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Phase equilibria of $Cr(NO_3)_3$–Met–H_2O system with synthesis and characterization of solid complexes

Sheng-li Gao*, San-ping Chen, Huan-yong Li, Rong-zu Hu, Qi-zhen Shi

Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, PR China

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Abstract

The solubility property of the ternary complex $Cr(NO_3)_3$–methionine (Met)–H_2O has been investigated in the whole concentration range by phase equilibrium method, and the phase diagram has been constructed. It was indicated that the new complexes of $Cr(Met)(NO_3)_3\cdot 2H_2O$ (D) and $Cr(Met)_2(NO_3)_3\cdot 2H_2O$ (E) exist in the system of $Cr(NO_3)_3$–Met–H_2O. These complexes that are congruently in water have not been reported in literature. Under the guidance of the phase diagram, the two complexes have been prepared and characterized by chemical analysis, elemental analysis, IR and TG–DTG. Their combustion energies have been determined by a RBC-type I rotating-bomb calorimeter, and their standard enthalpies of formation, $\Delta_f H_m^\circ$, have been calculated which are -1842.01 ± 2.13 and -1136.16 ± 4.45 kJ mol^{-1}, respectively.

Keywords: Chromium nitrate; L-α-Methionine; Solubility; Solid complex; Characterization; Standard enthalpy of formation

1. Instruction

GTF, the indispensable cofactor of insulin, is a complex by amino acid and niacin coordination to microelement-chromium. Insulin does not keep the normal sugar metabolic unless GTF has affinity for its complexity [1]. It is not surprising that a good understanding of coordination behavior of chromium with amino acid is basic to acquaintance with GTF. So, there is considerable practical and fundamental importance to focus on the complex of chromium and amino acid.

With respect to the investigations of the complexes of chromium with valine (Val), Leucine (Leu), methionine (Met) and phenylanine (Phe), including the preparations and properties on spectrum, NMR and magnetism in the mixture solvent of water and alcohol, they have been reported in literatures [2–8]. The complexes of the chromium–amino acid in the mole ratio of chromium to amino acid of 1:2 as well as the relationships of the complexes with GTF, were elucidated from the viewpoints of the structure, biological activity, chromatography and spectrum [1]. However, the phase equilibrium and thermochemical property of the solid complexes of chromium (III) and amino acid have not been investigated anywhere. In this manuscript, the solubility property of the ternary systems of $Cr(NO_3)_3$–Met–H_2O have been investigated at 298.15 K by semi-micro phase equilibrium method [9], and the construction of phase diagram of the system has been completed. Based on the experimental results, two new solid complexes of $Cr(Met)(NO_3)_3\cdot 2H_2O$ and $Cr(Met)_2(NO_3)_3\cdot 2H_2O$, which are presented as sym-

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[*] Corresponding author. Fax: +86-29-833-3511.
E-mail address: weizhang@nwu.edu.cn (S.-l. Gao).

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bols of D and E in this paper, have been prepared and characterized by chemical analysis, elemental analysis, IR and TG–DTG, while their combustion energies have been determined by a RBC-type I rotating-bomb calorimeter, and their standard enthalpies of formation, $\Delta_f H_m^\circ$, have been calculated as well.

2. Experimental

2.1. Material and experimental equipment

$Cr(NO_3)_3{\cdot}9H_2O$ (Beijing Hongxing Chemical Plant, A.R.) and L-α-methionine (Shanghai Kangda Ammonia Factory, B.R.) were recrystalized with the purity of 99.95%. The conductivity of the deionized water is 1.4 $\mu s\,cm^{-1}$, the others are A.R. grade reagents. The thermostat is with a temperature fluctuation of ±0.05 K. Elementary analyses of the complexes were carried out with a 2400 analyzer made by Perkin Elmer Company. The IR spectra of the compounds were obtained with a BRUKER EQ UINOX-550 infrared spectrophotometer (KBr paller). 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 $ml\,min^{-1}$, the heating rate used $10^\circ\,min^{-1}$ and sample masses approximated 1 mg. The constant-volume combustion energy of compound was determined by the RBC-type I precision rotating-bomb [10]. The mainly experimental procedures have been described in the literature [11]. The initial temperature was regulated to 25.0000± 0.0005 °C by a thermostat and the initial oxygen pressure was 2.5 MPa. The correction of the heat exchange was performed according to the Linio–Pyfengdelel–Wsava formula [12]. The calorimeter was calibrated with benzoic acid with the purity of 99.999%. Benzoic acid had isothermal heat of combustion at 298.15 K of $-26\,434 \pm 3.00\,J\,g^{-1}$. The energy equivalent of calorimeter was 17 936.23± 9.08 $kJ\,K^{-1}$. The analytical methods of final products (gas, liquid, solid) were the same as the literature [11]. The analytical results of the final products indicated that the combustion reactions were complete. Neither carbon deposits nor carbon monoxide was formed during the combustion reactions, and the amount of NO_x in the final gas phase were neglected.

2.2. Analysis method

Cr^{3+} was determined complexometrically with ammonium ferrous sulfate. Met content was analyzed by iodimetric method. The contents of carbon, hydrogen and nitrogen were carried out on the elemental analyzer.

2.3. Experimental method

Solubility property on the system was determined by semi-micro phase equilibrium method [9]. Distribution of the synthesized compounds were estimated roughly according to the solubility of chromium nitrate and L-α-Met in water at 298.15 K. The components of the synthesized compound were precisely weighed out, followed by sealing into a group of small polythene tubes, and then the tubes were fixed in a rotating plate immersed in water of a thermostat. Chemical compositions of these samples were determined after a certain time. When it remained constant, the system was assumed to be in the equilibrium state. The ternary systems of $Cr(NO_3)_3$–Met–H_2O came to equilibrium after 30 days. The compositions of liquid phase and wet–solid phase were analyzed by the same method above-mentioned.

3. Results and discussion

3.1. Result of studies on phase equilibrium

The solubility property of the ternary of $Cr(NO_3)_3$–Met–H_2O has been investigated in the whole concen-

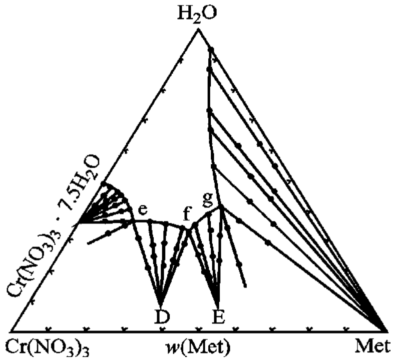

Fig. 1. Solubility diagram of the ternary system of $Cr(NO_3)_3$–Met–H_2O at 25 °C.

Table 1
Results of phase equilibrium of ternary system of $Cr(NO_3)_3$–Met–H_2O at 25 °C[a]

No.	Composition of liquid phase (100*w*)		Composition of solid phase (100*w*)		Composition of synthetic phase (100*w*)		Equilibrium solid phase
	$Cr(NO_3)_3$	Met	$Cr(NO_3)_3$	Met	$Cr(NO_3)_3$	Met	
1	51.03	–	–	–	–	–	$Cr(NO_3)_3{\cdot}7.5H_2O$
2	49.75	2.40	57.02	1.23	52.98	2.10	$Cr(NO_3)_3{\cdot}7.5H_2O$
3	48.69	5.36	56.11	2.89	53.74	3.68	$Cr(NO_3)_3{\cdot}7.5H_2O$
4	48.52	6.45	56.97	3.04	51.13	5.27	$Cr(NO_3)_3{\cdot}7.5H_2O$
5	47.93	8.51	55.62	4.70	51.86	6.64	$Cr(NO_3)_3{\cdot}7.5H_2O$
6	48.29	11.15	55.99	5.82	50.09	9.87	$Cr(NO_3)_3{\cdot}7.5H_2O$
7	49.33	13.94	56.88	6.96	52.20	11.04	$Cr(NO_3)_3{\cdot}7.5H_2O + D$
8	49.29	14.03	57.96	9.43	52.61	12.33	$Cr(NO_3)_3{\cdot}7.5H_2O + D$
9	49.41	14.14	53.00	25.81	50.74	18.29	$Cr(NO_3)_3{\cdot}7.5H_2O + D$
10	45.13	18.48	49.62	25.45	48.16	23.21	D
11	41.02	23.37	48.86	19.43	44.78	26.32	D
12	37.79	28.41	45.67	31.70	42.53	30.64	D
13	36.11	30.94	45.12	33.01	39.59	31.77	D + E
14	36.23	31.09	38.60	41.34	37.62	36.48	D + E
15	33.55	31.47	38.12	43.93	35.26	36.14	E
16	28.13	33.09	33.96	41.14	30.02	35.90	E
17	23.96	35.16	32.87	43.68	28.74	39.76	E + Met
18	23.84	35.12	28.04	49.61	25.43	40.66	E + Met
19	23.79	35.04	16.83	53.76	21.17	42.21	E + Met
20	19.98	26.75	12.14	52.29	14.93	42.06	Met
21	13.45	20.09	9.03	47.14	10.15	38.40	Met
22	10.47	17.00	6.86	47.20	8.82	29.79	Met
23	3.74	10.27	2.25	42.63	2.76	35.35	Met
24	–	5.67	–	–	–	–	Met

[a] *w*: mass fraction. $Cr(Met)(NO_3)_3{\cdot}2H_2O = D$, $Cr(Met)_2(NO_3)_3{\cdot}2H_2O = E$.

tration by phase equilibrium method at 298.15 K. Based on 24 sets of phase equilibrium data of the system of $Cr(NO_3)_3$–Met–H_2O, the phase diagram has been constructed and depicted in Fig. 1. The solubility data were presented in Table 1.

Clearly, the solubility curves of the system were composed of four branches, respective corresponding to chromium salts, the complexes D and E along with Met. The complexes of D and E are congruently soluble compounds.

3.2. Preparation and characterization of the complexes

Under the guidance of the phase diagram, the complexes of D and E were synthesized directly from the water through a general method, and dried in the desiccator containing P_4O_{10}. Both of them are excellent than the yield of 95% and not hydroscopic, while they do not dissolve in organic solvents but in water. The composition of the complexes is depicted in Table 2. The data from Table 2 indicated that the compositions of the solid complexes were consistent with those of the new phases existing in the phase diagram, which showed that the equilibrium phase diagram contributed to the preparation of the new complexes.

The IR absorption of main groups of the complexes and ligands were summarized in Table 3, which was interpreted as follows:

(1) As compared with the ligand of Met, nitrogen and oxygen atoms in the complexes coordinated to Cr^{3+} in a bidentate fashion. In addition, methyl-sulfenyl group in the complexes shifting to the low wave-number compared with that of the ligand illustrated that sulfate atom of methyl-sulfenyl group combined with chromium in coordination bond.

Table 2
Analytical results of composition of solid complexes (%)[a]

Complex	Cr^{3+}	Met	C	H	N
$Cr(Met)(NO_3)_3{\cdot}2H_2O$	12.43 (12.28)	35.14 (35.23)	14.38 (14.19)	3.68 (3.57)	13.17 (13.24)
$Cr(Met)_2(NO_3)_3{\cdot}2H_2O$	9.14 (9.08)	52.41 (52.10)	20.98 (20.98)	4.63 (4.58)	12.20 (12.23)

[a] The data in brackets were calculated values.

Table 3
Data of IR absorption for main groups of ligands and complexes (cm^{-1})

Compound	$\nu^{as}_{NH_3^+}$, $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$, $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$, $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$, $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	ν_{OH}	ν_{OH}	ν_{SCH_3}
L-α-Met	3124	2100	1620	1510	1582	1410	–	–	1340
$Cr(Met)(NO_3)_3{\cdot}2H_2O$	2921	2273	1624	1446	1508	1384	3421	826	1140
$Cr(Met)_2(NO_3)_3{\cdot}2H_2O$	2977	2361	1660	1456	1508	1384	3428	825	1140

(2) The characteristic absorption of the wave-number of 3390–3423 and 823–828 cm^{-1} in the complexes were assigned to that of water. The existence of water molecular for the complexes was believable.

3.3. Thermostability of the solid complexes

Thermostability of the solid complexes was investigated by TG–DTG. The curves of TG–DTG concerning the compounds were presented in Fig. 2. The residual amounts of loss of weight were in best agreement with the calculated results. The intermediate and final products of the thermal decomposition of the complexes were identified via IR spectrophotometer as well. It was thus assumed that the thermal decomfposition processes of the complexes were summarized in Table 4.

To the complexes of D and E, the thermal decomposition processes were proceeded in three steps. The first step was the loss of water from the complexes, which indicated that the role of water in the complexes was crystal water. The following step was loss of Met and chromic nitrate was produced. Finally, the complexes were completely decomposed into chromium hemitrioxide.

3.4. Standard enthalpies of the complexes

The constant-volume combustion energy, $\Delta_{c,\mathrm{complex\,(s)}}U$, of the two complexes was determined by using the same procedure and instrument in literature

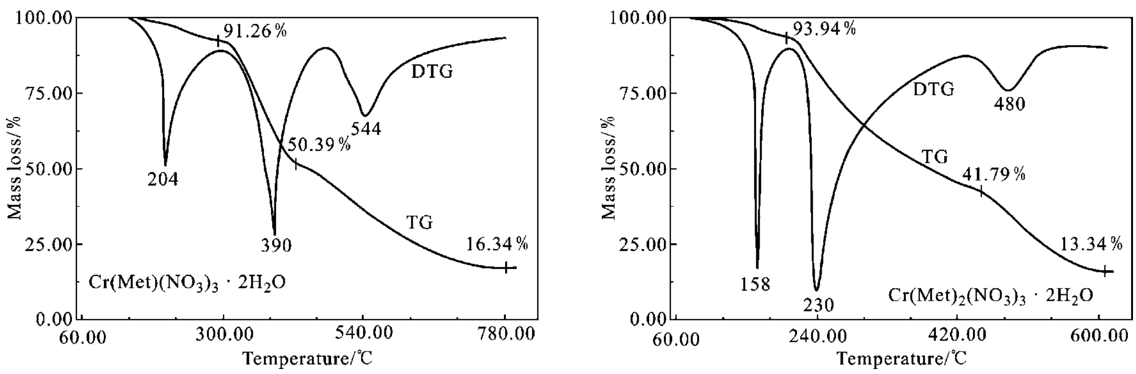

Fig. 2. TG–DTG curves of the complexes.

Table 4
Thermoanalytical results of the complexes

$Cr(Met)(NO_3)_3{\cdot}2H_2O$			
Decomposition product	$Cr(Met)(NO_3)_3$	$Cr(NO_3)_3$	Cr_2O_3
Decomposition temperature (°C)	51–204–300[a]	300–390–460	460–544–800
Residual rate (%)	91.26 (91.49)[b]	50.39 (50.71)	16.34 (16.19)
$Cr(Met)_2(NO_3)_3{\cdot}2H_2O$			
Decomposition product	$Cr(Met)_2(NO_3)_3$	$Cr(NO_3)_3$	Cr_2O_3
Decomposition temperature (°C)	51–158–200	200–230–450	460–480–600
Residual rate (%)	93.94 (93.71)	41.79 (41.58)	13.34 (13.28)

[a] The intermediate data are peak temperatures of DTG curves.
[b] The data in brackets are calculated values.

[10]. The values of $\Delta_{\mathrm{c,complex\,(s)}}U$ are -7432.52 ± 4.72 and $-13\,424.34 \pm 7.37\ \mathrm{J\,g^{-1}}$, respectively. The standard combustion enthalpies, $\Delta_{\mathrm{c,complex\,(s)}}H^\circ$, refer to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa:

$$\begin{aligned}&\mathrm{Cr(Met)(NO_3)_3 \cdot 2H_2O\,(s) + 4O_2\,(g)}\\&\quad = \tfrac{1}{2}\mathrm{Cr_2O_3\,(s)} + 5\mathrm{CO_2\,(g)} + \tfrac{15}{2}\mathrm{H_2O\,(l)}\\&\qquad + \mathrm{SO_2\,(g)} + 2\mathrm{N_2\,(g)}\end{aligned} \tag{1}$$

$$\begin{aligned}&\mathrm{Cr(Met)_2(NO_3)_3 \cdot 2H_2O\,(s)} + \tfrac{47}{4}\mathrm{O_2\,(g)}\\&\quad = \tfrac{1}{2}\mathrm{Cr_2O_3\,(s)} + 10\mathrm{CO_2\,(g)} + 13\mathrm{H_2O\,(l)}\\&\qquad + 2\mathrm{SO_2\,(g)} + \tfrac{5}{2}\mathrm{N_2\,(g)}\end{aligned} \tag{2}$$

The standard combustion enthalpies of the complexes were calculated from the combustion energies by Eq. (3):

$$\Delta_{\mathrm{c,complex\,(s)}}H^\circ = \Delta_{\mathrm{c,complex\,(s)}}U + \Delta nRT \tag{3}$$

The standard combustion enthalpies of the complexes of D and E, $\Delta_{\mathrm{c,complex\,(s)}}H^\circ$ are -3135.93 ± 2.00 and $-7678.20 \pm 4.22\ \mathrm{kJ\,mol^{-1}}$, respectively.

The standard enthalpies of formation, $\Delta_{\mathrm{f,complex\,(s)}}H^\circ$, of the complexes were calculated by Hess's law according to the thermochemistry equations (1) and (2):

$$\begin{aligned}&\Delta_{\mathrm{f,Cr(Met)(NO_3)_3\cdot 2H_2O}}H^\circ\\&\quad = \tfrac{1}{2}\Delta_{\mathrm{f,Cr_2O_3\,(s)}}H^\circ + 5\Delta_{\mathrm{f,CO_2\,(g)}}H^\circ + \tfrac{15}{2}\Delta_{\mathrm{f,H_2O\,(l)}}H^\circ\\&\qquad + \Delta_{\mathrm{f,SO_2\,(g)}}H^\circ - \Delta_{\mathrm{C,Cr(Met)(NO_3)_3\cdot 2H_2O}}H^\circ\end{aligned} \tag{4}$$

$$\begin{aligned}&\Delta_{\mathrm{f,Cr(Met)(NO_3)_3\cdot 2H_2O}}H^\circ\\&\quad = \tfrac{1}{2}\Delta_{\mathrm{f,Cr_2O_3\,(s)}}H^\circ + 10\Delta_{\mathrm{f,CO_2\,(g)}}H^\circ + 13\Delta_{\mathrm{f,H_2O\,(l)}}H^\circ\\&\qquad + 2\Delta_{\mathrm{f,SO_2\,(g)}}H^\circ - \Delta_{\mathrm{C,Cr(Met)_2(NO_3)_3\cdot 2H_2O}}H^\circ\end{aligned} \tag{5}$$

where $\Delta_{\mathrm{f,Cr_2O_3\,(s)}}H^\circ = -1139.70\ \mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{f,CO_2\,(g)}}H^\circ = -393.51 \pm 0.13\ \mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{f,H_2O\,(l)}}H^\circ = -285.83 \pm 0.04\ \mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{f,SO_2\,(g)}}H^\circ = -296.81 \pm 0.02\ \mathrm{kJ\,mol^{-1}}$ [13]. The standard enthalpies of formation, $\Delta_{\mathrm{f,complex\,(s)}}H^\circ$ are -1842.01 ± 2.13 and $-1136.31 \pm 4.45\ \mathrm{kJ\,mol^{-1}}$, respectively.

Acknowledgements

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