THERMOCHEMISTRY OF THE COMPLEXES OF SOME MICROELEMENTS AND HISTIDINE

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Abstract

Solid complexes of $M(His)_2Cl_2 \cdot nH_2O$ (M=Mn, Co, Ni, Cu) of $MnCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and L-α-histidine (His) have been prepared in 95% ethanol solution and characterized by elemental analyses, chemical analyses, IR and TG-DTG. The constant-volume combustion energies of the complexes have been determined by a rotating-bomb calorimeter. The standard enthalpies of formation of the complexes have been calculated as well.

Introduction

As noted earlier, trace elements of manganese, cobalt, nickel, and copper are necessary for the life. L-α-Amino acids are structural units of proteins. L-α-histidine is one of eight species of amino acids which have to be absorbed from foods due to being not synthesized by organism. In view of the complexes of L-α-histidine and essential elements as addictives widely used in such fields as foodstuff, medicine and cosmetic, they have a broaden prospect for application. Simply put, a better understanding of the research for the complexes of the microelements and L-α-histidine is thus of considerable practical and fundamental importance.

The coordination behavior of the microelements and amino acids has been expounded in the literature. On the preparation and characterization, along with the determination of the stability constant in water for histidine complexes, there have been reported in literatures [1–9]. In our laboratory, phase chemistry, the determination of reaction heat and thermokinetics of the complexes zinc salts with α-histidine have been explicated [10]. As one of the basic thermochemical data, the constant-volume combustion energies of compounds have not been described anywhere. The gains of these thermodynamic quantities have contributed to the progress in the new use for these complexes and have provided the numerical basis of the related study.

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In our present work, the solid complexes of chloride salts inclusive of manganese, cobalt, nickel and copper with histidine have been prepared in 95% ethanol solution and characterized by chemical analyses, element analyses, IR and TG-DTG. And the constant-volume combustion energies of these complexes have been determined by a RBC – type rotating-bomb calorimeter. These parameters will provide a scientific basis for technological processing of preparing the complexes of microelements and histidine.

Experimental

Preparation and composition of the complexes

$MCl_2 \cdot n H_2O$ including $MnCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and *L*-α-histidine were dissolved with an appropriate amount of 95% ethanol, respectively, then mixed in the mole ratio of 1:2 (M:His). After refluxing on 70–80°C water bath for several hours, the solution was condensed for removing a large amount of ethanol solution, filtered and rinsed with 95% ethanol, finally the aim products of $Mn(His)_2Cl_2 \cdot 4H_2O$, $Cu(His)_2Cl_2 \cdot H_2O$, $Co(His)_2Cl_2 \cdot H_2O$ and $Ni(His)_2Cl_2 \cdot H_2O$ were obtained. $MnCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ (Beijing Shuanghuan Chemical Plant, A. R.) and *L*-α-histidine (Shanghai Kanda Ammonia Factory, B. R.) were recrystallized with the purity ≥99.5%. The analytical results on the compositions of the complexes were summarized in Table 1. The purity of the complexes checked by HPLC was greater than 99.99%.

Table 1 Analytical results on the composition of the complexes (%)[*]

Compound	C	H	N	M^{2+}	Cl^-
$Mn(His)_2Cl_2 \cdot 4H_2O$	28.39 (28.36)	5.21 (5.16)	16.51 (16.54)	10.79 (10.81)	14.02 (13.96)
$Co(His)_2Cl_2 \cdot H_2O$	31.53 (31.46)	4.47 (4.40)	18.48 (18.34)	11.42 (11.35)	13.69 (13.66)
$Ni(His)_2Cl_2 \cdot H_2O$	31.52 (31.48)	4.43 (4.40)	18.33 (18.35)	12.89 (12.82)	15.67 (15.48)
$Cu(His)_2Cl_2 \cdot H_2O$	31.17 (31.14)	4.39 (4.36)	18.12 (18.16)	13.69 (13.73)	15.37 (15.32)

Mn^{2+} was determined oxidation–reduction by ammonium peroxydisulfate,
Co^{2+} and Ni^{2+} were determined complexometrically with EDTA,
Cu^{2+} was determined by iodimetry, Cl^- was determined by Fajans method.
Carbon, hydrogen, and nitrogen analyses were carried out on a 2400-type elemental analyzer of P.E. Company.
The data in brackets were calculated values

Apparatus and experimental procedure

It was a RBC-type rotating-bomb calorimeter by which the constant volume combustion energies of the complexes have been determined [11]. Benzoic acid had an iso-

thermal 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 literature [11].

The IR spectra of the compounds were obtained with a Bruker EQ Uinox-550 model infrared spectrophotometer (KBr pellet). TG and DTG data were determined by a Perkin Elmer thermogravimetric analyzer. All TG-DTG tests were performed under a dynamic atmosphere of dry nitrogen at a flow rate of 60 mL min^{-1}, the heating rate used 10°C min^{-1} and sample mass approximated to 1 mg.

Results and discussion

The IR absorption of main groups for the complexes and ligand were designated [13, 14] and depicted in Table 2. Compared with those in the ligand of His, the characteristic absorption peaks of amino group ($v^{as}_{NH_3^+}, v^{s}_{NH_3^+}$) and carboxyl group ($v^{as}_{COO^-}$, $v^{s}_{COO^-}$) in the IR spectra of the complexes had great shifts. $\Delta v^{as-s}_{-NH_3^+}$ and $\Delta v^{as-s}_{-COO^-}$ of the complexes shifted to lower frequencies by 21–78 and 53–136 cm^{-1}, while $\Delta \delta^{as-s}_{-NH_3^+}$ shifted to higher frequencies by 45–94 cm^{-1}. It indicated that nitrogen and oxygen atoms in the complexes coordinated to M^{2+}. In addition, characteristic absorption peak of imidazolyl group ($v^{as}_{CCN}, v^{s}_{CCN}$) in the complexes shifted intensely, Δv^{as-s}_{CNN} shifted to lower frequencies by 371–445 cm^{-1}. This showed that nitrogen atom in the imidazolyl group coordinated to M^{2+} as well. The peaks close to that of 3410 and 815 cm^{-1} in the IR spectra of the complexes were assigned to hydroxyl absorption of water, which was evidence for the presence of water molecule in the complexes.
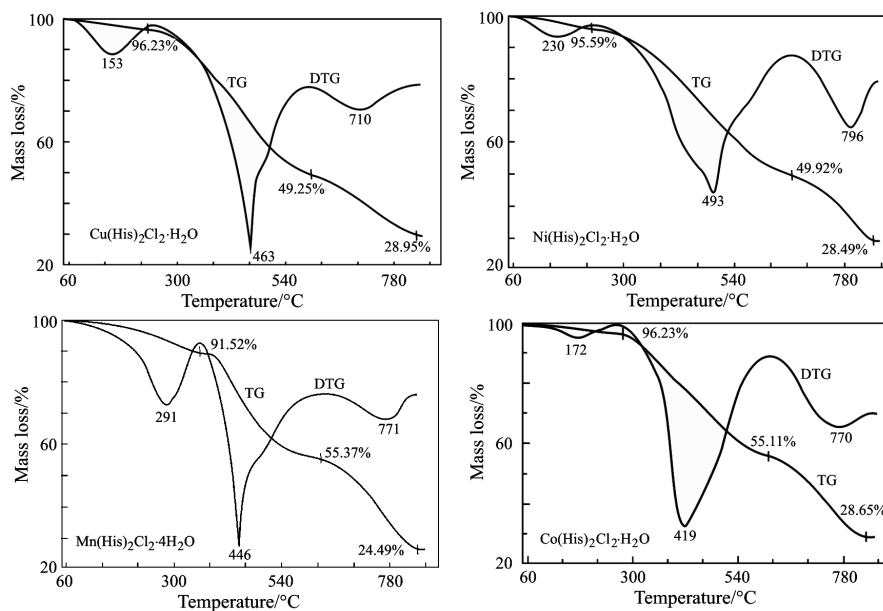

Fig. 1 TG curves of the complexes at an atmosphere of oxygen

Table 2 Data of IR absorption for main groups of ligand and complexes/cm^{-1}

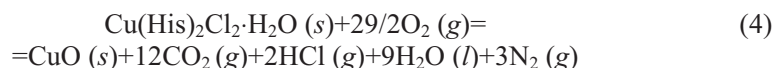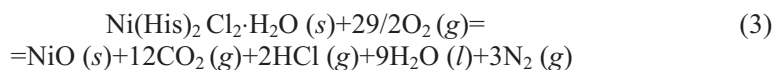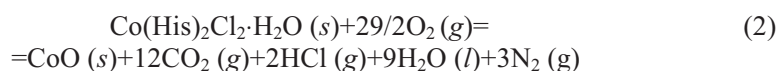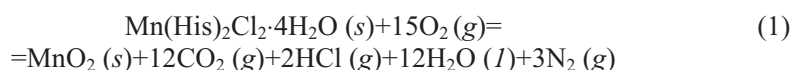| Compound	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	ν_{OH}	ν^{as}_{CCN}	ν^{s}_{CCN}
L-α-His	3025	2860	1590	1456	1635	1415	–	1315	744
Mn(His)$_2$Cl$_2$·4H$_2$O	3116	3011	1629	1409	1499	1332	3420	1082	956
Co(His)$_2$Cl$_2$·H$_2$O	3119	3032	1635	1407	1500	1336	3415 827	1146	966
Ni(His)$_2$Cl$_2$·H$_2$O	3251	3154	1593	1414	1497	1334	3408 821	1170	970
Cu(His)$_2$Cl$_2$·H$_2$O	3275	3134	1613	1395	1428	1344	3423 826	1144	971

Thermostability of the complexes

Thermostability of the solid complexes was investigated by TG-DTG and the TG curves of the complexes were depicted in Fig. 1. The curves of TG-DTG concerning the compounds reflected that the experimental results for the residual amount of loss of mass were in good agreement with the calculated results, and the intermediate and final products of the thermal decomposition of the complexes were identified by IR spectra as well. It was thus assumed that the thermal decomposition processes of the complexes were summarized in Table 3.

Obviously, the complexes were completely decomposed into chlorides after processing water loss and skeleton splitting of histidine.

The constant volume combustion energies and standard enthalpies of formation

The constant volume combustion energies of the complexes determined by a RBC-type rotating-bomb calorimeter were summarized in Table 4.

The standard combustion enthalpies of the complexes, $\Delta_{c,coor}H_m^\theta$, referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 101.325 kPa.

$$Mn(His)_2Cl_2 \cdot 4H_2O \ (s)+15O_2 \ (g)= \tag{1}$$
$$=MnO_2 \ (s)+12CO_2 \ (g)+2HCl \ (g)+12H_2O \ (l)+3N_2 \ (g)$$

$$Co(His)_2Cl_2 \cdot H_2O \ (s)+29/2O_2 \ (g)= \tag{2}$$
$$=CoO \ (s)+12CO_2 \ (g)+2HCl \ (g)+9H_2O \ (l)+3N_2 \ (g)$$

$$Ni(His)_2 \ Cl_2 \cdot H_2O \ (s)+29/2O_2 \ (g)= \tag{3}$$
$$=NiO \ (s)+12CO_2 \ (g)+2HCl \ (g)+9H_2O \ (l)+3N_2 \ (g)$$

$$Cu(His)_2Cl_2 \cdot H_2O \ (s)+29/2O_2 \ (g)= \tag{4}$$
$$=CuO \ (s)+12CO_2 \ (g)+2HCl \ (g)+9H_2O \ (l)+3N_2 \ (g)$$

The standard combustion enthalpies of the complexes were calculated from the combustion energy by the Eqs (1)–(4).

$$\Delta_{c,coor}H_m^\theta=\Delta_{c,coor}E+\Delta nRT \tag{5}$$

herein n_{gas} was the total amount (in moles) of gas present as products or as reactants, $R=8.314$ J mol^{-1} K^{-1}, $T=298.15$ K. The results of the calculations were also shown in Table 5.

The standard formation enthalpies of the complexes, $\Delta_{f,coor}H_m^\theta$, were calculated by Hess's law according to the thermochemical Eqs (1)–(4).

$$\Delta_{f,Mn(His)_2 Cl_2 \cdot 4H_2O(s)}H_m^\theta=[\Delta_{f,MnO_2 \ (s)}H_m^\theta+12\Delta_{f,CO_2 \ (g)}H_m^\theta+$$
$$+2\Delta_{f,HCl(g)}H_m^\theta+12\Delta_{f,H_2O(l)}H_m^\theta]-\Delta_{c,Mn(His)_2 Cl_2 \cdot 4H_2O(s)}H_m^\theta \tag{6}$$

Table 3 Thermoanalytical results of the complexes

Complex	Decomposition product	Decomposition temperature/°C	Residue/%
	$Mn(His)_2Cl_2 \cdot 1.5H_2O$	51–291–360[a]	91.52(91.54)[b]
$Mn(His)_2Cl_2 \cdot 4H_2O$	$Mn(His)_2Cl_2+MnCl_2$	360–446–650	55.37(55.29)
	$MnCl_2$	650–771–840	24.49(22.76)
	$Co(His)_2Cl_2$	51–172–281	95.47(96.07)
$Co(His)_2Cl_2 \cdot H_2O$	$4Co(His)_2Cl_2+7CoCl_2$	281–419–610	55.11(55.13)
	$CoCl_2$	610–770–840	28.65(28.34)
	$Ni(His)_2Cl_2$	51–230–341[a]	95.59(96.07)
$Ni(His)_2Cl_2 \cdot H_2O$	$4Ni(His)_2Cl_2+2NiCl_2$	341–493–665	49.92(50.89)
	$NiCl_2$	665–796–845	28.49(29.30)
	$Cu(His)_2Cl_2$	51–153–237	96.23(96.11)
$Cu(His)_2Cl_2 \cdot H_2O$	$4Cu(His)_2Cl_2+9CuCl_2$	237–463–598	49.25(49.68)
	$CuCl_2$	598–710–830	28.95(29.05)

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

Table 4 The experimental results for combustion energies of the complexes

Complex	No.	Mass of sample a/g	Calibrated heat of combustion wire q_c/J	Calibrated heat of acid containing nitrogen q_N/J	Calibrated ΔT/K	Combustion energy of sample $-\Delta_{c,coor}E$/J g^{-1}
Mn(His)$_2$Cl$_2\cdot$4H$_2$O	1	0.86480	12.60	134.24	0.7826	16119.9
	2	0.84226	12.60	130.74	0.7629	16134.4
	3	0.85731	12.60	133.08	0.7755	16113.0
	4	0.85435	9.90	132.62	0.7743	16147.2
	5	0.87587	12.60	135.96	0.7918	16103.3
	6	0.83213	12.60	129.17	0.7531	16120.7
	mean					16123.1±6
Co(His)$_2$Cl$_2\cdot$H$_2$O	1	0.83680	12.60	148.94	0.7668	16301.8
	2	0.82357	12.60	146.59	0.7536	16278.0
	3	0.84585	12.60	150.55	0.7745	16289.4
	4	0.83712	12.60	149.00	0.7682	16325.6
	5	0.82169	10.80	146.25	0.7533	16311.3
	6	0.84587	9.90	150.55	0.7742	16285.8
	mean					16289.7±7
Ni(His)$_2$Cl$_2\cdot$H$_2$O	1	1.6110	12.60	192.02	0.7454	11379.8
	2	1.00523	12.60	166.25	0.6462	11393.6
	3	1.10631	12.60	182.96	0.7116	11401.6
	4	1.11389	9.90	184.22	0.7136	11357.6
	5	1.12473	12.60	186.01	0.7224	11685.0
	6	1.13508	12.60	187.72	0.7284	11374.8
	mean					11382.1±6
Cu(His)$_2$Cl$_2\cdot$H$_2$O	1	1.00360	12.60	222.40	0.8242	14548.8
	2	0.99586	12.60	220.68	0.8185	14560.5
	3	0.99320	10.80	220.10	0.8129	14500.4
	4	0.98498	12.60	218.27	0.8078	14528.3
	5	0.99035	12.60	219.46	0.8126	14535.5
	6	0.99437	9.90	220.43	0.8163	14540.2
	mean					14535.6±8

$$\Delta_{f,Co(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta = [\Delta_{f,CoO(s)}H_m^\theta + 12\Delta_{f,Co_2\,(g)}H_m^\theta +$$
$$+2\Delta_{fHCl(g)}H_m^\theta + 9\Delta_{fH_2O(1)}H_m^\theta] - \Delta_{c,Co(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta \tag{7}$$

$$\Delta_{f,Ni(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta = [\Delta_{f,NiO(s)}H_m^\theta + 12\Delta_{f,CO_2\,(g)}H_m^\theta +$$
$$+2\Delta_{fHCl(g)}H_m^\theta + 9\Delta_{fH_2O(1)}H_m^\theta] - \Delta_{c,Ni(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta \tag{8}$$

$$\Delta_{f,Cu(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta = [\Delta_{f,CuO(s)}H_m^\theta + 12\Delta_{f,CO_2\,(g)}H_m^\theta +$$
$$+2\Delta_{fHCl(g)}H_m^\theta + 9\Delta_{fH_2O(1)}H_m^\theta] - \Delta_{c,Cu(His)_2\,Cl_2\cdot H_2O(s)}H_m^\theta \tag{9}$$

where $\Delta_{f,MnO_2\,(s)}H_m^\theta = -530.03$ kJ mol^{-1}, $\Delta_{f,CoO(s)}H_m^\theta = -237.94$ kJ mol^{-1}, $\Delta_{f,NiO(s)}H_m^\theta = -239.70$ kJ mol^{-1}, $\Delta_{f,CuO(s)}H_m^\theta = -157.30$ kJ mol^{-1}, $\Delta_{f,CO_2\,(g)}H_m^\theta = (-393.51\pm 0.13)$ kJ mol^{-1}, $\Delta_{fHCl(g)}H_m^\theta = (-92.31\pm0.03)$ kJ mol^{-1}, $\Delta_{f,SO_2\,(g)}H_m^\theta = (-296.81\pm 0.02)$ kJ mol^{-1}, $\Delta_{fH_2O(1)}H_m^\theta = (-285.83\pm0.042)$ kJ mol^{-1} [15]. Combustion energies, standard enthalpies of combustion and standard enthalpies of formation of the complexes were presented in Table 5. Obviously, the standard formation enthalpies of the complexes varied with the structures of amino acids.

Table 5 Combustion energies, standard enthalpies of combustion and standard enthalpies of formation of the complexes (in kJ mol^{-1})

Complex	$-\Delta_{c,coor}E$	$-\Delta_{c,coor}H_m^\theta$	$-\Delta_{f,coor}H_m^\theta$
Mn(His)$_2$Cl$_2$·4H$_2$O	8194.05±3.24	8189.09±3.24	667.6±3
Co(His)$_2$Cl$_2$·H$_2$O	7467.53±3.32	7461.33±3.32	255.8±3
Ni(His)$_2$Cl$_2$·H$_2$O	6212.14±2.87	6205.94±2.87	1512.9±3
Cu(His)$_2$Cl$_2$·H$_2$O	6726.82±3.88	6720.62±3.88	915.9±4

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