Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 323-330

THERMAL BEHAVIOUR OF THE COMPLEXES OF ZINC AMINO ACIDS

J. Liu[1], *Y. Hou*[1], *S. Gao*[1*], *M. Ji*[1], *R. Hu*[2] *and Q. Shi*[1]

[1]Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069
[2]Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, P. R. China

Abstract

The eight solid complexes of zinc with *L*-α-methionine or *L*-α-histidine were prepared. The thermal decomposition processes of these complexes were determined by means of TG-DTG. The results show that their decomposition processes can be divided into three steps except for the complex $Zn(Met)_2$ the decomposition of which is completed in one step. All the final products are ZnO.

Keywords: *L*-α-histidine, *L*-α-methionine, thermal decomposition, zinc complex

Introduction

Zinc is one of essential trace elements for human body; α-amino acids are the basic structural units of protein. The complexes of zinc with α-amino acids as additives have wide applied prospects in medicines, foodstuff and cosmetics [1, 2]. There are many reports on preparation and structure of zinc amino acids in literature [3–9]. However, studies on their thermal stabilities have not yet been reported in literature.

In this paper 8 solid complexes of zinc with *L*-α-methionine (Met) or *L*-α-histidine (His) were prepared referred to literature. The processes of thermal decomposition of the complexes have been investigated by using TG-DTG techniques.

Experimental

Preparation and composition of the complexes

The eight solid complexes were prepared according to [1, 2, 9] and put into desiccator containing P_4O_{10} until the weight of the complexes became constant. Chemical analysis proved that the composition of the complexes are $Zn(Met)Cl_2$ (I), $Zn(Met)_2Cl_2{\cdot}2H_2O$ (II), $Zn(Met)SO_4{\cdot}H_2O$ (III), $Zn(Met)_2$ (IV), $Zn(His)Cl_2{\cdot}0.5H_2O$ (V), $Zn(His)Ac_2{\cdot}0.5H_2O$ (VI), $Zn(His)SO_4{\cdot}H_2O$ (VII) and $Zn(His)_2{\cdot}1.5H_2O$ (VIII), respectively. The analytical results of composition of the complexes are given in Table 1.

* Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Table 1 Analytical results of chemical composition for the complexes (%)

Complex	Zn^{2+}	Am	C	H	N
I	22.91(22.90)	51.94(52.31)	21.11(21.04)	3.92(3.88)	4.96(4.91)
II	14.01(13.90)	63.27(63.39)	25.58(22.52)	4.47(4.71)	6.01(5.95)
III	20.23(19.90)	45.27(45.40)	18.35(18.27)	3.41(3.37)	4.29(4.26)
IV	18.10(18.07)	81.48(81.93)	32.75(33.17)	5.87(5.57)	7.36(7.74)
V	21.34(21.76)	51.73(51.64)	24.03(23.99)	3.36(3.35)	13.55(13.99)
VI	18.95(18.81)	44.98(44.63)	34.90(34.55)	4.49(4.35)	12.26(12.09)
VII	19.38(19.54)	46.12(46.37)	21.37(21.54)	3.42(3.31)	12.63(12.56)
VIII	16.34(16.32)	77.44(77.19)	35.62(35.97)	5.05(4.87)	20.97(20.97)

*The data in brackets are calculated values. Zn^{2+} was determined complexometrically with EDTA. Am (Met or His) was analysed by formalin method. Carbon, hydrogen and nitrogen analyses were made on a 1106 model elemental analyser (Italy)

Apparatus and experimental conditions

TG and DTG data were simultaneously obtained using a Perkin Elmer TGA-7 thermogravimetric analyser. All TG-DTG tests were carried out under a dynamic atmosphere of dry oxygen at a flow rate of 60 cm^3 min^{-1}. The heating rate was of 10 K min^{-1}. The sample masses were about 1 mg.

The IR spectra (KBr pellet) of the intermediates and final products were obtained by the use of IR-440 model infrared spectrophotometer (Japan).

Results and discussion

Figures 1 and 2 are TG-DTG curves of two series complexes. The data of decomposition products, decomposition temperature and residue amount read from the figures are given in Table 2. It can be seen from the figures that the thermal decomposition for complex, $Zn(Met)_2$, was completed in a single step, but for the others completed in three steps: dehydration, skeleton broken, and then decomposition via intermediates to give the zinc oxide as final products.

The IR analytical results of ligands, zinc salts, complexes and their decomposition products are given in Table 3, from which the following points can been seen.

1. In the first stage of decomposition process, the main vibrational band of IR spectra of the products are consistent with those of the complexes themselves except for the disappearing of the vibrational peak of H_2O at about 3450 cm^{-1}. It indicates that this stage is a dewatering process for all the complexes except for complexes I and IV.

2. In the second stage, the IR spectra show the main vibrational peaks of the complexes as well as those of zinc salts. It indicates that all the intermediate products are mixtures of complexes with zinc salts except for the complexes III and VII that form

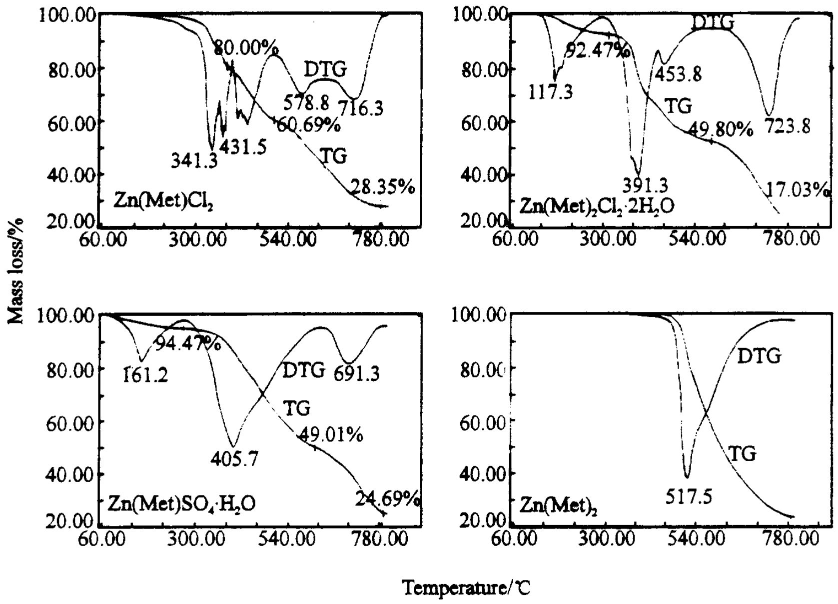

Fig. 1 TG-DTG curves of complexes of zinc with L-α-methionine

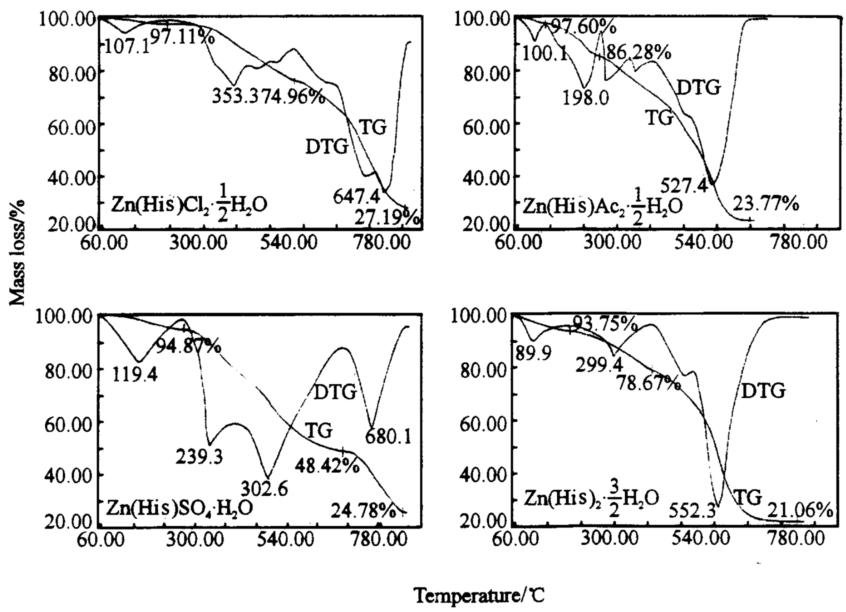

Fig. 2 TG-DTG curves of complexes of zinc with L-α-histidine

Table 2 The data of decomposition processes of the complexes *

Complex	Product	Decomp. temp./°C	Residue/ %	Product	Decomp. temp./°C	Residue/ %	Product	Decomp. temp./°C	Residue/ %
I	$3Zn(Met)Cl_2\cdot 2ZnCl_2$	51–341–382	80.00 (79.09)	$Zn(Met)Cl_2\cdot 3ZnCl_2$	382–432–504	60.69 (60.80)	ZnO	504–716–783	28.35 (28.51)
II	$Zn(Met)_2Cl_2$	51–173–310	92.47 (92.35)	$2Zn(Met)Cl_2\cdot ZnCl_2$	310–391–580	49.80 (50.08)	ZnO	580–724–791	17.03 (17.29)
III	$Zn(Met)SO_4$	51–161–272	94.47 (94.52)	$ZnSO_4$	272–409–610	49.01 (49.12)	ZnO	610–691–791	24.69 (24.76)
IV	–	–	–	–	–		ZnO	51–518–788	23.01 (22.50)
V	$Zn(His)Cl_2$	50–107–196	97.11 (97.00)	$3ZnCl_2\cdot 4Zn(His)Cl_2$	196–335–462	74.96 (74.87)	ZnO	462–647–696	27.19 (27.09)
VI	$Zn(His)Ac_2$	50–100–127	97.60 (97.41)	$Zn(His)Ac_2\cdot ZnAc_2$	127–198–256	86.28 (86.25)	ZnO	256–527–620	23.77 (23.41)
VII	$Zn(His)SO_4$	50–120–242	94.87 (94.62)	$ZnSO_4$	242–303–600	48.42 (48.25)	ZnO	600–680–746	24.78 (24.32)
VIII	$Zn(His)_2$	50– 90–190	93.75 (93.26)	$ZnO\cdot 4Zn(His)_2$	190–299–387	78.67 (78.67)	ZnO	387–552–739	21.06 (20.31)

* The data in brackets are calculated values

Table 3 IR analytical results of ligands, zinc salts, complexes and decomposition products (cm^{-1})

Sample	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	δ_{S-CH_3}	ν^{as}_{CCN}	ν^{s}_{CCN}	ν_{OH}	$\nu^{*}_{X^{n-}}$	ν_{ZnO}
L-α-Met	3124	2100	1620	1510	1582	1410	2910 1340 970	–	–	–	–	–
L-α-His	3025	2860	1590	1456	1635	1415	–	1143	980	–	–	–
$ZnCl_2$	–	–	–	–	–	–	–	–	–	–	1200 1026 780	–
$ZnSO_4$	–	–	–	–	–	–	–	–	–	–	1152 1010 620	–
$ZnAc_2$	–	–	–	–	–	–	–	–	–	–	1545 1450 690	–
ZnO	–	–	–	–	–	–	–	–	–	–	–	490 410
Complex I	3260 3350	2100	1650	1540	1640	1425	2910 1340 970	–	–	–	1200 1025 785	–
$3Zn(Met)_2Cl_2\cdot$ $2ZnCl_2$	3258 3350	2100	1648	1538	1639	1425	2910 1340 970	–	–	–	1205 1023 780	–
$Zn(Met)Cl_2\cdot$ $3ZnCl_2$	3258 3350	2100	1648	1539	1639	1425	2910 1340 970	–	–	–	1205 1023 780	

Table 3 Continued

Sample	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	δ_{S-CH_3}	ν^{as}_{CCN}	ν^{s}_{CCN}	ν_{OH}	$\nu^{*}_{X^{n-}}$	ν_{ZnO}
Complex II	3150	2100	1620	1510	1540	1412	2910 1340	–	–	3450	1205 1020 800	–
$Zn(Met)_2Cl_2$	3150	2100	1620	1510	1540	1412	2910 1340	–	–	–	1205 1020 800	–
$2Zn(Met)_2Cl_2\cdot$ $ZnCl_2$	3148	2100	1620	1510	1540	1412	2910 1340	–	–	–	1205 1020 796	
Complex III	3150	2100	1640	1540	1620	1415	2910 1340	–	–	3445	1150 1010 620	–
$Zn(Met)SO_4$	3150	2100	1640	1540	1620	1415	2910 1340	–	–	–	1150 1010 620	–
Complex IV	3250 3310	–	–	–	1640	1428	2910 1340	–	–	–	–	–
Complex V	3150	3000	1590	1456	1600	1400	–	1110	970	3420	1210 1036 857	–
$3ZnCl_2\cdot$ $4Zn(His)Cl_2$	3150	3000	1591	1456	1600	1400	–	1110	970	–	1200 1030 795	–

Table 3 Continued

Sample	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	δ_{S-CH_3}	ν^{as}_{CCN}	ν^{s}_{CCN}	ν_{OH}	$\nu^{*}_{X^{n-}}$	ν_{ZnO}
Complex VI	3150	3006	1560	–	1590	1392	–	1110	968	3410	1540 1410 710	–
$Zn(His)Ac_2$	3150	3006	1560	–	1590	1390	–	1110	970	–	1540 1410 710	–
$Zn(His)Ac_2\cdot ZnAc_2$	3150	3000	1560	–	1590	1390	–	1110	970	–	1545 1450 700	–
Complex VII	3150	3004	1562	–	1610	1410	–	1110	968	3450	1145 1000 527	–
$Zn(His)SO_4$	3150	3004	1562	–	1610	1410	–	1110	970	–	1145 1002 530	–
Complex VIII	3310	–	1550	–	1640	1410	–	1110	970	3450	–	–
$Zn(His)_2$	3310	–	1550	–	1640	1410	–	1110	970	–	–	–
$ZnO\cdot 4Zn(His)_2$	3310	–	1550	–	1638	1410	–	1110	970	–	–	490 410

$ZnSO_4$ directly (the IR spectra is consistent with the band spectra of $ZnSO_4$ in Sadtler Standard).

3. The IR spectra of the final products are consistent with those of ZnO in Sadtler Standard. It indicates that the final products are all ZnO.

In order to prove the steps of decomposition existing, the chemical composition of the intermediates and final products were analysed. The analytical results for the intermediates and the final products also show the thermal decomposition mechanisms shown in Table 2 exist.

* * *

We thank the National Science Foundation of China and Education Committee of Shaanxi Province for financial support.

References

1 M. M. Abdel-Monem, St. Paul and Minn, U. S. Pat., US 4 039 681, 1997-08-02.
2 S. Taguchi, M. Inokuchi, N. Nakajima, M. Inomata and Y. Naitoh, WO Patent, Wo 10 178, 1992-06-25.
3 T. Kentaro, J. Pharm. Bull., 79 (1959) 737 (Japanese).
4 H. A. Harvey, U. S. Pat., US 4 830 716, 1989-05-06.
5 V. Sushama, Kamaluddin and N. Matrh, Bull. Chem. Soc., 66 (1993) 2922 (Japanese).
6 C. A. Mcan Liff, J. V. Quaglinao and M. Vliarinol, Inorg. Chem., 5 (1966) 1996.
7 S. A. Best, P. Brant and R. D. Fetham, Inorg. Chem., 16 (1977) 1976.
8 H. A. Harvey, U.S. Pat., US 4 599 152, 1986-06-08.
9 G. Shengli, L. Jianrui, J. Mian, Y. Xuwu, Z. Fengxing and L. Zhongjin, Chinese Sci. Bull., 18 (1998) 1527 (English).