Phase Chemistry and Thermochemistry of Coordination of Chromium Chloride to Histidine

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The solubility properties of the ternary systems CrCl$_3$—His—H$_2$O at 298.15 K in the entire concentration range have been investigated by the phase equilibrium method and the corresponding solubility diagrams (phase diagrams) have been constructed. The congruently soluble complexes Cr(His)Cl$_3 \cdot$ H$_2$O, Cr(His)$_2$Cl$_3 \cdot$ H$_2$O, and Cr(His)$_3$Cl$_3 \cdot$ H$_2$O have been prepared. The compositions of these complexes were determined by chemical and elemental analyses. The enthalpies of reaction of chromium chloride with histidine in water have been measured by microcalorimeter. On the basis of experimental and calculated results, three thermodynamic parameters (the activation enthalpy, the activation entropy, and the activation Gibbs energy), the rate constant, three kinetic parameters (the activation energy, the pre-exponential constant, and the reaction order) are obtained.

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

Considering the complexes of chromium with valine, leucine, methionine, and phenylanine, much effort has been expended toward their preparations and studies of their properties, spectra, and magnetism in the mixed solvent of water and alcohol [2—8]. The structure, biological activity, chromatography and spectra of the complexes of chromium and amino acid (x_r = 1:2) and the relationship between the complexes and GTF were studied by *Cooper* [1]. However, the phase chemistry related to chromium(III) with amino acid in water and the formation thermokinetics of these complexes have not been reported in literature.

In the present work, the solubility of the ternary system CrCl$_3$—His—H$_2$O has been investigated at 25 °C by the semimicrophase equilibrium method [9] and the construction of phase diagram of the system has been completed. Based on the results of the experiments, three new solid complexes, the mole ratio of chromium to histidine being 1:1, 1:2, and 1:3, respec-

tively, have been prepared. In addition, the enthalpies of formation of the complexes have been determined by microcalorimeter, and the fundamental parameters for reaction of preparing chromium histidine complexes, including the reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (a), the activation enthalpy, the activation entropy, the activation Gibbs energies, and the enthalpies have been calculated as well. These parameters will provide a scientific basis for technology of the preparation of chromium histidine complexes.

EXPERIMENTAL

CrCl$_3 \cdot$ 6H$_2$O (Beijing Shuanghuan Chemical Plant, A.R.) and L-α-His (Shanghai Kanda Ammonia Factory, B.R.) were recrystallized with the purity > 99.5 %. During the calorimetric experiment, CrCl$_3 \cdot$ 6H$_2$O and L-α-His were aqueous solutions of c = 0.1000 mol dm^{-3}. The molar ratio n(CrCl$_3 \cdot$ 6H$_2$O) to n(L-α-His) was 1:1, 1:2, and 1:3, respectively. The conductivity of the deionized water was 1.4 μS cm^{-1}, the remaining chemicals were anal. grade reagents. The thermostat with a temperature fluctuation of $\pm$ 0.05 °C and the ZD-Z type automatic potential titrator of Shanghai Leici Company manufacture were used. The RD496-III type microcalorimeter was made in the Southwest Institute of Electron Engineering of China [10]. The operation temperature was 298.15 K, 303.15 K,
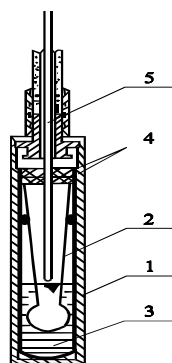

Fig. 1. Sketch of the device used for the study of the formation reaction. *1.* Calorimetric cell; *2.* tube containing chromium chloride solution; *3.* tube containing histidine solution; *4.* silicone rubber cover; *5.* glass rod (on depressing the bottom of tube *2* is broken. The two solutions are mixed in *1* and *2*).

Fig. 2. Isothermal solubility diagram of the ternary system $CrCl_3$—His—H_2O at 25 °C.

313.15 K, 318.15 K, and 323.15 K, respectively. Under experimental temperature, the calorimetric constants were determined by the Joule effect experiment, the results were (63.994 ± 0.042) μV $(mW)^{-1}$, (64.499 ± 0.040) μV $(mW)^{-1}$, (64.638 ± 0.078) μV $(mW)^{-1}$, (64.733 ± 0.77) μV $(mW)^{-1}$, and (64.739 ± 0.059) μV $(mW)^{-1}$. The accuracy and precision of instruments were determined through chemical calibration. At 298.15 K, the enthalpy of solution of KCl (spectral purity) in deionized water was measured and compared with the literature [10]. The experimental value of $\Delta_{sol}H^{\circ\neq} = (17.238 \pm 0.048)$ kJ mol^{-1} is in good agreement with that of $\Delta_{sol}H^{\circ\neq} = (17.241 \pm 0.018)$ kJ mol^{-1} reported in the literature [10]. The calorimetric accuracy was 0.02 % and the precision was 0.3 %, which indicates that the device for measurement used in the experiment is reliable.

Cr^{3+} was determined complexometrically with ammonium ferrous sulfate. Histidine content was analyzed by the formalin method. Cl^- was determined by the Fajans method. Carbon, hydrogen, and nitrogen analyses were performed on a 2400 type elemental analyzer (PE Company, U.S.A.).

Solubility properties of the system were determined by the semimicrophase equilibrium method. The experimental results showed that the equilibrium of the system was reached after 30 d. The compositions of liquid phase and wet-solid phase were analyzed by the same method mentioned above. Calorimetric experiment was carried out after the calibration. The two stainless sampling pools with volume of 15 cm^3, including the sample cell and the reference cell, were packed with the sample (Fig.1). When heat balance was reached, the sample cell and the reference cell were pulled down with shutter line at the same time. So reactants were mixed and heat effect curves were recorded.
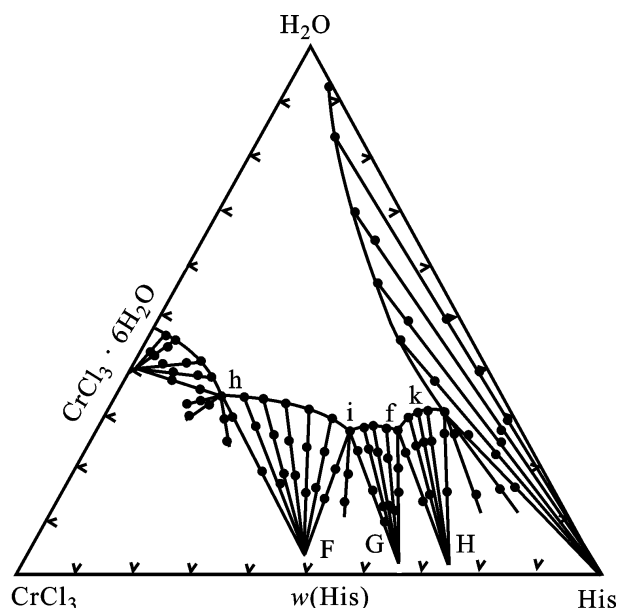
RESULTS AND DISCUSSION

Based on the 36 sets of phase equilibrium data (the compositions of the critical points are listed in Table 1), the phase diagram of the ternary systems was constructed (Fig. 2), which indicated that each liquid phase point, corresponding wet-solid phase point, and matter point were excellently on the same line. The solubility curves of the systems consisted of five branches, corresponding to $CrCl_3 \cdot 6H_2O$, $Cr(His)Cl_3 \cdot H_2O$ (F), $Cr(His)_2Cl_3 \cdot H_2O$ (G), and $Cr(His)_3Cl_3 \cdot H_2O$ (H) and L-α-His crystal, respectively. F, G, and H, being congruently soluble compounds, are synthesized in water by the general methods. The results of composition of these complexes are given in Table 2. IR spectra of the complexes were compared with those of ligands. The characteristic absorption peak of amino group shifted 71 cm^{-1}, 103 cm^{-1}, and 120 cm^{-1}, the characteristic absorption peak of carboxyl had shifting of 127 cm^{-1}, 128 cm^{-1}, and 185 cm^{-1}, while the characteristic absorption peak of imidazolyl ring had only a little shifting of 1—9 cm^{-1}. This indicated that N atom of amino group and O atom of carboxyl coordinated to Cr^{3+} strongly while imidazolyl was coordinated weakly in the complexes. Strong characteristic absorption peak appearing at 3390 cm^{-1} and 825 cm^{-1} was evidence of water molecule in the complexes.

In the calculation of thermodynamics and kinetics of the formation of complexes, the following equations could represent the formation reaction of chromium histidine complexes

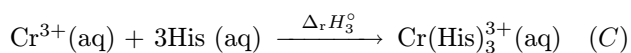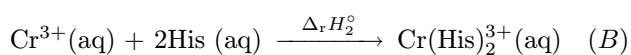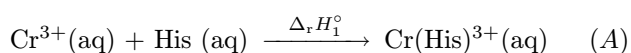**Table 1.** Results of Phase Equilibrium of Ternary System $CrCl_3$—His—H_2O at 25 °C

No.	Composition of liquid phase (w_i/%)		Composition of solid phase (w_i/%)		Composition of synthetic phase (w_i/%)		Equilibrium solid phase
	CrCl₃	His	CrCl₃	His	CrCl₃	His	
1	52.02	0.00	59.50	0.00	–	–	$CrCl_3 \cdot 6H_2O$
2	50.33	2.50	59.41	1.11	52.73	1.87	$CrCl_3 \cdot 6H_2O$
3	49.21	4.98	59.50	1.78	51.43	4.00	$CrCl_3 \cdot 6H_2O$
4	47.30	10.49	59.46	4.20	49.55	8.91	$CrCl_3 \cdot 6H_2O$
5	47.01	14.24	59.44	6.56	49.56	11.34	$CrCl_3 \cdot 6H_2O$
6	47.01	18.00	59.38	8.00	50.23	13.44	$CrCl_3 \cdot 6H_2O$ + F
7	47.00	18.04	53.71	13.10	50.80	15.31	$CrCl_3 \cdot 6H_2O$ + F
8	47.03	17.98	54.32	14.95	49.82	17.01	$CrCl_3 \cdot 6H_2O$ + F
9	47.01	18.01	50.33	23.22	48.61	20.22	$CrCl_3 \cdot 6H_2O$ + F
10	47.05	18.03	47.36	32.11	48.00	22.31	$CrCl_3 \cdot 6H_2O$ + F
11	43.41	22.01	46.00	36.00	48.11	26.89	F
12	40.64	25.21	44.03	36.00	42.08	30.10	F
13	37.10	29.71	42.61	38.21	39.80	34.00	F
14	33.83	34.00	41.93	41.25	37.87	37.46	F
15	30.94	38.98	39.45	43.00	35.02	40.90	F
16	28.88	43.20	39.92	44.22	34.73	44.21	F + G
17	28.90	43.18	36.00	47.01	33.02	47.00	F + G
18	28.86	43.17	30.80	53.30	29.10	46.00	F + G
19	26.33	44.79	29.02	52.99	28.12	47.88	G
20	24.34	46.2	29.22	56.10	26.00	50.00	G
21	22.02	49.00	29.00	57.96	24.69	51.92	G
22	21.89	50.98	28.98	59.00	24.11	54.21	G + H
23	21.92	51.00	27.35	59.82	23.00	54.30	G + H
24	21.87	51.02	23.00	62.70	21.82	54.60	G + H
25	17.90	51.81	21.50	62.41	19.00	55.46	H
26	15.81	52.34	20.25	62.67	17.78	56.50	H
27	13.98	53.97	20.35	64.61	16.00	57.82	H
28	10.75	57.02	18.48	65.00	12.00	59.05	H + His
29	10.80	57.06	13.87	70.55	11.50	60.5	H + His
30	10.77	57.00	9.00	73.79	10.20	61.00	H + His
31	10.81	57.03	6.02	76.34	9.21	62.79	H + His
32	11.67	41.54	6.02	69.96	9.50	52.10	His
33	9.98	29.87	4.65	69.10	8.66	41.11	His
34	7.11	22.05	3.00	68.00	6.91	27.90	His
35	3.70	12.20	1.95	63.21	3.50	18.00	His
36	0.00	4.78	0.00	0.00	–	–	His

F: $Cr(His)Cl_3 \cdot H_2O$; G: $Cr(His)_2Cl_3 \cdot H_2O$; H: $Cr(His)_3Cl_3 \cdot H_2O$; w_i: mass fraction.

Table 2. Analytical Results of Composition of Compounds* (w_i/%)

Complexes	Cr^{3+}	His	Cl^-	C	H	N
$Cr(His)Cl_3 \cdot H_2O$	15.71(15.69)	46.79(46.80)	32.11(32.08)	21.68(21.74)	3.31(3.34)	12.81(12.67)
$Cr(His)_2Cl_3 \cdot H_2O$	10.77(10.69)	63.81(63.76)	21.47(21.85)	29.68(29.61)	4.19(4.14)	17.26(17.27)
$Cr(His)_3Cl_3 \cdot H_2O$	8.13 (8.10)	72.57(72.52)	16.11(16.57)	34.00(33.68)	4.60(4.55)	19.47(19.64)

*The data in brackets are calculated values.

$$Cr^{3+}(aq) + His\ (aq) \xrightarrow{\Delta_r H_1^\circ} Cr(His)^{3+}(aq) \quad (A)$$

$$Cr^{3+}(aq) + 2His\ (aq) \xrightarrow{\Delta_r H_2^\circ} Cr(His)_2^{3+}(aq) \quad (B)$$

$$Cr^{3+}(aq) + 3His\ (aq) \xrightarrow{\Delta_r H_3^\circ} Cr(His)_3^{3+}(aq) \quad (C)$$

The enthalpies of the above reactions are determined and given in Table 3.

According to the heat effect curves, reaction (A) is exothermic reaction at 298.15 K. It is in the temperature range of 303.15—323.15 K when the reaction (A) firstly shows a small endothermic peak, then followed by the exothermic reaction, and the endothermic reaction time induced with temperature going up. Heat effect increased with the temperature rising. Like the reaction (A), the reaction (B) was also exothermic after absorption of a small amount of heat at 303.15 K.

Table 3. Thermokinetic Data of $x_r = 1:1$ Reaction (A) for Chromium Chloride and Histidine

t/s	303.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	308.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	313.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	318.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	323.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}
600							0.1394	8.747	0.2394	12.35
700					0.1627	6.050	0.2113	8.066	0.3159	11.08
800					0.2029	5.863	0.2822	7.387	0.3885	9.820
900			0.1532	3.749	0.2454	5.322	0.3511	6.536	0.4563	8.587
1000	0.1689	2.273	0.2312	3.442	0.2910	5.114	0.4189	5.863	0.5195	7.529
1100	0.2104	2.198	0.3074	3.137	0.3419	4.657	0.4801	5.207	0.5782	6.599
1200	0.2542	1.984	0.3806	2.757	0.4056	4.271	0.5488	4.619	0.6326	5.723
1300	0.3011	1.902	0.4494	2.427	0.4698	3.897	0.5995	4.049	0.6824	5.052
1400	0.3533	1.722	0.5155	2.168	0.5272	3.491	0.6560	3.631	0.7285	4.378
1500	0.4183	1.571	0.5781	1.884	0.5985	2.910	0.7087	3.091	0.7700	3.819
1600	0.4836	1.426	0.6371	1.662	0.6890	2.449				
1700	0.5417	1.269	0.6933	1.482						
1800	0.6185	1.081	0.7449	1.250						
1900	0.7038	0.871								

H_0/J = 0.364, 0.475, 0.638, 0.759, and 0.946.

Table 4. Thermokinetic Data of $x_r = 1:2$ Reaction (B) for Chromium Chloride and Histidine

t/s	303.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	308.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	313.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	318.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}	323.15 K $(H_t/H_0)_i$	$(\mathrm{d}H/\mathrm{d}t)\cdot10^4$ J s^{-1}
600									0.4292	44.18
700									0.4572	41.00
800			0.3169	10.98	0.4024	16.44	0.4592	23.49	0.5133	37.50
900			0.3734	10.31	0.4426	15.31	0.5345	20.57	0.5648	33.79
1000			0.4273	9.506	0.4819	14.37	0.6000	17.70	0.6111	30.01
1100	0.4403	4.835	0.4783	8.653	0.5203	13.42	0.6565	15.21	0.6525	26.60
1200	0.4826	4.475	0.5256	7.816	0.5578	12.37	0.7050	13.12	0.6891	23.42
1300	0.5235	4.178	0.5699	7.149	0.5935	11.19	0.7464	11.30	0.7215	20.53
1400	0.5632	3.880	0.6115	6.466	0.6278	10.30	0.7816	9.650	0.7499	18.23
1500	0.6014	3.552	0.6494	5.753	0.6606	9.412	0.8113	8.387	0.7751	16.20
1600	0.6375	3.185	0.6847	5.396	0.6925	8.771	0.8367	7.355		
1700	0.6717	2.911	0.7180	4.869	0.7232	7.944	0.8584	6.408		
1800	0.7042	2.639								
1900	0.7354	2.444								
2000	0.7649	2.195								

H_0/J = 1.064, 1.504, 1.968, 2.262, and 2.626.

Within the range of 308.15—323.15 K it was exothermic reaction. With the temperature increase, the heat effect increased and the reaction time shortened. In the scope of experimental temperature, reaction (C) was exothermic reaction.

The thermodynamic and kinetic parameters were obtained from the TK curve. The energy of reaction system varied with the reaction processing. Reaction rate constant k and reaction order a were derived from (1)

$$\ln\left\{\frac{1}{H_0}\frac{\mathrm{d}H_t}{\mathrm{d}t}\right\} = \ln\{k\} + a\ln\left(1 - \frac{H_t}{H_0}\right) \qquad (1)$$

where H_0 denotes the total reaction heat (correspond-ing to the volume under the TK curve). H_t is the re-action heat for a period of time (corresponding to part volume under the TK curve). $\mathrm{d}H_t/\mathrm{d}t$ is the exother-mic rate at the time t.

Based on eqns (2—4), the apparent activation en-ergy E, the pre-exponent constant A, the activation Gibbs energy $\Delta G^{\circ\neq}$, and the activation entropy $\Delta S^{\circ\neq}$ were calculated.

$$\ln\{k\} = \ln\{A\} - \left\{\frac{E}{RT}\right\} \qquad (2)$$

$$\Delta G^{\circ\neq} = RT\cdot\ln\left(\frac{RT}{N_A hk}\right) \qquad (3)$$

Table 5. Thermokinetic Data of $x_r = 1:3$ Reaction (C) for Chromium Chloride and Histidine

t/s	298.15K $\mathcal{H}$ (J s^{-1})		303.15 K $\mathcal{H}$ (J s^{-1})		308.15 K $\mathcal{H}$ (J s^{-1})		313.15 K $\mathcal{H}$ (J s^{-1})		318.15 K $\mathcal{H}$ (J s^{-1})		323.15 K $\mathcal{H}$ (J s^{-1})	
100											0.2197	4.47
150											0.3522	9.65
200									0.4059	43.35	0.4791	1.86
250							0.3635	29.94	0.4926	36.92	0.5970	36.96
300			0.1527	17.69	0.4462	16.08	0.5065	24.36	0.5800	31.25	0.7179	27.20
350	0.1617	10.69	0.1897	16.89	0.5837	11.99	0.6078	20.14	0.6318	26.48	0.8172	17.37
400	0.2005	10.18	0.2198	16.51	0.6877	9.877	0.6800	16.81	0.6871	22.42	0.8856	11.47
450	0.2321	9.942	0.2421	15.99	0.7608	7.454	0.7329	14.30	0.7347	19.10	0.9224	7.989
500	0.2554	9.613	0.2671	15.53	0.8116	5.924	0.7727	12.22	0.7758	16.36	0.9479	6.251
550	0.2815	9.321	0.2860	14.88	0.8432	4.959	0.8033	10.33	0.8113	13.98	0.9613	4.072
600	0.3012	8.906	0.3124	14.49	0.8683	4.369	0.8274	8.928	0.8419	11.98		
650	0.3286	8.664	0.3388	14.03	0.8867	3.538	0.8464	7.762	0.8681	10.20		
700	0.3561	8.371	0.3652	13.46	0.9038	2.994	0.8615	6.949				
750	0.3833	8.014	0.4048	12.82	0.9215	2.563						
800	0.4237	7.608										

$H_0/\text{J} = 1.239,\ 1.416,\ 1.517,\ 2.085,\ 2.299,$ and 2.537.
$\mathcal{H} = (H_t/H_0)_i (\mathrm{d}H/\mathrm{d}t) \cdot 10^4$

Table 6. Kinetic, Thermodynamic Parameters of $x_r = 1:1$ Reaction for Chromium Chloride and Histidine

T/K	Eqn (1) $\frac{k \cdot 10^3}{\text{s}^{-1}}$	a	r	Eqn (2) $\frac{E}{\text{kJ mol}^{-1}}$	$\ln(A/\text{s}^{-1})$	r	Eqn (3) $\frac{\Delta G^{\circ\neq}}{\text{kJ mol}^{-1}}$	Eqn (4) $\frac{\Delta H^{\circ\neq}}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^{\circ\neq}}{\text{kJ mol}^{-1}}$	r
303.15	0.728	0.930	0.998	33.33	5.998	0.999	92.50	30.74	−191.4	0.998
308.15	0.909	0.925	0.998				93.50			
313.15	1.101	0.931	0.997				94.56			
318.15	1.322	0.968	0.999				95.63			
323.15	1.680	0.993	0.999				96.53			

r – the correlation coefficient.

Table 7. Kinetic, Thermodynamic Parameters of $x_r = 1:2$ Reaction for Chromium Chloride and Histidine

T/K	Eqn (1) $\frac{k \cdot 10^3}{\text{s}^{-1}}$	a	r	Eqn (2) $\frac{E}{\text{kJ mol}^{-1}}$	$\ln(A/\text{s}^{-1})$	r	Eqn (3) $\frac{\Delta G^{\circ\neq}}{\text{kJ mol}^{-1}}$	Eqn (4) $\frac{\Delta H^{\circ\neq}}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^{\circ\neq}}{\text{kJ mol}^{-1}}$	r
303.15	0.773	0.921	0.999	53.44	14.00	0.993	92.35	50.85	−137.2	0.992
308.15	1.058	0.945	0.999				93.11			
313.15	1.364	0.956	0.999				94.00			
318.15	1.910	0.979	0.999				94.66			
323.15	2.976	1.040	0.998				94.99			

r – the correlation coefficient.

$$\ln\left\{\frac{k}{T}\right\} = -\frac{\Delta H^{\circ\neq}}{RT} + \frac{\Delta S^{\circ\neq}}{R} + \ln\left\{\frac{k_B}{h}\right\} \quad (4)$$

where R is the gas constant, N_A is Avogadro constant, h is Planck constant, and k_B is Boltzmann constant.

The thermokinetic parameters are given in Tables 3—5 according to the TK curves of three exothermic reactions. The kinetic and thermodynamic parameters procured from eqns (1—4) are listed in Tables 6—8.

It is assumed on the basis of experimental results that the three reactions were the first-order reactions. With the temperature increase, the reaction rate constant and the heat effect increased. The reaction rate constant of the reaction of $n(\text{CrCl}_3 \cdot 6\text{H}_2\text{O})$ and $n(\text{L-}\alpha\text{-His})$ (the mole ratio $x_r = 1:2$) was little bigger than that of the reaction with the mole ratios of compounds 1:1 and 1:3. Reaction activation energies were very low in the sequence of $E(x_r = 1:1) < E(x_r = 1:3)$

Table 8. Kinetic, Thermodynamic Parameters of $x_r = 1:3$ Reaction for Chromium Chloride and Histidine

T/K	Eqn (1)			Eqn (2)			Eqn (3)	Eqn (4)			
	$\dfrac{k \cdot 10^3}{s^{-1}}$	a	r	$\dfrac{E}{kJ\ mol^{-1}}$	$\ln(A/s^{-1})$	r	$\dfrac{\Delta G^{\circ\neq}}{kJ\ mol^{-1}}$	$\dfrac{\Delta H^{\circ\neq}}{kJ\ mol^{-1}}$	$\dfrac{\Delta S^{\circ\neq}}{kJ\ mol^{-1}}$	r
298.15	1.015	0.926	0.998	42.07	10.12	0.998	90.11	39.49	−169.4	0.998
303.15	1.458	0.933	0.998				90.75			
308.15	1.882	0.947	0.999				91.64			
313.15	2.335	0.962	0.997				92.60			
318.15	3.077	0.969	0.999				93.39			
323.15	3.893	0.978	0.998				94.27			

r – the correlation coefficient

$< E(x_r = 1:2)$, and activation enthalpy was high in the order of $\Delta H^{\circ\neq}(x_r = 1:1) > \Delta H^{\circ\neq}(x_r = 1:3) > \Delta H^{\circ\neq}(x_r = 1:2)$. Reaction activation enthalpy was less with activation enthalpy of reaction (C) being minor to that in the ratios of 1:1 and 1:2. The experimental results indicated that the title reactions took place easily in the sequence $x_r = 1:1$, $x_r = 1:3$, $x_r = 1:2$.

After the calorimetric experiment, the final solution was collected and concentrated on a 343.15—353.15 K water bath till crystal membrane was formed on the surface, then it was put into a desiccator containing P_4O_{10} to remove trace water. The analytical results given in Table 3 indicated that the complexes had the same composition of $Cr(His)Cl_3 \cdot H_2O$, $Cr(His)_2Cl_3 \cdot H_2O$, and $Cr(His)_3Cl_3 \cdot H_2O$.

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