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Spectral, thermoanalytical and XRD study of zinc(II) complexes containing adenine and guanosine

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Abstract

Guanosine (Guo) and adenine (Ade) zinc(II) complexes were synthesized by the reaction of the zinc(II) acetate and the respective base. Spectroscopic and thermal properties of the two complexes $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ and $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ ($Ade^- =$ adenine monoanion) are reported. Combination of thermal investigations with IR spectroscopy and powder XRD studies showed that pyrolysis of zinc(II) acetate took place in the first step of the thermal decomposition followed by release and pyrolysis of adenine or guanosine. The decomposition differs from those of zinc(II) carboxylates with N-donor organic molecules (nicotinamide, caffeine) studied elsewhere, in which the organic ligand is released in the first stage of decomposition followed by pyrolysis of the carboxylate.

Keywords: Zinc acetate; Adenine; Guanosine; Thermal analysis; IR; XRD

1. Introduction

Interests in interaction of zinc(II) ion with N-donor bases and DNA constituents have been aroused by several reasons. First, zinc has structural, chemical and regulatory roles in biological systems and is an essential ingredient of the active site in many enzymes. Over 300 enzymes are known to contain zinc(II) ion in the active centre [1,2]. The mechanisms of the interaction of enzymes with a substrate can be studied using synthetic model compounds. Second, zinc stabilizes the structure of proteins and nucleic acids and it is also found in the proteins involved in the control of gene expression. The zinc binding peptide motifs in these proteins are collectively termed ''zinc fingers'' [3,4]. Zinc–nucleic acid interactions can be investigated using small model metal complexes containing purine and pyrimidine bases, nucleosides and nucleotides (see Scheme 1).

In our previous work, we have studied the interaction of theophylline, which is a close analogue of guanine, with zinc(II) acetate. Depending on basicity of the reaction media, we have prepared zinc(II) theophylline complexes with the composition $[Zn(B)_2(Tph^-)_2]$ and $[Zn_2(OH)(CH_3COO)(Tph^-)_2]$ ($B = NH_3$, ethanolamine, isopropylamine, $Tph^- =$ theophyllinate monoanion) [5].

In a continuation of this work, we have carried out reactions of zinc(II) acetate with two of DNA constituents guanosine (Guo) and adenine (Ade), which are known to form complexes preferentially through their N^7 atoms [6–8]. Here, we present the results of

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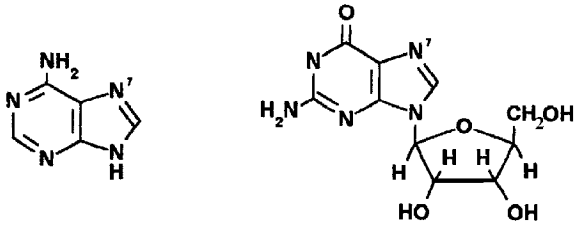

Scheme 1. Molecular structure of adenine and guanosine.

spectral, thermal and powder XRD study of the two prepared complexes, namely $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ and $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$.

2. Experimental

2.1. Materials

Adenine (Ade), guanosine (Guo), zinc(II) acetate and methanol were commercially available (Aldrich Chemie) and used without further purification.

2.2. Preparation of the complexes

2.2.1. $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$

The complex $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ was prepared by mixing methanolic suspension of guanosine (0.28324 g; 1 mmol) in 40 cm^3 MeOH with methanolic solution of zinc acetate dihydrate (0.43888 g; 2 mmol) in 40 cm^3 MeOH. The mixture was then stirred at room temperature for 3 h yielding a white solid, which was dissolved in cold water. A small amount of undissolved solid, which contained unreacted guanosine was filtered off and the filtrate left for slow evaporation. After several days, a white compound crystallized. The compound was washed with methanol and dried over silica gel. The dried sample contains two crystal water molecules. Anal. Calcd. for $C_{18}H_{29}N_5O_{15}Zn_2$: C, 31.51; H, 4.26; N, 10.21; Zn, 19.06%. Found: C, 31.35; H, 4.21; N, 10.08; Zn, 19.35%.

2.2.2. $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$

A batch of 0.27026 g (2 mmol) of adenine was dissolved in 70 cm^3 of hot water. Zinc acetate dihydrate (0.43888 g; 2 mmol) dissolved in 30 cm^3 of water was then added dropwise to the adenine solution with stirring. A white precipitate $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ was formed immediately. The solid was filtered off, washed with hot water and dried over silica gel. Anal. Calcd. for $C_7H_9N_5O_3Zn$: C, 30.40; H, 3.28; N, 25.33; Zn, 23.64%. Found: C, 30.29; H, 3.60; N, 25.24; Zn, 23.43%.

3. Instrumentation

IR spectra of the compounds were recorded on a Specord M-80 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets.

TG/DTG and DTA measurements were carried out using Derivatograph (MOM OD-102) under dynamic conditions in air atmosphere, with heating rate 10°C min^{-1} and sample weight 100 mg. To identify the solid products of thermal decomposition, XRD patterns were measured using a Mikrometa 2 diffractometer equipped with CrKα (V-filtered) radiation ($\lambda = 2.29092$ Å).

Elemental analyses were performed using a Perkin-Elmer 2400 CHN analyser. The zinc content was determined complexometrically.

4. Results and discussion

The reaction of zinc(II) acetate with guanosine and adenine yielded white, air-stable microcrystalline products with the formulae $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ and $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$. The guanosine complex was prepared by the reaction of guanosine with zinc(II) acetate in the 1:2 molar ratio. The same product was also found in the 1:1 molar ratio. Adenine is known to form complexes in its various forms: adenine monoanion, neutral adenine and adenine cation [8]. During the studied reaction of zinc(II) acetate with adenine, deprotonation of adenine nitrogen takes place and adenine coordinates as a monoanion (see also IR spectra). Both complexes are insoluble in common organic solvents.

4.1. Spectral study

The most important IR absorption bands of the complexes as well as those of the free guanosine

monohydrate and adenine are summarized in Table 1. Band assignments were carried out on the basis of data available in the literature [6,7,9].

Fig. 1 shows the IR spectra of the complex, $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ (Fig. 1b), together with the spectra of guanosine monohydrate (Fig. 1a). Compared with guanosine, differences in ν(C−H), ν(N−H) and ν(C=O) stretching vibrations are observed in the complex. The band assigned to ν(C=O) for guanosine (1736 cm^{-1}), shows a negative shift of 16 cm^{-1} and lower intensity upon coordination. It is well known from the structure studies of various guanosine complexes that the C=O group does not participate in coordination via its oxygen atom, but nitrogen N^7 atom of the purine ring [6,8]. Thus, the observed shift of the band is probably not due to coordination of the oxygen atom of the C=O group to metal, but can be attributed to rearrangement of the inter-ligand hydrogen bonding.

Differences are also found in the 2900–2700 cm^{-1} region. In free guanosine, ν(C−H) and ν(N−H) stretching vibrations can be observed, whereas in the complex, there is only one. The presence of the acetate groups in the complex is evident from $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching frequencies at 1608 and 1440 cm^{-1}, respectively.

It can be seen from Table 1 and Fig. 2 that the IR spectra of the complex $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ and those of free adenine are very similar. Differences can be observed near 3400 cm^{-1} as a consequence of ν(OH) vibration, which is not present in free adenine, only in the hydrated complex. The same holds for δ(OH) vibration. Very important differences can be observed in the 2900–2550 cm^{-1} region, which can indicate whether the metal-bonded adenine is present in its neutral or monoanionic form [7].

Neutral adenine-containing complexes show four strong ν(NH) absorption bands in this region, whereas the complex containing monodeprotonated adenine exhibit only one or two weak maxima [7]. A comparison of spectra of the free adenine (Fig. 2a) and the adenine complex (Fig. 2b) suggests coordination of the adenine as monoanion. Deformation vibrations of the NH_2 group in the complex undergo only small changes compared with the free adenine ligand.

Bands at 1560 and 1476 cm^{-1} in the complex have been assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching frequencies of the carboxylate group. The value of separation $\Delta = \nu_{as}(COO) - \nu_s(COO) = 94\ cm^{-1}$ indicates bidentate mode of carboxylate coordination [9].

4.2. Thermoanalytical and XRD study

4.2.1. $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$

Thermoanalytical curves of the complex $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ are shown in Fig. 3. As it can be seen, the dried sample contains two molecules of water, which is released in the temperature range 60–140°C (weight loss 5.5%; calcd. 5.26%).

The next two steps of the gradual decomposition occur in the temperature range 140–320 and 320–460°C with the observed weight losses of 15 and 15.5%, respectively. They are accompanied by endothermic process with maximum at 220°C and exothermic process with maximum at 420°C on the DTA curve. Taking into account the XRD patterns of the complex at 380°C (Fig. 4b) as well as the IR spectrum of the complex after heating to 320°C (Fig. 1c), the following explanation can be given. Two molecules of zinc(II) acetate which are present in the complex decompose to CO_2 and acetone during this process (calcd. weight loss 14.9%) with ZnO as the solid residue. According to the powder XRD of the complex heated to 380°C, zinc oxide forms in these steps of decomposition (Fig. 4b). The IR spectrum of the complex heated to 320°C also confirms decomposition of acetate at this stage. The presence of guanosine bands and absence of bands arising from acetate group can be seen in the spectrum.

The results are in accordance with the thermal investigation of zinc(II) carboxylates in air or in inert atmosphere [10–12]. These studies showed decomposition of zinc(II) carboxylates to CO_2 and ketones and formation of final solid residue ZnO using one of the carboxylate oxygens.

The next weight loss (460–600°C) corresponds to the release and pyrolysis of guanosine (weight loss 40%; calcd. 41.4%). This step is accompanied by strong exothermic process on the DTA curve with maximum at 560°C.

The final decomposition product detected by XRD corresponds with the data given for ZnO (solid residue 24%; calcd. 23.8%) [13].

Table 1
Infrared spectra (cm^{-1}) of guanosine hydrate, $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$, adenine and $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$

Band assignment	Guanosine hydrate	$[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$	Adenine	$[Zn(CH_3COO)(Ade^-)]\cdot H_2O$
ν(OH)	3360	3320		3376
$\nu(NH_2)$	2728		3280, 3144, 2792, 2704, 2600	
ν(CH)	2864	2920	2968	2932
ν(C=O)	1736	1720		
$\delta(NH_2)$[a]	1684	1676	1676	1676
$\delta(OH_2)$	1636	1640		1640
ν(C=O), ν(C=N)	1576, 1540, 1492, 1424	1576, 1540, 1488, 1424	1608, 1512, 1452, 1424, 1368	1608
$\nu_{as}(COO^-)$		1608		1560
$\nu_s(COO^-)$		1440		1476
$\delta(CH_2) + \gamma(CH_2)$ + ring vibrations	1400, 1344	1408, 1344	1336, 1312	1408, 1280
$\delta(NH_2)$[b]	1248		1256	1224
Ring mode	1180, 1132	1184, 1128	1160, 1128	1152
$\rho(NH_2)$	1088	1088, 1044	1024	1004
$\delta(NH_2)$[c]	920	928	944, 912	936
NH_2 rock + ring skeleton vibrations	884, 824	876	876, 848, 800	800
$\delta(NH_2)$[d]	776	784	724	744
Main ring skeleton vibrations	688, 624, 456, 416	688, 636, 584, 564, 520, 504, 480	640, 544	648, 580, 528, 496, 480

[a] Sym. in-plane.
[b] Asym. out-of-plane.
[c] Sym. out-of-plane.
[d] Asym. in-plane.

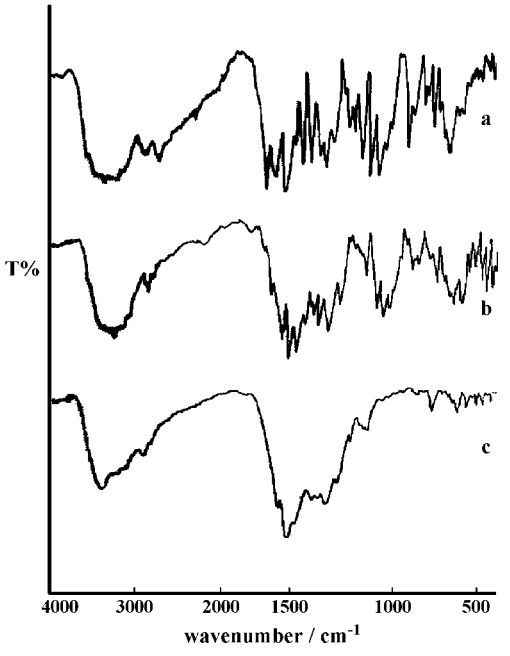

Fig. 1. IR spectra of: (a) guanosine hydrate; (b) $[Zn_2(CH_3COO)(Guo)]\cdot 2H_2O$; (c) $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ heated to 320°C.

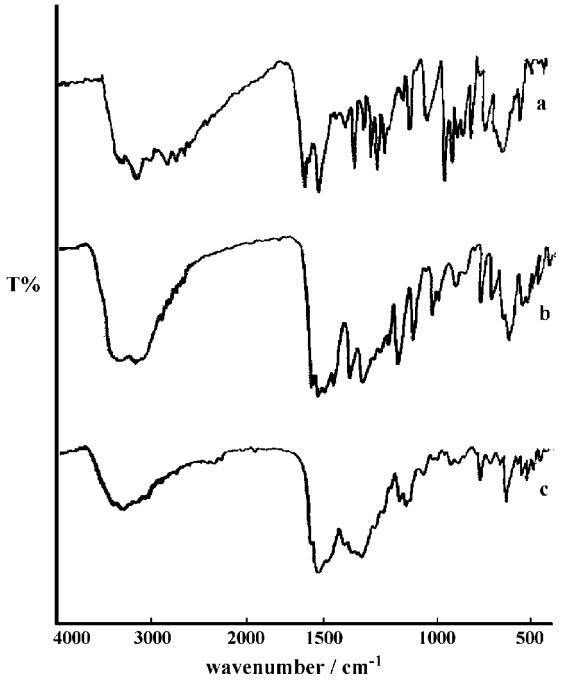

Fig. 2. IR spectra of: (a) adenine; (b) $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$; (c) $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ heated to 380°C.

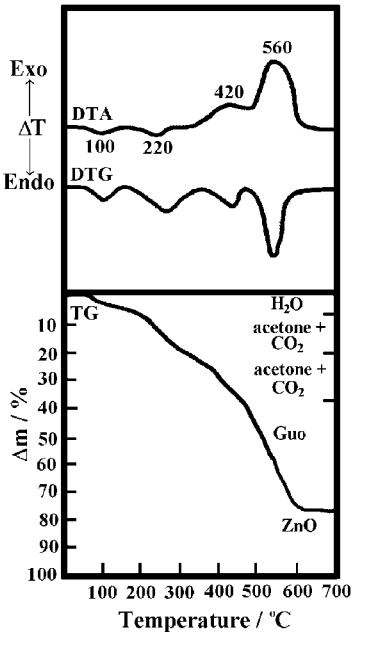

Fig. 3. Thermoanalytical curves of $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$.

4.2.2. $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$

Thermoanalytical curves of the $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ complex are shown in Fig. 5. As can be seen from the figure, the dried sample contains one molecule of the water, which is gradually released in the temperature range 50–160°C (weight loss 7%; calcd. 6.5%) with a weak endothermic effect on the DTA curve at 100°C.

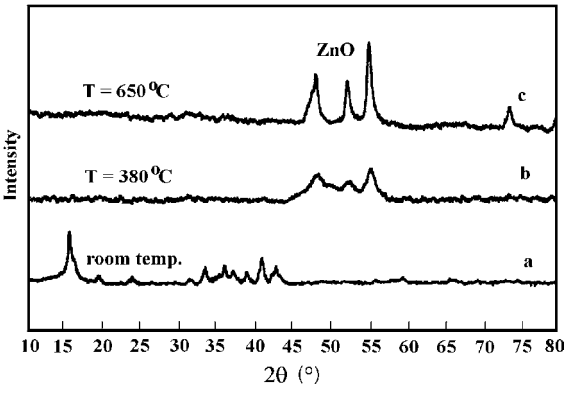

Fig. 4. XRD spectrum of $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ at: (a) room temperature; (b) 380°C; (c) 650°C.

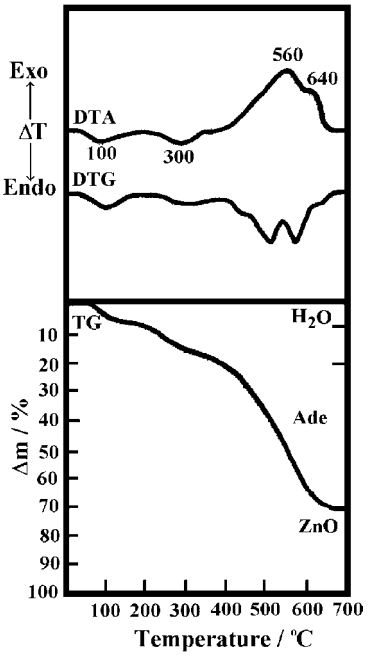

Fig. 5. Thermoanalytical curves of $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$.

The next weight loss step (160–380°C) corresponds to decomposition of the acetate including formation of ZnO. This fact is evident from IR and XRD spectra. After heating the sample to 380°C, the peaks arising from ZnO can be seen in the XRD pattern (Fig. 6b), similarly to the guanosine complex. IR spectrum of the sample heated to 380°C (Fig. 2c) shows the presence of adenine bands and the absence of acetate bands.

The next weight loss (380–660°C) corresponds to the release and pyrolysis of adenine (weight loss 49%; calcd. 48.50%). The process of decomposition of $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ is accompanied by endothermic processes at 100 and 300°C and exothermic processes with maxima at 560 and 640°C.

The final decomposition product ZnO (solid residue 30%; calcd. 29.42%) was detected by XRD [13].

5. Conclusion

The reaction of zinc(II) acetate with adenine and guanosine gave the complexes $[Zn_2(CH_3COO)_4(Guo)]\cdot 2H_2O$ and $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$, respectively. Combination of thermal investigation with IR and powder XRD studies showed that pyrolysis of zinc(II) acetate took place in the first step of the thermal decomposition followed by release and pyrolysis of guanosine or adenine. This process of decomposition differs from the decompositions of zinc(II) carboxylates with N-donor organic molecules (nicotinamide, caffeine) studied elsewhere, in which the organic molecule is released at the first stage of decomposition followed by pyrolysis of the carboxylate [14–16]. This fact may be associated with higher

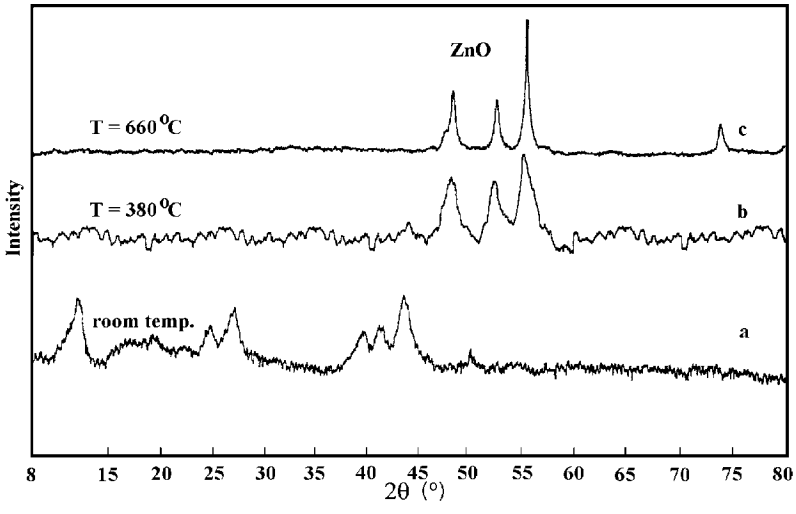

Fig. 6. XRD spectrum of $[Zn(CH_3COO)(Ade^-)]\cdot H_2O$ at: (a) room temperature; (b) 380°C; (c) 650°C.

thermal stability of guanosine and adenine ligands than the acetate ligands, which in the native zinc(II) acetate are totally decomposed at 300°C [10].

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