condition

$$2{:}1\,\mathrm{HAc(aq)} + \text{‘s’} = \text{solution B}$$

The dissolution enthalpies of *trans*-Cu(Ala)$_2$(s) in solution B were measured under the same condition as the above.

$$\textit{trans}\text{-}\mathrm{Cu(Ala)_2(s)} + \text{solution B} = \text{solution A1}$$

The measurement results of dissolution enthalpies for the reactants and products of reaction (1) are listed in

Table 1
Dissolution enthalpies of [$Cu(Ac)_2 \cdot H_2O(s) + 2Ala(s)$] and [2:1 HAc(aq)] in 2 mol l^{-1} HCl and [*trans*-$Cu(Ala)_2(s)$] in 2:1 HAc(aq) at 298.15 K[a]

System	Solvent	Number	m (g)	ΔE_e (mV)	ΔE_s (mV)	Q_e (J)	Q_s (J)	$\Delta_S H_m^{\Theta}$ (kJ mol^{-1})
$\Delta_S H_m^{\Theta}$ [$Cu(Ac)_2 \cdot H_2O(s)$ + 2Ala(s)] = 8.10 ± 0.04 kJ mol^{-1}								
$Cu(Ac)_2 \cdot H_2O(s)$ + 2Ala(s)	2 mol l^{-1} HCl	1	0.3145	1.25	1.60	5.280	6.758	8.113
		2	0.3141	1.15	1.57	4.840	6.610	7.955
		3	0.3159	1.14	1.61	4.845	6.843	8.176
		4	0.3132	1.16	1.57	4.959	6.712	8.092
		5	0.3122	1.15	1.60	4.862	6.765	8.181
$\Delta_S H_m^{\Theta}$ [2:1 HAc(aq)] = − 1.36 ± 0.01 kJ mol^{-1}								
2:1 HAc(aq)	2 mol l^{-1} HCl	1	0.4062	1.87	1.67	7.732	−6.905	−1.327
		2	0.4114	1.68	1.74	6.846	−7.091	−1.346
		3	0.4063	1.83	1.76	7.331	−7.331	−1.405
		4	0.4001	1.64	1.71	7.057	−7.057	−1.337
		5	0.4063	1.73	1.73	7.149	−7.149	−1.374
$\Delta_S H_m^{\Theta}$ [*trans*-$Cu(Ala)_2(s)$] = − 37.81 ± 0.04 kJ mol^{-1}								
Trans-$Cu(Ala)_2(s)$	2:1 HAc(aq) + 2 mol l^{-1} HCl	1	0.1986	6.49	7.49	27.168	−31.377	−37.873
		2	0.1016	2.55	3.86	10.612	−16.064	−37.901
		3	0.0981	3.21	3.68	14.495	−15.425	−37.693
		4	0.0962	3.38	3.65	14.167	−15.173	−37.808
		5	0.0985	3.36	3.70	14.098	−15.521	−37.774

[a] $R = 1666.0\ \Omega$, $I = 10.000$ mA; m is mass of sample (g); ΔE_e, the voltage change during the electrical calibration (mV); ΔE_s, the voltage change during the sample dissolution (mV); Q_e electrical energy of electrical calibration (J); Q_s heat effect (J); $\Delta_S H_m^{\Theta} = (\Delta E_s/\Delta E_e) I^2 R t_e (M/m)$, where R is the electro-resistance; I, the electrical current; M, the molar mass; t_e, heating period of electrical calibration.

Table 1. In addition, the enthalpy change of mixing HAc(l) with $H_2O(l)$ in the mole ratio of $n(HAc)/n(H_2O) = 2:1$ can be obtained from literature [7]: $\Delta_d H_m^{\Theta} = -3.58$ kJ mol^{-1}. The enthalpy change of the solid-state coordination reaction (1) can be calculated in accordance with a thermochemical cycle and the experimental results as follows:

$$\begin{aligned}\Delta_r H_m(1) &= \Delta_s H_m^{\Theta}[Cu(Ac)_2 \cdot H_2O(s) + 2Ala(s)] \\ &\quad - \Delta_s H_m^{\Theta}[2{:}1\ HAc(aq)] \\ &\quad - \Delta_s H_m^{\Theta}[trans\text{-}Cu(Ala)_2(s)] - \Delta_d H_m^{\Theta} \\ &= 50.85 \pm 0.06\ \text{kJ mol}^{-1}.\end{aligned}$$

3.3. The determination of enthalpy change of the solid-state coordination reaction of $Cu(Ac)_2 \cdot H_2O(s)$ with glycine

The determination of the enthalpy change of the reaction (2) was similar to that of the reaction (1) described in Section 3.2 except that [2:1HAc(aq)+ ‘s’ = solution B] was replaced by [HAc(l) + ‘s’ = solution B]. The enthalpy change of reaction (2) did not include the enthalpy change of mixing HAc(l) with $H_2O(l)$ in the mole ratio of $n(HAc)/n(H_2O) = 2:1$.

The measurement results of dissolution enthalpies for the reactants and products of the reaction (2) are listed in Table 2. The enthalpy change of the solid-state coordination reaction (2) can be also calculated according to a thermochemical cycle and the experimental results as follows:

$$\begin{aligned}\Delta_r H_m(2) &= \Delta_s H_m^{\Theta}[Cu(Ac)_2 \cdot H_2O(s) + 2Gly(s)] \\ &\quad - 2\Delta_s H_m^{\Theta}[HAc(l)] \\ &\quad - \Delta_s H_m^{\Theta}[trans\text{-}Cu(Gly)_2 \cdot H_2O(s)] \\ &= 29.99 \pm 0.05\ \text{kJ mol}^{-1}.\end{aligned}$$

3.4. The standard molar formation enthalpies of trans-$Cu(Ala)_2(s)$ and trans-$Cu(Gly)_2 \cdot H_2O(s)$

The two reaction schemes are used to derive the standard molar formation enthalpies of *trans*-$Cu(Ala)_2(s)$ and *trans*-$Cu(Gly)_2 \cdot H_2O(s)$ are given in Tables 3 and 4, respectively. The experimental values of the dissolution enthalpies of the reactants and

Table 2
Dissolution enthalpies of [$Cu(Ac)_2{\cdot}H_2O(s)$ + 2Gly(s)] and [HAc(l)] in 2 mol l^{-1} HCl and [*trans*-$Cu(Ala)_2(s)$] in [HAc(l) + 2 mol l^{-1} HCl] at 298.15 K[a]

System	Solvent	Number	m (g)	ΔE_e (mV)	ΔE_s (mV)	Q_e (J)	Q_s (J)	$\Delta_S H_m^{\Theta}$ (kJ mol^{-1})
$\Delta_S H_m^{\Theta}$ [$Cu(Ac)_2{\cdot}H_2O(s)$ + 2Gly(s)] = 13.59 ± 0.03 kJ mol^{-1}								
$Cu(Ac)_2{\cdot}H_2O(s)$ + 2Gly (s)	2 mol l^{-1} HCl	1	0.3269	2.78	2.77	12.804	12.758	13.657
		2	0.3303	2.78	2.82	12.726	12.909	13.672
		3	0.3324	2.53	2.77	11.464	12.552	13.524
		4	0.3337	2.76	2.86	12.447	12.898	13.518
		5	0.3289	2.96	2.84	13.298	12.759	13.564
$\Delta_S H_m^{\Theta}$ [HAc(l)] = − 0.93 ± 0.03 kJ mol^{-1}								
HAc(l)	2 mol l^{-1} HCl	1	0.2052	1.00	1.70	4.508	−3.156	−0.925
		2	0.3060	1.19	1.06	5.292	−4.714	−0.925
		3	0.3064	1.05	1.06	4.696	−4.741	−0.929
		4	0.3114	1.02	1.11	4.541	−4.942	−0.953
		5	0.3056	0.96	1.04	4.287	−4.644	−0.913
$\Delta_S H_m^{\Theta}$ [*trans*-$Cu(Gly)_2.H_2O(s)$] = − 14.64 ± 0.02 kJ mol^{-1}								
trans-$Cu(Gly)_2{\cdot}H_2O(s)$	HAc(l) + 2 mol l^{-1} HCl	1	0.2194	3.13	3.09	13.830	−14.009	−14.665
		2	0.2181	3.12	3.07	13.660	−13.883	−14.619
		3	0.2057	2.85	2.55	11.736	−13.117	−14.646
		4	0.2069	2.84	2.69	12.531	−13.230	−14.686
		5	0.2058	2.83	2.82	13.073	−13.027	−14.590

[a] $R = 1666.0\ \Omega$, $I = 10.000$ mA.

products in the two solid-state coordination reactions (1) and (2) were combined with auxiliary thermodynamic data of $\Delta_f H_m^{\Theta}[H_2O(l)] = -285.83 \pm 0.04$ kJ mol^{-1} [9], $\Delta_f H_m^{\theta}[Cu(Ac)_2 \cdot H_2O(s)] = -1193.70$ kJ mol^{-1} [8], $\Delta_f H_m^{\Theta}[HAc(l)] = -484.131$ kJ mol^{-1} [9], $\Delta_f H_m^{\Theta}[Ala(s)] = -563.33 \pm 0.60$ kJ mol^{-1} [10] and $\Delta_f H_m^{\Theta}[Gly(s)] = -528.5 \pm 0.5$ kJ mol^{-1} [10] to derive the standard molar formation enthalpies of *trans*-$Cu(Ala)_2(s)$ and *trans*-$Cu(Gly)_2{\cdot}H_2O(s)$

$$\begin{aligned} &\Delta_f H_m^{\Theta}[\textit{trans}\text{-}Cu(Ala)_2\,(s)] \\ &= \Delta_r H_m\,(1) - 2\Delta_S H_m^{\Theta}[HAc\,(l)] - \Delta_S H_m^{\Theta}[H_2O\,(l)] \\ &\quad + \Delta_S H_m^{\Theta}[Cu(Ac)_2 \cdot H_2O\,(s)] + 2\Delta_S H_m^{\Theta}[Ala\,(s)] \\ &= \Delta H_9 = \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 - 2\Delta H_5 - \Delta H_6 \\ &\quad + \Delta H_7 + 2\Delta H_8 = -1015.42 \pm 1.20\,\text{kJ mol}^{-1}. \end{aligned}$$

Table 3
Reaction scheme used to determine the standard molar formation enthalpy of the complex $Cu(Ala)_2(s)$ at 298.15 K[a]

Number	Reactions	Solution	$\Delta_f H_m^{\Theta}$ or $\Delta_S H_m^{\Theta} \pm \sigma_a^*$ (kJ mol^{-1})
1	$\{Cu(Ac)_2 \cdot H_2O(s) + 2Ala(s)\}$ + 's'	A	8.10 ± 0.04
2	$2HAc(l) + H_2O(l) = 2:1\ HAc(aq)$		−3.579[b]
3	2:1 HAc(aq) + 's'	B	−1.36 ± 0.01
4	$Cu(Ala)_2(s)$ + 'B'	A_1	−37.81 ± 0.04
5	$2H_2(g) + O_2(g) + 2C(s) = HAc(l)$		−484.131
6	$H_2(g) + (1/2)O_2(g) = H_2O(l)$		−285.380 ± 0.042
7	$Cu(s) + 4H_2(g) + (5/2)O_2(g) + 4C(s) = Cu(Ac)_2{\cdot}H_2O(s)$		−1193.695
8	$3C(s) + (7/2)H_2(g) + O_2(g) + (1/2)N_2(g) = Ala(s)$		−563.33 ± 0.6
9	$Cu(s) + N_2(g) + 7H_2(g) + 2O_2(g) + 6C(s) = Cu(Ala)_2(s)$		−1015.421

[a] The solvent 's' is 2 mol l^{-1} HCl.

[b] According to [7] $\sigma_a^* = \sqrt{\sum_{i=1}^{5}(x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

Table 4
Reaction scheme used to determine the standard molar formation enthalpy of the complex $Cu(Gly)_2{\cdot}H_2O(s)$ at 298.15 K[a]

Number	Reactions	Solution	$\Delta_f H_m^{\Theta}$ or $\Delta_S H_m^{\Theta} \pm \sigma_a^*$ (kJ mol^{-1})
1	$\{Cu(Ac)_2 \cdot H_2O(s) + 2Gly(s)\} + \text{'s'}$	A′	13.59 ± 0.03
2	$2HAc(l) + \text{'s'}$	B′	−0.93 ± 0.03
3	$Cu(Gly)_2{\cdot}H_2O(s) + \text{'B'}$	A'_1	−14.64 ± 0.02
4	$2H_2(g) + O_2(g) + 2C(s) = HAc(l)$		−484.131
5	$Cu(s) + 4H_2(g) + (5/2)O_2(g) + 4C(s) = Cu(Ac)_2{\cdot}H_2O(s)$		−1193.695
6	$2C(s) + (5/2)H_2(g) + O_2(g) + (1/2)N_2(g) = Gly(s)$		−528.5 ± 0.5
7	$Cu(s) + N_2(g) + 6H_2(g) + (5/2)O_2(g) + 4C(s) = \textit{trans}\text{-}Cu(Gly)_2{\cdot}H_2O(s)$		−1252.363

[a] The solvent 's' is 2 mol l^{-1} HCl.

in which $\Delta H_1 \sim \Delta H_9$ are the enthalpy changes of the reactions corresponding to the number of reaction in Table 3.

$$\begin{aligned}
&\Delta_f H_m^{\Theta}[\textit{trans}\text{-Cu(Gly)}_2 \cdot H_2O\,(s)] \\
&= \Delta_r H_m(2) - 2\Delta_S H_m^{\Theta}[\text{HAc (l)}] + 2\Delta_S H_m^{\Theta}[\text{Gly (s)}] \\
&\quad + \Delta_S H_m^{\Theta}[\text{Cu(Ac)}_2 \cdot H_2O\,(s)] = \Delta H'_7 \\
&= \Delta H'_1 - \Delta H'_2 - \Delta H'_3 - 2\Delta H'_4 + \Delta H'_5 + 2\Delta H'_6 \\
&= -1252.36 \pm 1.00\,\text{kJ mol}^{-1}.
\end{aligned}$$

in which $\Delta H'_1 \sim \Delta H'_7$ are the enthalpy changes of the reactions corresponding to no. of reaction in Table 4.

In this paper, all of the reactants and products of the two solid-state coordination reactions can be easily dissolved in the corresponding solvent. Solution A and solution A′ are in thermodynamic equivalent states to solution A_1 and solution A'_1, respectively, which has been verified by UV spectroscopy and the data of the refrangibility.

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