

SYNTHESIS, SPECTRAL AND THERMAL PROPERTIES OF MACROCYCLIC ZINC(II) COMPLEXES

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Abstract

The new zinc ternary complexes $[\text{Zn}(\text{cyclen})\text{NO}_3]\text{ClO}_4$ (**I**), $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ (**II**), $[\text{Zn}_2(\text{cyclen})_2(\text{-pic})](\text{ClO}_4)_3$ (**III**) (*cyclen*=1,4,7,10-tetraazacyclododecane; *nic*=nicotinic acid; *pic*=picolinic acid) were synthesized and their spectral and thermal properties were investigated. The compounds were characterized by elemental analysis, IR spectroscopy and TG/DTG, DTA methods. Moreover, the way of coordination of pyridinecarboxylate anions was proposed on the basis of the spectral data and consequently proved with results of X-ray structure analysis.

Keywords: infrared spectroscopy, macrocyclic complexes, thermal behaviour, zinc(II) pyridinecarboxylate

Introduction

The pyridinecarboxylic acids belong to ligands occurring in biological systems. Nicotinic acid and nicotinamide are present in cells as the pyridine nucleotides (NAD^+ , NADP^+), which belong to the coenzymes and vitamins and are necessary for their metabolisms. Nicotinamide transfers reversible hydride anion from alcohols to nicotinamide adenosine dinucleotide (NAD^+). Few models of zinc(II) enzymes were built up to understand the interaction between enzymes, coenzymes and the substrate itself. One of these models are macrocyclic polyamines. Kimura [1–3] has described the 1,5,9-triazacyclododecane–Zn–OH species as a new alcohol dehydrogenase and carbonic anhydrase models. Moreover, he reported the syntheses and characterization of zinc(II) cyclen complexes and their various pendant derivatives [4–7]. Such compounds have been extensively studied as the enzyme models and artificial carriers for thymidine and uridine nucleosides useful in antiviral chemotherapy [8]. Some of zinc(II) complexes show antimicrobial activity and fungistatic effect [9–11].

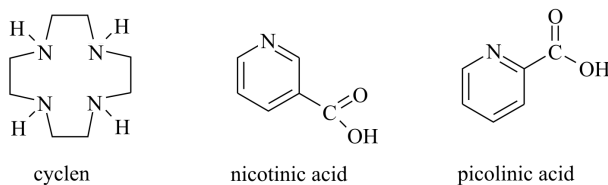
This paper reports the synthesis, spectral and thermal properties of the new compounds $[\text{Zn}(\text{cyclen})(\text{NO}_3)](\text{ClO}_4)$ (**I**), $[\text{Zn}(\text{cyclen})\text{-nic-Zn}(\text{cyclen})](\text{ClO}_4)_3$ (**II**), $[\text{Zn}(\text{cyclen})\text{-pic-Zn}(\text{cyclen})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**III**).

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Experimental

Synthesis of the compounds

The following A.R. grade chemicals were used for the preparation of the compounds under study: $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Lachema Neratovice), HNO_3 68%, cyclen (1,4,7,10-tetraazacyclododecane, *m.p.* 110–113°C, *F.W.* 172.28), nicotinic acid 99% (*m.p.* 236–239°C, *F.W.* 123.11), picolinic acid 99% (*m.p.* 139–142°C, *F.W.* 123.11), (Sigma).



Scheme 1

Preparation of $[\text{Zn}(\text{cyclen})(\text{NO}_3)]\text{ClO}_4$ (**I**)

A solution of 345 mg cyclen (2.00 mmol) soluble in 20 mL water was added to the 20 mL aqueous solution containing 378 mg HNO_3 (6.00 mmol). Subsequently zinc perchlorate (745 mg 2.00 mmol) was added to the mixture. 1 M NaOH solution were necessary to add to adjust pH to 5.8–6.0. The mixture was allowed to stand in covered vessel 24 h at room temperature. Then ethanol was added to the mixture in ratio water:ethanol=1:1. The solution was left to stand in the air and after few days colorless crystals were obtained.

Preparation of $[\text{Zn}(\text{cyclen})\text{-nic-Zn}(\text{cyclen})](\text{ClO}_4)_3$ (**II**)

86 mg zinc perchlorate (0.232 mmol) soluble in 3 mL water was added to the 7 mL aqueous solution containing 40 mg cyclen (0.232 mmol). Reaction mixture was allowed to stand in covered vessel 24 h. Equimolar amount of 10 mL aqueous solution of 29 mg nicotinic acid (0.232 mmol) was added to the mixture that was left to stand at room temperature in the air (pH=4.3). After several days colorless and pellucid crystals were obtained from the aqueous solution.

Preparation of $[\text{Zn}(\text{cyclen})\text{-pic-Zn}(\text{cyclen})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**III**)

The 5 mL aqueous solution of 172 mg zinc perchlorate (0.462 mmol) was slowly added to the 5 mL aqueous solution of 80 mg cyclen (0.462 mmol). Reaction mixture was allowed to stand in covered vessel 24 h. Then equimolar amount of 58 mg picolinic acid (0.462 mmol) in 5 mL water was added to the reaction mixture. After two hours pH of solution was adjusted by 1 M NaOH from 4.49 to 5.55. The solution was left to stand and after 24 h 10 mL acetone was added to the solution. After few days colorless crystals were obtained.

Instrumentation

Infrared spectra were recorded on a Perkin Elmer spectrophotometer in the range 4000–400 cm^{-1} using KBr discs.

The content of C, H, N in prepared compounds was determined by means of Perkin Elmer 2400 CHN analyzer and zinc content complexometrically, using Complexone III as an agent and Eriochrome black as an indicator.

The TG/DTG and DTA measurements were carried out using TA instruments Setaram TG-DTA. The mass of the used samples was within 5.68–7.87 mg range. The samples have been heated in air atmosphere in the temperature range to 1000°C.

Results and discussion

Spectral behaviour

The prepared compounds are colorless, lightproof and stable in the air. The results of elemental analysis are in a good agreement with the calculated ones.

The IR spectra were used for determination of the presence of characteristic absorption bands. The observed absorption bands of prepared complexes are given in Table 1 and Fig. 1.

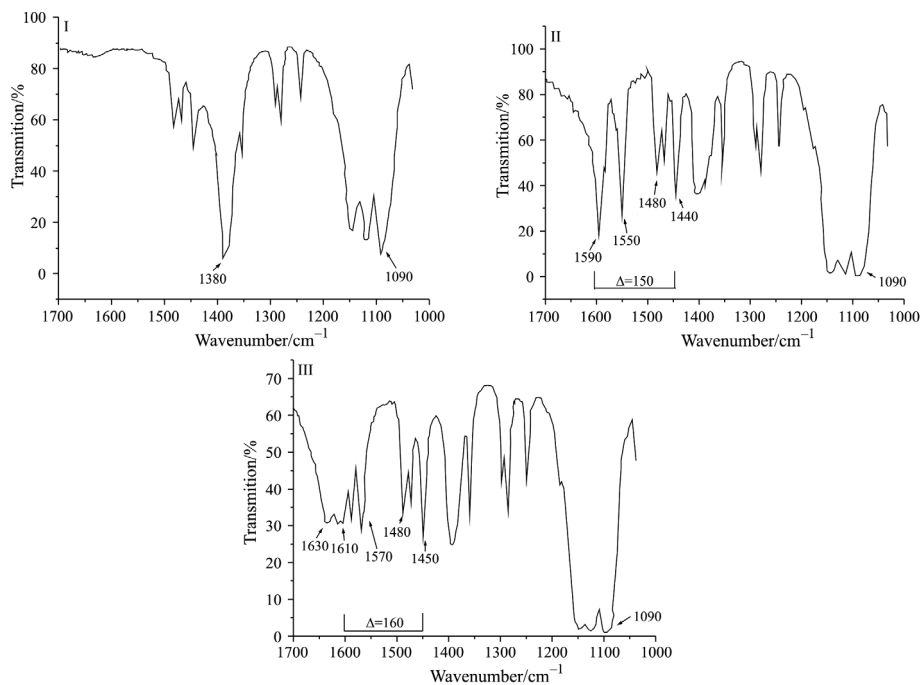


Fig. 1 Characteristic absorption bands of ternary complexes $[\text{Zn}(\text{cyclen})\text{NO}_3]\text{ClO}_4$ (I), $[\text{Zn}_2(\text{cyclen})_2(-\text{nic})](\text{ClO}_4)_3$ (II), $[\text{Zn}_2(\text{cyclen})_2(-\text{pic})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (III)

Table 1 Characteristic absorption bands of zinc(II) complexes in IR spectra

Compound	Assignment/cm ⁻¹					
	(N-H) _{cn}	(C-H) _{cn}	as(OCO ⁻)	s(OCO ⁻)	v(ClO ₄ ⁻)	v(NO ₃ ⁻)
[Zn(cn)NO ₃] ₃ ClO ₄ (I)	3180s	2940s 2910vs 2860s	–	–	1090vs	1380vs 830m 730w
[Zn ₂ (cn) ₂ (-nic)](ClO ₄) ₃ (II)	3160s	2940s 2910vs 2860s	1590s 1550s	1440m	1090vs	–
[Zn ₂ (cn) ₂ (-pic)](ClO ₄) ₃ H ₂ O (III)	3180s	2960s 2930vs 2860s	1610m 1570m	1450m	1090vs	–

cn – cyclen, as – asymmetric, s – symmetric, vs – very strong, s – strong, m – medium, w – weak, =_{as}(OCO⁻) – _v(OCO)

Infrared spectra are in good accordance with [12]. The presence of nitrate ligand and perchlorate anion was confirmed by characteristic stretching vibration at 1380 and 1090 cm^{-1} . Picolinate and nicotinate anions show characteristic absorption bands in the range 1630–1200 cm^{-1} [13]. Asymmetric stretching vibration of carboxylate anion shows at 1590 and 1550 cm^{-1} in complex **(II)** and at 1610 and 1570 cm^{-1} in the case of complex **(III)**. Moreover, the presence of wide absorption band in the range 1630–1610 cm^{-1} assume the overlap of asymmetric stretching vibration of carboxylate anion with deformation vibration of water molecule. The presence of water in this complex was really confirmed by X-ray structural analysis [14]. Therefore, the value 1630 cm^{-1} we have assigned to deformation vibration of water molecule. The values 1440 and 1450 cm^{-1} respond to symmetric vibration of carboxylate anion in complex **(II)** and **(III)**. The symmetric stretching vibrations (C–C) and (C–N) of pyridine ring were spotted at 1480 cm^{-1} in both complexes. The other characteristic absorption bands for the compounds **(II)** and **(III)** are in the range 1400–1000 cm^{-1} .

Martini studied spectral properties of some carboxylates and found out, that value ($\nu_{\text{as}}(\text{OCO}^-) - \nu_{\text{s}}(\text{OCO})$) for acetates changes in the following order [15]:

$$\begin{array}{ccccccc} \text{unidentate} & > & \text{ionic} & > & \text{bridging bidentate} & > & \text{chelating bidentate} \\ <190 \text{ cm}^{-1} & & 170\text{--}160 \text{ cm}^{-1} & & <140 \text{ cm}^{-1} & & <140 \text{ cm}^{-1} \end{array}$$

In our complexes, for the compound $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ **(II)** value is 150 cm^{-1} and for $[\text{Zn}_2(\text{cyclen})_2(\text{-pic})](\text{ClO}_4)_3$ **(III)** is value 160 cm^{-1} . The solved crystallographic data confirm monodentate coordination in the complex **(II)** through oxygen of carboxylate group and in **(III)** bridging bidentate coordination to two Zn(II) ions [14]. There are two independent zinc atoms in the structure **(II)**. Both are coordinated by four nitrogen atoms of the cyclen subunit. The fifth coordination position is occupied by oxygen atom of unidentate nicotinate carboxylate anion ($\text{O1-Zn2} = 1.9240(19) \text{ \AA}$) or the nitrogen atom of nicotinate pyridine ring ($\text{N1-Zn1} = 2.026(2) \text{ \AA}$), respectively. In the case of complex **(III)**, the monomeric unit also contains two independent zinc atoms, so two different chromophores are present ($\text{Zn(2)N}_4\text{O}$ and $\text{Zn(1)N}_5\text{O}$). The first coordination polyhedron adopts the shape of a distorted tetragonal pyramid and the second a distorted octahedron.

Thermal behaviour

The TG/DTG and DTA curves of compound $[\text{Zn}(\text{cyclen})\text{NO}_3]\text{ClO}_4$ **(I)** are depicted in Fig. 2. The first step of the thermal decomposition belongs to the release of cyclen molecule. This process is accompanied by strong exothermic effect at 330°C. The following course of the DTA curve displays one exothermic peak with the maximum at 420°C. This effect corresponds to the evaluation of oxygen and ZnO was found as a final product of thermal decomposition. The following reaction was proposed for the mechanism of the thermal decomposition:



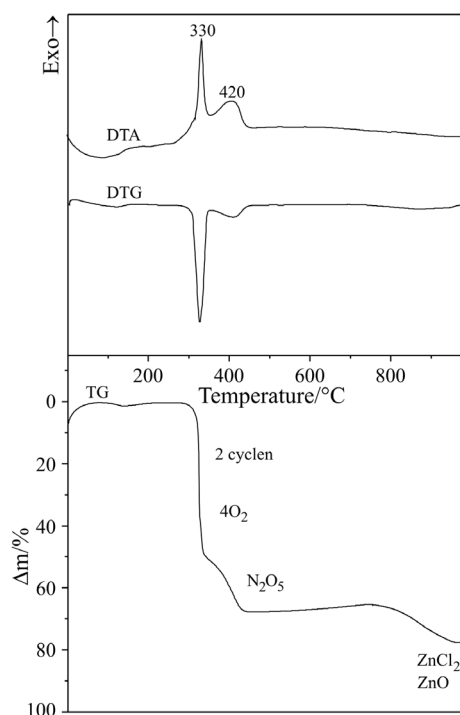
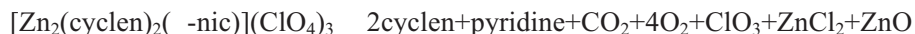


Fig. 2 TG/DTG and DTA curves of $[\text{Zn}(\text{cyclen})\text{NO}_3]\text{ClO}_4$ (**I**)

As it is obvious from the TG, DTG and DTA curves in Fig. 3, the complex $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ (**II**) is thermally stable up to 340°C . Above this temperature the sample loses cyclen, as demonstrated the mass loss on the TG curve and the exothermic effect on DTA curve at 355°C . At the next step of thermal decomposition pyridine, CO_2 , ClO_3 and oxygen are released with an exothermic peak at 550°C . Above 600°C the thermal decomposition continues by release of zinc chloride and zinc oxide is the final product of thermal decomposition. The mechanism of the thermal decomposition can be proposed in this way:



It was interested to compare thermal decomposition of $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ (**II**) compound with $\text{Zn}(\text{nic})_2(\text{H}_2\text{O})_4$ studied by Allan [16]. The compound $\text{Zn}(\text{nic})_2(\text{H}_2\text{O})_4$ is stable to 93°C . Above this temperature dehydration process was observed. The complex then decomposes at 140°C with loss of organic ligand and the formation of zinc oxide. In the DTA curve this decomposition process corresponds to an exothermic effect at 390°C [16]. In our case the thermal decomposition of nicotinate anion in complex $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ (**II**) is also accompanied by exothermic effect at higher temperature (550°C). The higher thermal stability is caused by different way of zinc coordination in complex compounds. In the case of compound (**II**) zinc is

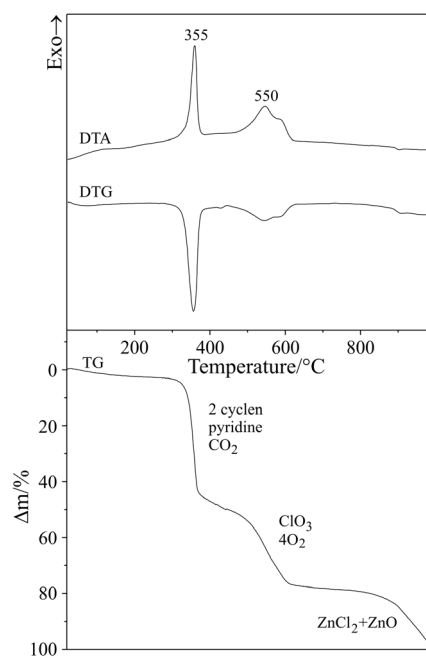


Fig. 3 TG/DTG and DTA curves of $[\text{Zn}_2(\text{cyclen}_2(-\text{nic}))(\text{ClO}_4)_3]$ (II)

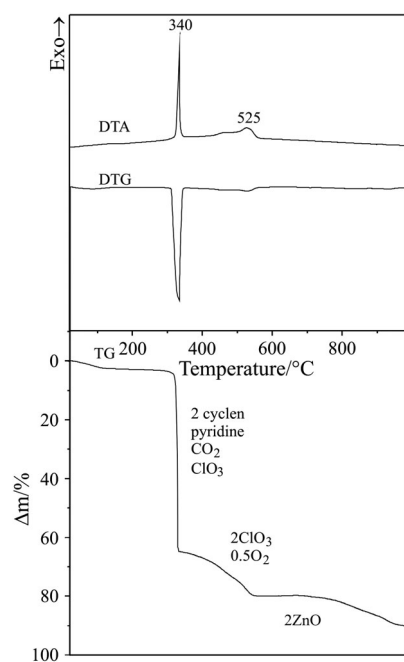


Fig. 4 TG/DTG and DTA curves of $[\text{Zn}_2(\text{cyclen}_2(-\text{pic}))(\text{ClO}_4)_3]$ (III)

surrounded by four nitrogen atoms from cyclen and oxygen or nitrogen atom from nicotinate anion [12]. On the other hand, zinc in complex $[\text{Zn}(\text{nic})_2(\text{H}_2\text{O})_4]$ is coordinated only through two nitrogen atoms [16].

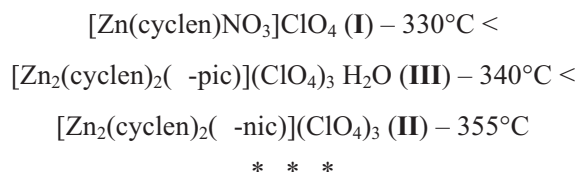
The TG/DTG and DTA curves of compound $[\text{Zn}_2(\text{cyclen})_2(\text{-pic})](\text{ClO}_4)_3$ (**III**) are given in Fig. 4. The first step of the thermal decomposition is the release of cyclen, pyridine, CO_2 and ClO_3 as it is displayed on the DTA curve with a maximum at 340°C . The next step of thermal decomposition is accompanied by weak exothermic effect on the DTA curve at temperature 525°C . It corresponds to the mass loss of ClO_3 and O_2 . Above 550°C the thermal decomposition is finished by formation of zinc oxide. The scheme of the thermal decomposition can be proposed like this:



Conclusions

We have found that the compounds $[\text{Zn}(\text{cyclen})\text{NO}_3]\text{ClO}_4$ (**I**), $[\text{Zn}_2(\text{cyclen})_2(\text{-nic})](\text{ClO}_4)_3$ (**II**), $[\text{Zn}_2(\text{cyclen})_2(\text{-pic})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**III**) are stable in the air atmosphere up to 300°C . When heated above this temperature, the release of cyclen and the decomposition of pyridinecarboxylate anions takes place and O_2 , N_2O_5 , ClO_3 and ZnCl_2 are evolved. The solid product of the thermal decomposition ZnO was proved by X-ray powder diffraction.

The thermal stability of the prepared complexes increases in the following order:



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