Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 839–846

THERMAL ANALYSIS OF MANGANESE(II) COMPLEXES WITH GLYCINE

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(Received June 15, 2000; in revised form October 13, 2000)

Abstract

The thermal decomposition behaviour of the manganese(II) complexes with glycine: $Mn(gly)Cl_2(H_2O)_2$, $Mn(gly)_2Cl_2$, $Mn(gly)Br_2(H_2O)_2$, $Mn(gly)_2Br_2(H_2O)_2$ was investigated by means of TG-DTG-DTA, Hi-Res-TA and DSC techniques. The evolved gas analysis was carried out by means of the coupled TG-FTIR system. Heating of the complexes results first in the release of water molecules. Next, the multi-stage decomposition process with degradation of glycine ligand occurs. Water, carbon dioxide and ammonia were detected in the gaseous products of the complexes decomposition. The temperature of NH_3 evolution from the complexes is higher than from free glycine. The final residue in the air atmosphere is Mn_2O_3 which transforms into Mn_3O_4 at 930°C. In a nitrogen atmosphere, the complexes decompose into MnO.

Keywords: DSC, manganese(II) complexes with glycine, TG-DTG, TG-FTIR, thermal analysis

Introduction

Manganese is an essential trace element which plays an important role in biological systems. Activity of the enzymes: enolase, xylose isomerase or arginase is stabilized by the presence of Mn(II) ions [1, 2]. In green plants, the oxygen evolving complex of photosystem II (OEC) contains a manganese cluster [3]. Thus the complexes of manganese(II) with O, N donor ligands have attracted increasing interest in recent years as manganoenzyme mimetic complexes [4, 5]. In our previous investigations the crystallographic and spectroscopic examinations of the complexes: $[Mn(pro)Cl_2](H_2O)$ [6], $[Mn(hyp)(H_2O)_4](SO_4)$ [7], $[Mn_4(ala)_4Cl_7(H_2O)_5]Cl\cdot 3H_2O$ [8], $[Mn(gly)Cl_2(H_2O)_2]$, $[Mn(gly)_2Cl_2]$ [9] have been made. All complexes have polymeric structures. The zwitterionic amino acids molecules bind Mn(II) ions through the carboxylate oxygen atom of COO^- groups. The thermal decomposition of the complexes $[Mn(pro)Cl_2](H_2O)$, $[Mn(hyp)(H_2O)_4](SO_4)$, $[Mn_4(ala)_4Cl_7(H_2O)_5]Cl\cdot 3H_2O$ was also studied. The less stable complex is $[Mn(pro)Cl_2](H_2O)$ [6] due to the presence of the only outer water molecule. The remaining complexes decompose above 70°C into corresponding oxides.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

This paper deals with thermal analysis of the manganese(II) complexes with glycine of the formulae: $[Mn(gly)Cl_2(H_2O)_2]$, $[Mn(gly)_2Cl_2]$, $Mn(gly)Br_2(H_2O)_2$, $Mn(gly)_2Br_2(H_2O)_2$. The thermal decomposition properties of complexes were investigated by means of TG-DTG-DTA, Hi-Res-TA, DSC and TG-FTIR.

Experimental

The crystals of the complexes $[Mn(gly)_2Cl_2]$, $[Mn(gly)Cl_2(H_2O)_2]$, have been obtained by means of the method described before [9]. The complexes $Mn(gly)Br_2(H_2O)_2$, $Mn(gly)_2Br_2(H_2O)_2$ were obtained by heating the mixture containing glycine (0.006 mole) and $MnBr_2{\cdot}4H_2O$ in the molar ratios 1:1 and 1:2 on the water bath at 50°C. After several hours, water soluble pink crystals were formed. The crystals were washed with ethyl alcohol and dried at room temperature.

The percentage of carbon, hydrogen and nitrogen were determined with Perkin Elmer CHN 2400 elemental analyser. The manganese content were estimated using standard methods. Elemental analysis data are summarized in Table 1.

Table 1 Elemental analysis data of complexes

Complex	Content/mass%			
	Mn	C	H	N
	calc. (found)	calc. (found)	calc. (found)	calc. (found)
$[Mn(gly)Cl_2(H_2O)_2]$	29.94 (29.93)	10.13 (10.20)	3.79 (3.69)	5.91 (5.86)
$[Mn(gly)_2Cl_2]$	25.72 (25.51)	17.39 (17.45)	3.62 (3.52)	10.15 (10.10)
$Mn(gly)Br_2(H_2O)_2$	49.06 (49.24)	7.36 (7.44)	2.76 (2.64)	4.29 (4.23)
$Mn(gly)_2Br_2(H_2O)_2$	39.88 (39.81)	11.97 (12.30)	3.49 (3.53)	6.98 (7.05)

The IR spectra of the compounds were recorded in the range 4000–400 cm^{-1} on a SPECORD M80 spectrophotometer at room temperature using the KBr pellet technique.

Magnetic susceptibility measurements were conducted at 19±1°C using a magnetic susceptibility balance MSB-MKI, Sherwood Scientific Ltd, Cambridge. The data were corrected for diamagnetic susceptibilities.

Thermal measurements were performed with a Q-1500D derivatograph in a static air atmosphere, at the heating rate of 10°C min^{-1}. The sample mass was 50 mg. For the complexes $[Mn(gly)Cl_2(H_2O)_2]$, $[Mn(gly)_2Cl_2]$, high resolution thermogravimetric technique was used. The samples of the mass about 10 mg were heated in the static air atmosphere and in flowing nitrogen (v=4–6 $dm^3\ h^{-1}$) using Hi-Res-TA apparatus (TA Instruments).

The gas-phase products of decomposition were identified using a Netzsch TG 209 apparatus coupled with a Bruker FTIR IFS66 spectrophotometer. The samples of about 10 mg were heated in flowing argon atmosphere to about 500°C.

DSC curves were obtained up to 250°C with a Netzsch DSC 204 apparatus, using an aluminium open crucible with ca 5–15 mg of sample, in argon atmosphere, at a heating rate of 1 or 2°C min^{-1}.

Results and discussion

All the studied complexes of the formulae $[Mn(gly)Cl_2(H_2O)_2]$ (1), $[Mn(gly)_2Cl_2]$ (2), $Mn(gly)Br_2(H_2O)_2$ (3), $Mn(gly)_2Br_2(H_2O)_2$ (4) are crystalline substances. The polymeric complexes (1) and (2) are built up of manganese(II) ions bridged by one (1) or two (2) carboxylate groups of glycine. In complex 1 the co-ordination sphere of Mn(II) ions is completed by two water molecules and two chloride ions. In complex 2

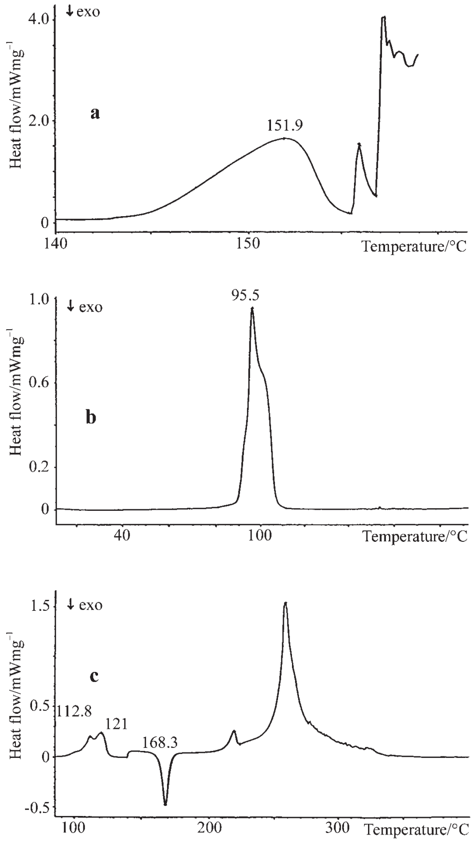

Fig. 1 DSC curves of complexes a – $[Mn(gly)Cl_2(H_2O)_2]$, b – $Mn(gly)Br_2(H_2O)_2$, c – $Mn(gly)_2Br_2(H_2O)_2$

Table 2 Thermogravimetric data of the compounds

	Air atmosphere				Inert gas atmosphere			
Complex	T_{range}/°C	Mass loss /%		Residue	T_{range}/°C	Mass loss /%		Residue
		found	calc.			found	calc.	
$[Mn(gly)_2Cl_2]$	150–220	5.04			150–280	33.20		
	220–285	34.75			280–800	75.84		MnO
	285–415	54.73						
	415–700	71.43	71.38	Mn_2O_3				
	850–930	72.13	72.34	Mn_3O_4				
$[Mn(gly)Cl_2(H_2O)_2]$	85–180	15.00	15.19	$Mn(gly)Cl_2$	85–195	15.21	15.19	$Mn(gly)Cl_2$
	185–315	37.99			200–360	39.01		
	315–420	55.46			360–615	63.62		
	420–700	66.86	66.67		615–800	70.12	70.04	MnO
	840–930	67.84	67.79	Mn_3O_4				
$Mn(gly)Br_2(H_2O)_2$	115–225	10.50	11.04	$Mn(gly)Br_2$	100–200	12.15	11.03	$Mn(gly)Br_2$
	235–335	27.50			260–350	29.65		
	335–550	76.50	75.75	Mn_2O_3				
$Mn(gly)_2Br_2(H_2O)_2$	95–135	8.20	8.96	$Mn(gly)_2Br_2$	110–145	7.43	8.96	$Mn(gly)_2Br_2$
	210–335	32.20			230–365	32.19		
	335–620	81.00	80.30	Mn_2O_3	365–390	45.41		

two chloride ions complete co-ordination polyhedron of Mn(II) ion. The both structures are stabilised by the network of hydrogen bonds [9]. Based on the IR spectra of the complexes and free glycine, also for the compounds Mn(gly)$Br_2(H_2O)_2$, Mn$(gly)_2Br_2(H_2O)_2$, co-ordination through carboxylate oxygen of organic ligand is postulated. The effective magnetic moments values being 5.39–5.82 M.B. of the complexes are characteristic for high-spin Mn(II) complexes of d^5 configuration.

All complexes are stable at room temperature. Upon heating, the multi-stage decomposition process occurs as follows from Table 2. The first mass loss on the TG curves corresponds to the dehydration process. The less stable hydrated complex is [Mn(gly)$Cl_2(H_2O)_2$]. The dehydration process in this complex begins at 85°C. The remaining complexes are more stable and the release of water molecules occurs at slightly higher temperature. As observed on the DSC curves, the release of water molecules is accompanied by an endothermic effect (Fig. 1). For the complex [Mn(gly)$Cl_2(H_2O)_2$] a broad endothermic peak with the maximum at 151.9°C is observed. The corresponding molar dehydration enthalpy (ΔH) value is 36.3 kJ mol^{-1}. The DSC curve of the complex Mn(gly)$Br_2(H_2O)_2$ shows a sharp endothermic peak at 95.5°C with the measured ΔH equal to 86.42 kJ mol^{-1}. Only for the complex Mn$(gly)_2Br_2(H_2O)_2$ in the temperature range of dehydration, a double-peak with the maxima at 112.8 and 121°C is observed with the corresponding total

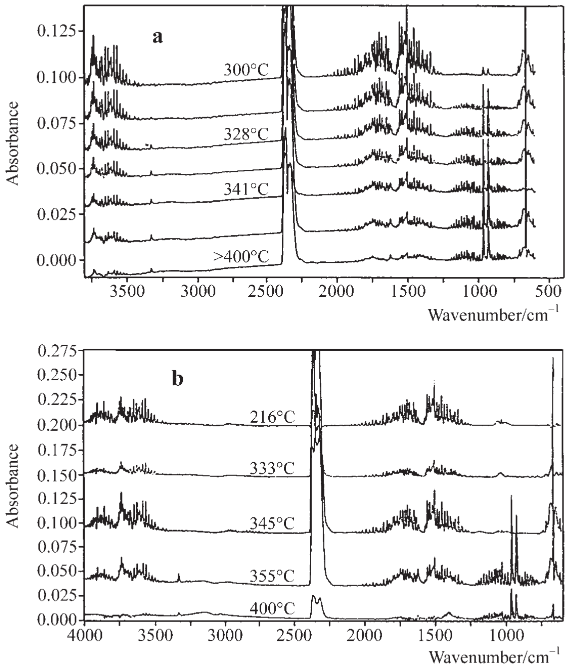

Fig. 2 FTIR spectra of gaseous products of thermal decomposition of a – [Mn$(gly)_2Cl_2$], b – [Mn(gly)$Cl_2(H_2O)_2$] (b)

ΔH=92.2 kJ mol^{-1}. It may indicate that the loss of water molecules is a two-stage process.

The loss of water molecules is reflected in by FTIR spectra of the gaseous products of decomposition. As is seen in Figs 2 and 3, the evolved H_2O molecules give characteristic valence and deformation vibration bands in the wavenumber ranges 3750–3500 and 1900–1300 cm^{-1}, respectively. In the FTIR spectra of the gas-phase products of heating of the complexes $Mn(gly)Br_2(H_2O)_2$, $Mn(gly)_2Br_2(H_2O)_2$ the H_2O bands were observed at 150°C while in the FTIR spectra of gaseous products of the complex $[Mn(gly)Cl_2(H_2O)_2]$ the water molecules bands were detected at 216°C. These observations can be related to the different binding of water molecules in the complexes.

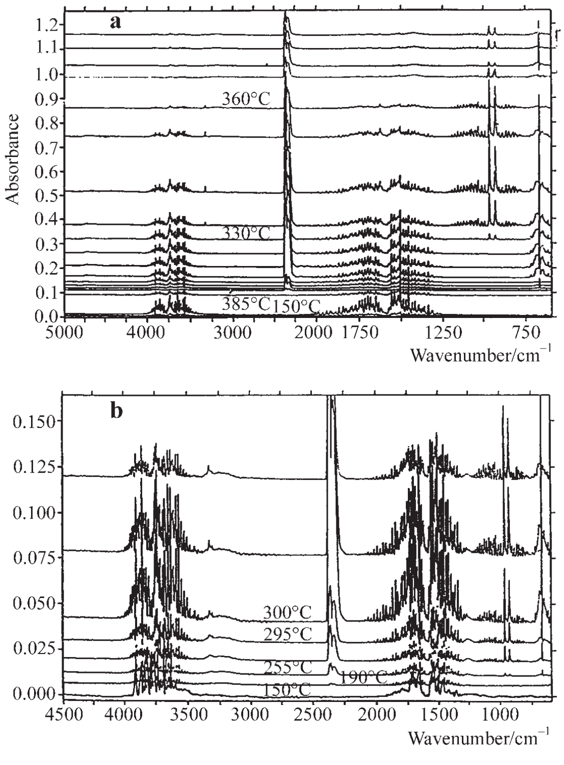

Fig. 3 FTIR spectra of gaseous products of thermal decomposition of a – $Mn(gly)Br_2(H_2O)_2$, b – $Mn(gly)_2Br_2(H_2O)_2$

The temperature of dehydration process in air and inert atmosphere differs slightly as can be seen in Table 2. The anhydrous compounds 1, 2, 3 are unstable in the air atmosphere. Compound $Mn(gly)_2Br_2$ being a product of dehydration of the complex $Mn(gly)_2Br_2(H_2O)_2$ is stable in the temperature range 135–210°C. On the DSC curve of the $Mn(gly)_2Br_2$ the exothermic peak is observed at 168.3°C due to the change in crystal structure or solid–solid interactions. In argon atmosphere also anhydrous Mn(gly)Br_2 is formed as a stable decomposition product of the complex Mn(gly)$Br_2(H_2O)_2$.

When the complexes are heated above the temperature of dehydration process the subsequent decomposition of the complexes with degradation of glycine takes place. The complex [Mn(gly)$_2Cl_2$] is stable up to 150°C in air atmosphere as well as in nitrogen. The remaining complexes begin to decompose in the temperature range 185–210°C.

In the IR spectra of gaseous products of the [Mn(gly)$_2Cl_2$] decomposition, measured at 300°C, besides the bands of water molecules there are observed the bands of carbon dioxide. CO_2 molecules absorb in the wavenumber ranges: 2300–2250 and 750–600 cm^{-1} due to valence and deformation vibrations, respectively. Additionally, at the same temperature very weak bands of ammonia are also detected. Vibrations of gaseous NH_3 give very characteristic double-peak bands with the maxima at 966 and 923 cm^{-1}. At higher temperature, intensities of NH_3, CO_2 and H_2O increase rapidly.

The scheme of decomposition for the remaining complexes is different. The first step of degradation of organic ligand is connected with release of CO_2 molecules. In the FTIR spectra of Mn(gly)$_2Br_2(H_2O)_2$ decomposition, the bands of H_2O and CO_2 appear at 190°C, while in the remaining complexes [Mn(gly)$Cl_2(H_2O)_2$] and Mn(gly)$Br_2(H_2O)_2$ at 333 and 285°C, respectively. Upon further heating, bands of gaseous ammonia are observed. As the FTIR spectra demonstrate, NH_3 is released from the Mn(gly)$Br_2(H_2O)_2$ at 255°C. The release of NH_3 takes place at 355 and 330°C from complexes (2) and (3), respectively. For comparison, the IR spectra of the gaseoius products of glycine decomposition were also recorded. The first stage of the uncoordinated glycine decomposition is connected with evolution of H_2O and NH_3 at 185°C. The bands of CO_2 appears at slightly higher temperature i.e. 220°C.

The temperature of NH_3 evolution from the complexes is higher than from glycine. It may be due to possible nitrogen–manganese bonding in the intermediate solid product.

Upon further heating in air atmosphere, Mn_2O_3 is formed as the final decomposition product. During heating up to 930°C, Mn_2O_3 transforms into Mn_3O_4 (complexes 1 and 2).

Conclusions

1. The studied complexes are stable at room temperature.

2. The first stage of complex decomposition begins as an endothermic process by release of the water molecules. The values of molar dehydration enthalpy are 36.3, 86.42 and 92.2 kJ mol^{-1} for complexes 2, 3, 4, respectively. In the FTIR spectra of gaseous products of complex dehydration, the bands in the wavenumber ranges: 4000–3500 and 1900–1300 cm^{-1} due to valence and deformation vibrations of H_2O are observed.

3. In the air atmosphere, only Mn(gly)$_2Br_2$ is a stable anhydrous product of dehydration.

4. At higher temperature the multi-step decomposition of complexes with degradation of glycine ligand occurs. The way of degradation of free glycine and co-ordinated glycine entirely differs.

5. Temperature of release of gas-phase decomposition products of the anhydrous complexes 2, 3, 4 changes in the order: $CO_2 \approx H_2O < NH_3$. The complex $[Mn(gly)_2Cl_2]$ decomposes with simultaneous evolution of all gas-phase products.

6. It is worth noting that the temperature of NH_3 evolution during the complex decomposition is significantly higher than during free glycine decomposition. This fact can suggest formation of intermediate solid compounds containing Mn–N bond. Temperatures of NH_3 evolution from the complexes are also different. The strongest bonding of ammonia is observed in $[Mn(gly)Cl_2(H_2O)_2]$ (355°C). In the remaining complexes, ammonia begins to evolve at: 330, 300, 255°C for complexes 3, 1, 4.

Temperature of CO_2 molecules evolution increases in the order of 190, 285, 300 and 333°C for $Mn(gly)Br_2(H_2O)_2$, $(Mn(gly)Br_2(H_2O)_2$, $[Mn(gly)_2Cl_2]$ and $[Mn(gly)Cl_2(H_2O)_2]$, respectively. This fact may point to the differences in Mn–O bonding strength in the studied complexes.

7. Upon heating of complexes in the air atmosphere up to about 500°C Mn_2O_3 is formed. The oxide at a higher temperature transforms into Mn_3O_4. In the nitrogen atmosphere MnO is formed as the final solid product of thermal decomposition.

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